Heterostructured Metaloxide Photocatalytic (Copper Oxide and Titanium Oxide) for Degradation and Removal of Organic Pollutants from Water

Thesis

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Heterostructure Metaloxide Photocatalyst (Copper Oxide and Titanium Dioxide) for Degradation and Removal of Organic Pollutants from Water

Thesis Submitted for The Award of The Degree Of

Doctor of Philosophy (Ph.D.)

by

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Supervised by

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March 2022
Metal oxides with favourable light absorption properties and charge transport characteristics play wide application as a photocatalyst. Titanium oxide and Copper oxide are the two major earth abundant metal oxides, and this dissertation is aimed to synthesize the heterostructured copper oxide and titanium oxide for the application of water treatment by enhancing their photocatalytic activity. Metal oxides are treated with atmospheric pressure plasma or by altering the structural level in nano size region to enhance the photocatalytic activity.

Cupric oxide (CuO) thin film has found widespread application as a low-cost material for photo catalytic applications. High surface wettability is a key factor to achieve enhanced efficiency in these catalytic applications. Here, we report a fast and environment friendly route to fabricate super hydrophilic CuO thin films using a low power (5–10 W) atmospheric pressure plasma jet (APPJ). With APPJ treatment for 5 min, the CuO surface transforms from hydrophobic to super-hydrophilic with increase in catalytic activity. APPJ introduces anisotropy in the crystal structure and creates unique three-dimensional surface morphology with distinct surface chemical and electronic features. The treated films exhibited a higher rate of photo degradation of Methylene Blue and phenol indicating efficient charge separation.

An environment friendly alternative to epitaxially grown process of copper oxide nanowires (NWs) on copper substrates using single step atmospheric pressure plasma jet assisted oxidation is used. NWs of average length 300 nm are grown rapidly in 5 minutes along with transforming the surface to superhydrophilic. This method introduces defects in the nanowire structure which is otherwise difficult to achieve due to the highly isotropic nature of nanowire growth. High resolution transmission electron microscopy reveals vacancies and structural defects such as lattice twinning and kinks. Copper oxide NWs have an excellent degradation activity towards organic pollutants Methylene Blue.

Two-dimensional (2D) Molybdenum disulfide (MoS$_2$) has become one of the most exciting areas of research for adsorbents due to its high surface area and abundant active sites. Mainly, 2D MoS$_2$ show promising removal of textile dye pollutants by adsorption process, but it shows high affinity for anionic type of dyes, that limits its performance in mixed dye pollutants treatment. Herein, we demonstrate an integrated approach to remove mixed dye pollutants (anionic and cationic) concurrently by combining adsorption and photocatalysis process. We synthesize MoS$_2$/TiO$_2$ nanocomposites for different weight percentages 2.5, 5, 10, 20, 30 and 50 wt% of pre-synthesized flower-like MoS$_2$ nanoparticle by a two-step hydrothermal method. We demonstrate a new process of two-stage adsorption / photocatalysis using high wt% of MoS$_2$ (Stage-I) and low wt% of MoS$_2$ (Stage-II) nanocomposites. The proposed two-stage integrated adsorption and photocatalysis process using 50% and 2.5% of MoS$_2$ coated TiO$_2$, respectively showed complete removal of methylene blue dye ~5 times faster than conventional single-stage (adsorption or photocatalysis) water treatment process. Furthermore, the feasibility of the proposed two-
stage method in mixed dye pollutants removal (anionic and cationic) showed excellent performance even in doubling the dye pollutant concentration. This work brings a deeper insight into understanding the morphology and concentration of 2-D MoS$_2$ in MoS$_2$/TiO$_2$ nanocomposite in tackling mixed dye pollutants and the possibilities of applying in textile dyeing industries wastewater treatment plants.
Acknowledgement

My journey as a doctoral student at Open University has been a tremendous learning. This doctoral thesis shaped into its current form because of the immense support and guidance of several people. I would therefore take this opportunity to offer my sincere thanks and love to all of them.

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# Contents

Abstract................................................................................................................................. II  
Acknowledgements................................................................................................................ IV  
Abbreviations........................................................................................................................ VII  
List of Figures........................................................................................................................ IX  
List of Tables........................................................................................................................ XIV  

## Chapter 1: Introduction

1. Water Treatment.............................................................................................................. 2  
   1.1. Conventional Water Treatment .............................................................................. 4  
1.2. Photocatalysis ........................................................................................................... 5  
   1.2.1. Influence of Photocatalysis in Water Treatment .............................................. 6  
1.3. Titanium Dioxide (TiO$_2$) as a Photocatalyst ......................................................... 7  
1.4. Copper oxide (CuO$_2$/CuO) as a Photocatalyst ....................................................... 9  
1.5. Molybdenum Disulfide (MoS$_2$) as a Co-catalyst .................................................... 10  
1.6. Motivation ................................................................................................................ 11  
1.7. Project Aim ............................................................................................................... 11  
1.8. References ................................................................................................................. 12  

## Chapter 2: Experimental methods

2. Synthesis methods .......................................................................................................... 19  
   2.1. Thermal Oxidation (Vapor-Liquid-Solid and Vapor-Solid Mechanisms) ............ 19  
   2.2. Atmospheric Pressure Plasma Jet (APPJ) assisted VS Mechanism ................. 21  
   2.3. Hydrothermal Method ......................................................................................... 22  
2. Synthesis of materials .................................................................................................... 23  
   2.2.1. Synthesis of Cupric Oxide (CuO) Thin Films ................................................... 23  
   2.2.2. Synthesis of Copper Oxide Nanowires by Thermal Oxidation (VS Mechanism) ........................................................................................................................................... 24  
   2.2.3. Synthesis of Copper Oxide Nanowires by APPJ assisted VS Mechanism ....... 24  
   2.2.4. Synthesis of MoS$_2$ nanoflakes in 3D flower structure .................................. 24  
   2.2.5. Preparation of TiO$_2$ nanopowder solution ..................................................... 24  
   2.2.6. Synthesis of MoS$_2$/TiO$_2$ nanocomposites .................................................... 25  
2.3. Characterization ......................................................................................................... 25  
   2.3.1. Electron Microscope Techniques .................................................................... 25  
   2.3.1.1. Scanning Electron Microscope (SEM) .......................................................... 25  
   2.3.1.2. Transmission Electron Microscope (TEM) .................................................... 26  
   2.3.2. Spectroscopic Techniques .............................................................................. 27  
   2.3.2.1. UV-Vis spectroscopy (UVS) ...................................................................... 27  
   2.3.2.2. X-ray photoelectron spectroscopy (XPS) .................................................... 27  
   2.3.2.3. Raman spectroscopy (RS) .......................................................................... 29  
   2.3.4. X-ray diffraction technique (XRD) ................................................................ 29  
   2.3.5. Zeta Potetial (ZP) ........................................................................................... 30  
   2.3.6. Contact Angle Measurement .......................................................................... 30  
2.4. Photocatalytic Activity Measurement ...................................................................... 31
### Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>APPJ</td>
<td>Atmospheric Pressure Plasma Jet</td>
</tr>
<tr>
<td>AES</td>
<td>Auger Electron Spectroscopy</td>
</tr>
<tr>
<td>BOD</td>
<td>Biochemical Oxygen Demand</td>
</tr>
<tr>
<td>COD</td>
<td>Chemical Oxygen Demand</td>
</tr>
<tr>
<td>Cu₂O</td>
<td>Cuprous Oxide</td>
</tr>
<tr>
<td>CuO</td>
<td>Cupric Oxide</td>
</tr>
<tr>
<td>CV</td>
<td>Crystal Violet</td>
</tr>
<tr>
<td>EXAFS</td>
<td>Extended X-ray Absorption Fine Structure</td>
</tr>
<tr>
<td>FTO</td>
<td>Fluorine Doped Tin Oxide</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full Width at Half Maxima</td>
</tr>
<tr>
<td>LPP</td>
<td>Low Pressure Plasma</td>
</tr>
<tr>
<td>MB</td>
<td>Methylene Blue</td>
</tr>
<tr>
<td>MoS₂</td>
<td>Molybdenum Disulfide</td>
</tr>
<tr>
<td>MO</td>
<td>Methyl Orange</td>
</tr>
<tr>
<td>NW</td>
<td>Nanowire</td>
</tr>
<tr>
<td>PVA</td>
<td>Polyvinyl Alcohol</td>
</tr>
<tr>
<td>RhB</td>
<td>Rhodamine B</td>
</tr>
<tr>
<td>RS</td>
<td>Raman Spectroscopy</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>SKPM</td>
<td>Scanning Kelvin Probe Microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscope</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Titanium Dioxide</td>
</tr>
<tr>
<td>UVS</td>
<td>UV-Vis Spectroscopy</td>
</tr>
<tr>
<td>VLS</td>
<td>Vapor-liquid-solid</td>
</tr>
<tr>
<td>VS</td>
<td>Vapor-solid</td>
</tr>
<tr>
<td>XAFS</td>
<td>X-ray Absorption Fine Structure Three Dimension</td>
</tr>
<tr>
<td>XANES</td>
<td>X-ray Absorption Near Edge Structure</td>
</tr>
<tr>
<td>XPS</td>
<td>X-Ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
<tr>
<td>ZLD</td>
<td>Zero Liquid Discharge</td>
</tr>
</tbody>
</table>
List of Figures

Figure 1.1a. Global Water withdrawals for agriculture, industry, and households............... 2
Figure 1.1b. Water withdrawals for agriculture, industry, and households in different world regions.................................................................................................................................................. 2
Figure 1.2. Conventional water treating system: (A) Stand-alone thermal process (B) RO Incorporated system.............................................................................................................................................................................. 4
Figure 1.3. Drawbacks involved in each stage of Conventional Water Treatment process........................................................................................................................................................................................................ 5
Figure 1.4. Schematic illustration of photocatalytic water splitting reaction in a semiconductor (photo-harvester) loaded with dual co-catalyst........................................... 6
Figure 2.1 Schematic diagram of the growth mechanism of 1D TiO$_2$ structures over Au coated Ti substrate by VLS growth mechanism ............................................................................................................................................................................................................. 19
Figure 2.2. Schematic diagram of the growth mechanism of Copper Oxide (Cu$_2$O/CuO) 1D nanostructure over the Cu substrate (a - b) ...................................................................................................................................................................................................... 21
Figure 2.3. Hydrothermal vessel (a), cross section view of hydrothermal vessel (b) and sub assemblies of hydrothermal vessel (c)........................................................................................................................................................................................................................................ 23
Figure 2.4. Schematic of (a) electron beam interaction with the sample surface and (b) scanning electron microscope ............................................................................................................................................................................................................................. 26
Figure 2.5 Schematic presentation of XPS instrument........................................................................................................................ 29
Figure 3.1. Water contact angle for (a) as deposited CuO (b) air-annealed CuO (A), (c) CuO annealed in presence of plasma (P), (d) variation in contact angle for the three CuO surfaces.......................................................................................................................................................................................................................................................... 34
Figure 3.2. Scanning electron microscope image of (a) CuO, (b) CuO(A), (c) CuO(P) thin films, (d) optical emission spectra corresponding to He + O$_2$ and He + N$_2$ plasma jet......... 35
Figure 3.3. (a) X-ray diffractogram and (b) Raman spectra comparing CuO, CuO(A), and CuO(P) thin films.......................................................................................................................................................................................................................................................................................... 37
Figure 3.4. X-ray photoelectron spectra of (a) Cu 2p, (b) Cu LMM, (c) O1s and (d) valence band of as-prepared, furnace-annealed and 10 W He + O$_2$ plasma treated copper oxide films .................................................................................................................................................................................................................................................................................................................. 39
Figure 3.5 (a) Cu K-edge XANES spectra of CuO thin films. The spectra are compared with standard CuO, Cu$_2$O and Cu samples. (b) first derivatives of the Cu K-edge spectra, (c) EXAFS oscillations in k- space, (d) Fourier transforms (FTs) of the EXAFS oscillations .................................................. 42
Figure 3.6. Kinetic Steps involved in VLS(a) Dark mode adsorption and light mode photocatalytic degradation of MB by batch-I samples of CuO, CuO(A) and CuO(P); (b) Photocatalytic degradation kinetics of MB by batch-I samples of CuO, CuO(A) and CuO(P);
(c) Light mode photocatalytic degradation of MB by batch-II samples of CuO, CuO(A) and CuO(P); (d) Photocatalytic degradation kinetics of MB by batch-II samples of CuO, CuO(A) and CuO(P); (e) UV–Vis absorption spectra depicting photocatalytic degradation of phenol at different time intervals. CuO thin films kept in 30 min dark(D) to reach equilibrium before exposure to simulated sunlight (L).

**Figure 3.7.** (a) Schematic illustration of CuO (or) CuO(A) with no characteristic surface morphology showing low MB dye adsorption and photocatalytic degradation; (b) CuO(P) with surface nanodots showing enhanced MB dye adsorption and enhanced photo degradation.

**Figure 3.8.** Surface potential map for (a) CuO, (b) CuO(A) (c) CuO(P) (d) Average surface potential value for the three CuO films. With plasma functionalisation the work function dropped by 80 mV.

**Figure 4.1.** SEM image of copper foil substrates with different oxidation temperature 300 °C, 375 °C and 450 °C showing the surface morphology cabbage (a1 and a2), rice grain (b1 and b2) and nanowire (c1 and c2) respectively.

**Figure 4.2.** Graph showing the temperature profile used to heat treat the copper substrates (wire mesh) for different soaking time.

**Figure 4.3.** TEM images of copper wire mesh heat treated at 450 °C for 1hr (a), 2 hr (b), 3 hr (c) and 4 hr (d) showing copper oxide nanowires on the surface of the copper mesh.

**Figure 4.4.** Schematic diagram copper foil showing bottom seeded Cu$_2$O nanoflake layer and top CuO nanowire structures (a); IPA solution mixture of highly dispersed CuO nanowires/nanowhiskers with sedemented Cu2O nanoflakes which are extracted from ultrasonication of oxidized copper foil sample (b); SEM image of CuO nanowires/nanowhiskers (c) and Cu2O nanoflakes dropcasted on silicon wafer (d).

**Figure 4.5.** TEM images of copper oxide nanowires which got exfoliated from oxidized copper substrates and drop casted on holey carbon TEM grids.

**Figure 4.6.** XRD pattern of copper foil oxidized at 450 °C for 4 hr showing the peaks for metallic copper, Cu2O and CuO.

**Figure 4.7.** Copper foil substrate with CuO nano-whiskers showed increase in contact angle (140°) compared to pure copper foil (65°).

**Figure 4.8.** SEM image of copper foil after 1min (a), 2 min (b), 3 min (c), 4 min (d), 5 min (e) of plasma assisted oxidation. SEM image of TEM grid after 5 mins of plasma oxidation (f).

**Figure 4.9.** SEM image of (a) as received copper foil and (b) copper foil after 5 mins of thermal annealing in He + O2 gas flow without plasma. (c) TEM image of copper grid after 5 mins of thermal annealing in He + O2 gas flow.
Table of Figures:

**Figure 4.10.** Optical emission spectra of the atmospheric pressure plasma jet taken on the sample surface (a). Schematic representation of the NW growth in the plasma atmosphere (b). Recombination, dissociation and adsorption of various oxygen species drives the growth.

**Figure 4.11.** EBSD inverse pole Figures of as received copper foil (a) after 5 mins of plasma oxidation (b). Showing the increase in grain size due to the heat treatment.

**Figure 4.12.** X-ray diffractogram (a) and Raman spectra (b) of the copper foil annealed at 400 °C for 4 hours (CuOa) and copper foil plasma functionalised at 375 °C for 5 mins (CuOp).

**Figure 4.13.** (a) Cu 2p spectra of as received, plasma oxidised (5 mins) and annealed (400 °C 4hour) copper substrates. (b) Cu LMM auger spectra of plasma oxidised (5 mins) and annealed (400 °C 4hour) copper substrates. (c) Valence band spectra for plasma oxidised (5 mins) and annealed (400 °C 4hour) copper substrates.

**Figure 4.14.** Comparison between (a) Cu 2p3/2 and (b) O 1s deconvoluted spectra for CuOp and CuOa NW electrode.

**Figure 4.15.** HRTEM image of (a) CuO nanowires grown using plasma functionalisation and (b) highly magnified single crystal CuO nanowire with lattice spacing d=0.257nm which corresponds to ⟨111⟩ crystal orientation.

**Figure 4.16.** (a) Transmission electron micrographs of CuO nanowires grown using plasma functionalisation, (b-d) High resolution images of different regions of NW highlighting the defects.

**Figure 4.17.** (a) Absorption spectra of methylene blue (MB) after photocatalytic degradation by CuOp, (b) adsorption and photocatalytic degradation of MB by the same CuOp sample for three cycle without intermediate plasma treatment; (c) dye removal (adsorption and photocatalytic) efficiency (%) of CuOp sample based on (b), (d) plot of photocatalytic degradation kinetics under light illuminated condition based on (b).

**Figure 4.18.** (a) Absorption spectra of methylene blue (MB) after photocatalytic degradation by CuOP; (b) adsorption and photocatalytic degradation of MB by the same CuOP sample for three repeatability cycle; (c) dye removal (adsorption and photocatalytic) efficiency (%) of CuOP sample; (d) plot of photocatalytic degradation kinetics under light illuminated condition.

**Figure 5.1.** SEM and TEM image of pure MoS2 and TiO2 [MoS2 SEM (a1, a2, a3); MoS2 TEM (b1, b2, b3); TiO2 SEM (c1, c2, c3); TiO2 TEM (d1, d2, d3)].

**Figure 5.2.** SEM image of MoS2/TiO2 nanocomposite TM 10%.

**Figure 5.3.** (a) SEM image of MoS2. HRTEM images of MoS2 measured at (b) 20 nm scale and (c) 5 nm scale. (d) High magnification TEM image of interlayers seen in Figure 2(c) at...
2nm scale, and (e) respective inverse FFT image of MoS2 interlayers. (f) HRTEM image of
TM 10% (TiO2/MoS2) composite, (g) High magnification TEM image of interlayers seen at
Figure 2(f) at 2nm scale, and Inverse FFT images of (h) MoS2 interlayers (i) TiO2 interlayers
marked in Figure 2(g). (j) HRTEM image of TM 50% (TiO2/MoS2) composite, (k) High
magnification TEM image of interlayers seen at Figure 2(j) at 2nm scale, and Inverse FFT
images of (l) MoS2 interlayers (m) TiO2 interlayers marked in Figure 2(k)

Figure 5.4. Plot showing the MoS2 (002) lattice spacing at different random location for
pristine MoS2, TM10% and TM50%

Figure 5.5. XRD pattern of MoS2, TiO2 and MoS2/TiO2 nanocomposites with different
weight percentage of MoS2

Figure 5.6. (a) Raman spectrum of TiO2 showing active modes of anatase phase and (b)
Raman spectra comparison of TiO2 and TM50% showing peak shift and peak broadening
in the insert Figure

Figure 5.7. Raman spectra of MoS2 vibrational peaks (E1g and A1g) in (a) MoS2 and (b) TM
50% showing Δk

Figure 5.8. XPS core level spectra of MoS2 - Mo3d (a), MoS2 - S2p (b), TM 2.5% - Mo3d
(c), TM 2.5% - S2p (d), TM 50% - Mo3d (e) and TM 50% - Mo3d (f)

Figure 5.9. UV-Visible absorption spectra (a) and valence band spectra (b) of TiO2, TM
2.5%, TM 50% and MoS2

Figure 5.10. Schematic illustration of the density of states for TiO2, MoS2, TM 2.5% and
TM 50%

Figure 5.11. Schematic diagram of predicted charge transfer mechanism in TM 2.5% and
TM 50%

Figure 5.12. Molecular structure of Methylene Blue (a), Crystal Violet (b), Methyl Orange
(c) and Rhodamine B (d)

Figure 5.13. Photocatalytic degradation (a) & dye removal efficiency (b) of MB by TiO2,
MoS2, TM 2.5%, TM 5%, TM 10%, TM 20%, TM 30% and TM 50%

Figure 5.14. Two-stage rapid adsorption and photocatalysis based dye pollutant removal

Figure 5.15. Dark Adsorption (stage 1) and Photocatalytic degradation (stage 2) (a) & dye
removal efficiency (b) of MB, MO, RhB and CV dyes by combined effect of TM 50% and
TM 2.5%

Figure 5.16. pH vs Zeta Potential of TiO2, TM 2.5%, TM 5%, TM 10%, TM 50% and MoS2
(a). pH vs Zeta Potential of MB, MO, RhB and CV dyes (b)
**Figure 5.17.** Absorbance spectra of mixed dye solution showing the corresponding spectrum of MB, CV, RhB nad MO dyes.................................................................92

**Figure 5.18.** Adsorption profile of dye (25mg/l) represented by the decrease in normalised absorbance spectra (a) and respective dye color change (b) over time in stage I using TM 50%............................................................................................................94

**Figure 5.19.** Photocatalytic degradation profile of dye (25mg/l) represented by the decrease in normalised absorbance spectra (a) and respective dye color change (b) over time in stage II using TM 2.5%......................................................................................................................94

**Figure 5.20.** Adsorption profile of dye (50mg/l) represented by the decrease in normalised absorbance spectra over time in stage I using TM 50%..............................................................................................95

**Figure 5.21.** Photocatalytic degradation profile of dye (50mg/l) represented by the decrease in normalised absorbance spectra over time in stage II using TM 2.5%.................................................................95

**Figure 5.22.** Adsorption (stage I) and photocatalytic degradation (stage II) curve of mixed dye (25 mg/l and 50 mg/l) using TM 50% and TM 2.5% respectively........................................................................................................96

**Figure 5.23.** Schematic illustration of dye adsorption in 3-D MoS$_2$ (a) and 2-D MoS$_2$ nanoflakes grown on TiO$_2$ (b).................................................................................................................................96
List of Tables

Table 1.1. List of the major textile processes and their corresponding effluent agents 3

Table 3.1. Structural parameters of CuO, CuO(A) and CuO(P) determined from EXAFS measurement........................................................................................................................................ 43

Table 4.1. Tabulation showing the length of the nanowires with respect to different soaking period........................................................................................................................................ 54

Table 5.1: The fitted Mo3d and S2p peak position and atomic percentage of TM 2.5%, TM 50% and pure MoS2........................................................................................................................................ 84
Heterostructured Metaloxide Photocatalysts (Copper Oxide and Titanium Dioxide) for Degradation and Removal of Organic Pollutants from Water
Chapter 1
Introduction

The current world population is around 7.6 billion (2018) and it is expected to reach 9.7 billion by 2050 [1]. As an average, each day about a quarter of a million people are added to the existing population. This rapid growth in population has already degraded, polluted and depleted the availability of natural resources like food, fresh water, air, soil, energy, and biodiversity. Around 2.1 billion people (27.5% of the global population) lack safe drinking water [2].

Only 1% of the liquid water on Earth is fresh and accessible for human use. This small portion of fresh water is consumed (Municipal, Industrial & Agricultural) and polluted in a rapid rate. Agriculture is the largest consumer of Earth’s available freshwater (70% by 2014) and the proportion is increasing for every year. The pollutants from agriculture (pesticides & fertilizers), industries (mining & textile) and municipal (sewage) are polluting our water resource (both surface and groundwater) in an unprecedented rate. The current multi-stage conventional water treating plants are not cost-effective and/or not energy efficient [5].

Figure 1.1. (a) Global Water withdrawals for agriculture, industry, and households, (b) water withdrawals for agriculture, industry, and households in different world regions [3].

1.1. Water treatment

Water treatment plants generally employ multi-stage interconnected processes and these multi-stage process vary with different industrial sectors. This project work is focused
on treating effluents from textile industries in a sustainable method which would replace/support the existing effluent treating technology. Textile production involves a range of processes to convert yarns into garments. Approximately 140-200 litres of water is used to produce 1 kg of garments by textile dyeing units. Some of the major processes which consume lots of water and chemicals are listed below:

<table>
<thead>
<tr>
<th>Process</th>
<th>Application</th>
<th>Major Agents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sizing of yarns</td>
<td>For additional strength, resistance to abrasion and better weaving efficiency during the weaving process</td>
<td>Starch (widely used), modified starch derivatives, polyvinyl alcohol (PVA), carboxy methyl cellulose (CMC) etc.</td>
</tr>
<tr>
<td>Desizing of fabrics</td>
<td>To remove sizing agents to allow further wet processing steps to occur at optimum efficiency.</td>
<td>Amylases &amp; maltase (widely used)</td>
</tr>
<tr>
<td>Bleaching</td>
<td>To remove natural colour, odour and impurities</td>
<td>Sodium hypochlorite, sodium chloride, sodium hydrosulphite, hydrogen peroxide etc</td>
</tr>
<tr>
<td>Mercerisation</td>
<td>To improve fibre strength, lustre, shrinkage resistance and dye affinity of cotton.</td>
<td>Sodium hydroxide</td>
</tr>
<tr>
<td>Dyeing</td>
<td>Adding colour (water soluble &amp; water insoluble) to yarns, fabrics or garments</td>
<td>Azo dyes (which release aromatic amines in water), reactive dyes (hydrolysis of water), acid dyes (lower the pH of water), sodium chloride, sodium sulfide, sodium hydroxide, formaldehyde etc</td>
</tr>
<tr>
<td>Printing</td>
<td>Water-insoluble pigments are used to design/printing the fabrics.</td>
<td>Colour dyes with toluene, methyl ethyl ketone, methanol, isopropyl alcohol etc</td>
</tr>
</tbody>
</table>

Table 1.1. List of the major textile process and its corresponding effluent agents [4].
All these processes will generate wastewater that has a high Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD); increase in alkalinity/pH, dissolved solids, suspended solids, and colour.

1.1.1. Conventional water treatment

Early textile industrial effluent treatment plants were based on stand-alone thermal processes, where wastewater was typically evaporated in a brine concentrator followed by a brine crystallizer or an evaporation pond. The condensed distillate water is collected for reuse, while the produced solids are either sent to a landfill or recovered as valuable salt by-products. In recent years membrane-based filtration technologies (reverse osmosis, nanofiltration etc.) are added to reduce the water volume entering the stand-alone thermal processing system (brine concentrator), which in turn reduces the energy consumption. This collective or multi-stage water treatment is also called Zero Liquid Discharge (ZLD). Figure 1.2 shows the stages involved in conventional water treatment process and Figure 1.3 highlights the essential challenges with each stage.

![Conventional water treating system](image)

**Figure 1.2.** Conventional water treating system: (A) Stand-alone thermal process (B) RO Incorporated system. [5]
1.2. Photocatalysis

A new approach to water treatment involves photo-induced splitting of water molecules to allow gaseous extraction and subsequent recombination. The word photocatalysis is a composite word which is composed of two parts, “photo” and “catalysis”. Catalysis is the process where a substance increases the rate of a reaction by reducing the activation energy without being altered or consumed at the end [6]. Photocatalysis is a reaction which uses light (photon) to activate a substance (photocatalyst) which modifies the rate of a chemical reaction without itself being involved itself. Photosynthesis in plants is a photocatalysis process driven by a typical natural photocatalyst – chlorophyll. When a semiconductor (artificial photocatalyst) is irradiated with light possessing energy greater than the semiconductor band-gap (hv > Eg), an electron (e⁻) from the valence band (VB) is excited to the conduction band (CB), leaving behind a photogenerated hole (h⁺) in the VB. Accordingly, the produced e⁻/h⁺ pairs are able to migrate to the surface of the semiconductor and participate in redox reactions. A semiconductor photocatalyst is composed of three components: photo-harvester, reduction co-catalyst, and oxidation co-catalyst. Associating the co-catalyst with the semiconductor promotes charge transfer and suppresses the charge recombination. Since most of the semiconductor photo-harvester also serves as an oxidation
site, the need for an oxidation co-catalyst is avoided – which leaves the structure only with a photo-harvester and a reduction co-catalyst.

**Figure 1.4.** Schematic illustration of photocatalytic water splitting reaction in a semiconductor (photo-harvester) loaded with dual co-catalyst [7].

### 1.2.1. Influence of photocatalysis in water treatment

Pollutant degradation in water using photocatalytic materials is facilitated mainly by a series of chain oxidative-reductive reactions that occur at the photo-activated surface, which are broadly proposed as [8]:

\[
\text{Photocatalyst} + h\nu \rightarrow h^+ + e^- \quad (1.1)
\]
\[
h^+ + H_2O \rightarrow OH^+ + H^+ \quad (1.2)
\]
\[
h^+ + OH^- \rightarrow OH^* \quad (1.3)
\]
\[
h^+ + \text{pollutant} \rightarrow (\text{pollutant})^+ \quad (1.4)
\]
\[
e^- + O_2 \rightarrow O_2^- \quad (1.5)
\]
\[
O_2^- + H^+ \rightarrow OOH^* \quad (1.6)
\]
\[
2 OOH^* \rightarrow O_2^- + H_2O_2 \quad (1.7)
\]
\[
H_2O_2 + O_2^- \rightarrow OH^* + OH^- + O_2 \quad (1.8)
\]
The Photocatalytic degradation reaction usually involves three main active species: a hydroxyl radical (OH\(^*\)), h\(^+\) and a superoxide radical (O\(_2\)\(^{-}\)), where OH\(^*\) is the primary oxidant in the photocatalytic degradation of the pollutant in the aqueous solution. The generation of OH\(^*\) radicals normally occurs via two routes,

(i) H\(_2\)O and OH\(^-\) in the water environment are readily oxidized by photogenerated h\(^+\) to form OH\(^*\) radicals (equations 1.2 & 1.3).

(ii) O\(_2\) presented in the aqueous solution is reduced by photogenerated e\(^-\) to form O\(_2\)\(^{-}\) radicals (equation 1.5), followed by reacting with H\(^+\) (forming OOH\(^*\) radicals – equation 1.6) and then further decomposition to produce OH\(^*\) radicals (equations 1.7, 1.8 & 1.9).

Moreover, the photogenerated h\(^+\) is widely considered as an oxidant for directly degrading organic contaminants, the capacity of which depends on the catalyst type and oxidation conditions [9-13]. Also, it was observed that the photocatalytic degradation of the pollutants depends upon various parameters such as, concentration of dye, pH of dye solution and catalyst, temperature, oxidizing agents, dopant content and catalyst loading [14-17]. In addition to this the selection of suitable light source is necessary for different type of the catalysts used [18-20]. It is therefore compulsory to investigate the various reaction conditions, as this will provide hints for better photocatalytic performance.

### 1.3. Titanium Dioxide (TiO\(_2\)) as a Photocatalyst

Photosensitization effect of TiO\(_2\) was first demonstrated by Fujishima and Honda in 1972 [21], since then TiO\(_2\) has been studied intensively for the application for light-driven photocatalytic water splitting due to its high chemical stability, abundance, non-toxic nature, low cost, and favourable bandgap structure which allows the redox reactions [22-26]. TiO\(_2\) crystallizes in three different allotropic forms: anatase, rutile, and brookite. Only anatase (3.2eV) and rutile (3.0 eV) phases exhibit photocatalytic property, in which anatase is a more active phase. This is due to indirect band gap in anatase crystal structure, which exhibits a longer lifetime of photoexcited electrons and holes than direct band gap rutile phase [27]. And the other reason is anatase phase has band gap \(\approx 0.2\) eV greater than rutile phase, which increases the reductive potential of electrons and facilitates better charge transfer from
anatase TiO$_2$ to adsorbed molecules [28]. However, the large band gap of TiO$_2$ limits the photocatalytic activity only to the UV region, which is just 3-5% of sunlight at Earth’s surface. The inefficient exploitation of visible light (42-43% of sunlight at Earth’s surface) by TiO$_2$ can be overcome by altering the electronic structure of TiO$_2$ by doping (non-metal & metal), loading co-catalyst and hydrogenation.

Nonmetal elements like B, C, N, P, S, and halides are doped with TiO$_2$ to improve light absorption at visible region and to enhance charge transport properties. TiO$_2$ doped with 5 and 8 weight % of B showed a weak absorption band in the range of 400-600nm and improved the photocatalytic activity of TiO$_2$ under visible light region [29]. Carbon-doped TiO$_2$ showed enhanced absorption in the entire visible light region and exhibited a high photocatalytic degradation activity of methylene blue under UV-Visible light irradiation [30]. Nitrogen doping with TiO$_2$ creates delocalized electronic states in both valence band (N 2p and O 2p) and conduction band (Ti 3d), reducing the band gap of TiO$_2$ to ≈2.6 eV which enables the photocatalytic activity under visible light spectrum [31]. TiO$_2$ doped with halides such as F, Cl and Br increase the photocatalytic activity in the visible spectral region [32, 33].

Metal ions doped in photocatalytic materials are extensively studied and some metal ions showed an effective photocatalytic activity of water splitting reactions. Wonyong Choi et al [34] synthesized TiO$_2$ doped with various metal ions and found not all metal ions enhance the photocatalytic activity. Metal ions like V$^{4+}$, Fe$^{3+}$, Mo$^{5+}$, Ru$^{3+}$, Rh$^{3+}$, Re$^{5+}$ and Os$^{3+}$ increased the photoactivity of TiO$_2$ nanoparticles while doping with Al$^{3+}$ and Co$^{3+}$ reduced the photoactivity of TiO$_2$. Cr$^{3+}$ metal ion is also one of the worst dopants among other metal ions because it traps the electrons generated from TiO$_2$ during optical irradiation [35]. The doping of lanthanide ions (e.g. Eu$^{3+}$, Gd$^{3+}$, Ho$^{3+}$ and Yb$^{3+}$) and the co-doping with Nd$^{3+}$ : Er$^{3+}$, Nd$^{3+}$ : Eu$^{3+}$ or Eu$^{3+}$ : Ho$^{3+}$ pairs were reported to improve the photocatalytic activity of TiO$_2$ [36,37]. Cerium ions Ce$^{3+}$ and Ce$^{4+}$ dopants in TiO$_2$ showed high and less photocatalytic activity respectively than pure TiO$_2$. This is because Ce$^{4+}$ traps the electrons which are photoexcited from TiO$_2$. [38]

Co-catalyst is loaded on TiO$_2$ instead of or in addition to doping non-metal or metal components. Though dopants help us to reduce the band gap of TiO$_2$ in-order to generate visible light active TiO$_2$, this in-turn reduces the reduction potential of photoexcited electrons. Heterostructure TiO$_2$ is created by loading different co-catalyst like pure metals (Au, Pt, Ru, Rh, Pd, Ag) [39-43], metal oxides (MnO$_x$, FeO$_x$, CoO$_x$, NiO$_x$, CuO$_x$) [44], and chalcogenides
(MoS$_2$, WS$_2$, CdS, CdSe, SnS$_2$) [45-48] to exhibit superior photocatalytic redox reaction. Loading dual co-catalysts increases the photocatalytic activity of the TiO$_2$ (WS$_2$/g-C$_3$N$_4$, CuS/NiS) [49-51].

Hydrogenation of TiO$_2$ extends the photon absorption spectrum from the UV region to UV-Visible region. This was first reported by Chen et al. [52], where pure TiO$_2$ (white powder) hydrogenated at high pressure (20 bar, H$_2$ atmosphere) and at high temperature (200°C) for 5 days. The hydrogenation process creates surface defects and oxygen vacancies, which leads to the formation of Ti$^{3+}$ centers. TiO$_2$ defects with Ti$^{3+}$ shifts the valence band upwards which narrows the band gap [53] and due to this the colour of TiO$_2$ changes into black. Ti$^{3+}$ and presence of oxygen vacancy reduces the charge recombination rate, thus improves the photocatalytic activity of TiO$_2$ [54]. Recent reports showed that hydrogenation of TiO$_2$ can also be achieved by plasma, which is much more effective and simple than conventional furnace heating process [55].

1.4. Copper Oxide (Cu$_2$O/CuO) as a Photocatalyst

Copper oxide is a promising material for large-scale, economic solar energy conversion due to the abundance of copper, suitable band gap, and ease of fabrication. Copper, depending on the valence state majorly exist in two different oxidation states: Cu$^{2+}$ (Cupric Oxide, CuO) and Cu$^{1+}$ (Cuprous Oxide, Cu$_2$O). Nanostructured CuO and Cu$_2$O are typical p-type semiconductors having a band gap in the range of 1.7eV and 2.2eV respectively. These two copper oxides recently attracted the interests of researchers due to their promising applications in the fields of water purification [56] and other photocatalytic applications [57,58]. The photocatalytic activity of CuO/Cu$_2$O is limited by two main drawbacks: (1) high charge recombination rate due to mismatch of the intrinsic carrier diffusion length (usually 20-100 nm) with the light absorption depth (approximately 10 μm); and (2) poor stability due to self-photo-corrosion in aqueous solution [59]. To achieve less charge recombination and better photocatalytic performance, 1D nanostructures with high aspect ratio are preferred in wastewater treatment [60]. To suppress photo-corrosion and enhance the photocatalytic activity copper oxide is loaded co-catalyst. Yongwoo Kwon et al. synthesized different morphology Cu$_2$O and studied its photo-corrosion rate with & without loading TiO$_2$ as co-catalyst. Cu$_2$O without co-catalyst within an aqueous solution under light irradiation experienced photo-corrosion. Whereas this was suppressed when Cu$_2$O got loaded with TiO$_2$.
Cu$_2$O nanowires coated with a thin layer of carbon, which avoids the Cu$_2$O from direct contact with the aqueous solution and exhibited remarkably improved photo-stability and reduced photo-corrosion during water splitting process [59,62]. Meenal Deo et al fabricated Cu$_2$O needle branched with ZnO. This Cu$_2$O/ZnO hetero-nanobrush structure degrades methyl orange dye effectively than only Cu$_2$O [63]. Recently, Youn Jeong Jang et al fabricated branched CuO without any co-catalyst or protective layer and their research reported the highest value of photocurrent -4.4 mA cm$^{-2}$ at 0 V$_{RHE}$ [64]. Definitely, the photocurrent value and photocatalytic activity of CuO can be enhanced by adding appropriate co-catalyst.

1.5. Molybdenum Disulfide (MoS$_2$) as a Co-catalyst

Molybdenum disulfide (MoS$_2$) with 2D nanostructure has become one of the most promising co-catalysts due to its high photocatalytic activity. MoS$_2$ has a two-dimensional layered structure, with the individual layers stacked upon each other by weak van der Waals forces to form the bulk and each layer consists of a plane of Mo atoms sandwiched between two planes of S atoms [65]. The bulk MoS$_2$ has a small indirect bandgap (1.3 eV), which is not sufficient to induce photocatalytic reactions and not beneficial for the separation of charge carriers. However when the size of MoS$_2$ is reduced to the 2-D scale (e.g. MoS2 nanosheets), the indirect bandgap transfers to a direct bandgap of 1.9 eV [66]. Thus, the low-dimensional MoS$_2$ is considered as a promising visible light-responsive photocatalyst. According to the stacking sequence of MoS$_2$-layers and atomic coordination between a central Mo atom and surrounding S atoms, the MoS$_2$ crystal structure can be classified into 4 types: 1H, 1T, 2H and 3R [67]. In the MoS$_2$ crystal structure, 2H (semiconductor) is the most common phase and exhibit promising photocatalytic activity. Recent research is focused on exploring the photocatalytic activity of MoS$_2$ with a combination of 2H and 1T crystal structure. 2H (semiconductor) phase can be transformed into 1T (metallic) phase by different phase engineering process [68]. Zhipeng Liu et al. synthesized MoS$_2$ with the combination of 2H and 1T phase through a scalable hydrothermal method. 2H-MoS$_2$ with locally introduced 1T phase (1T/2H-MoS$_2$) is measured to have an exchange current density of 4.43x10$^{-4}$ A/cm$^2$, whereas pristine 2H-MoS$_2$ has only 2.03x10$^{-4}$ A/cm$^2$ [69]. This proves that 1T/2H-MoS$_2$ increases the charge transport rate which would directly influence the enhancement of photocatalytic activity. Recently, Jianqi Zhu et al. (2017) used low-pressure Argon plasma to induce the phase transformation of MoS$_2$ that is 2H $\rightarrow$ 1T [70].
1.6. Motivation
The global freshwater requirement has pushed us towards a situation where we need not only to fill the demand gap but also to achieve sustainability in the environment. Researchers and technologists are looking for efficient solutions to deal with water treatment, and one of these efficient solutions is the photocatalytic water splitting process [10-13].

1.7. Project aim
We aimed at understanding how the low powered atmospheric pressure plasma spray of the CuO under the oxygen atmosphere effect its inherent properties such as structural, electronic, morphological, hydrophilicity etc. Furthermore, we aimed to study the photocatalytic performance of MoS$_2$-TiO$_2$ nanocomposite with varied weight ratio of cocatalyst MoS$_2$. Brief pointwise description of our aims are as follow:

(1) The first aim is to understand the effect of the atmospheric pressure plasma spray of CuO to enrich its surface with hydroxyl groups that could help achieve the high photocatalytic activity. The plasma spray in the presence of an oxygen atmosphere causes superhydrophilic CuO surface that exhibited a higher degree of pollutant adsorption and faster degradation rate. Furthermore, we are aiming to investigate the changes in the crystal structure and morphology after 5 min plasma spraying of CuO. It was also aimed to compare the APPJ spraying of the catalyst under different atmospheres. Finally, to utilize the synthesised photocatalyst to remove the dye pollutant molecules from the wastewater under simulated solar light. It is expected that these development would bring potential opportunities to develop highly active low cost, nontoxic and large scale photocatalysts for industrial wastewater treatment.

(2) The Second aim is to use the single-step plasma technique for epitaxial growth of the copper oxide nanowires onto Cu substrate with highly hydrophilic surface properties. Further to investigate the changes in the isotropic properties of rapidly formed nanowire. Finally, to utilize the nanocomposite to remove the pollutant molecules phenol and paracetamol from the wastewater under solar light irradiations.

(3) Finally, a 2D MoS$_2$/TiO$_2$ nanocomposite has been synthesized with a varied weight ratio of MoS$_2$ for hybrid adsorption-degradation catalysis to achieve a high rate of pollutants removal from wastewater. The high surface area and abundant active sites of the synthesised
photocatalyst show promising textile dye pollutants removal. Specifically, to exploit an integrated approach of adsorption and photocatalysis to remove mixed dye pollutants (anionic and cationic). In addition, the thesis aimed to bring a deeper understanding of various parameters (catalyst amount, morphology, dye concentration etc.) in tackling mixed dye pollutants.

1.8. References:


Chapter 2
Experimental methods

In chapter 2, it was suggested the importance of photocatalyst with type II heterostructures and the material of interest (Cu$_2$O/CuO & TiO$_2$/MoS$_2$). This chapter will provide information about the procedures involved in the synthesis of nanostructures and the characterization techniques which will be used to optimize/understand the material properties.

2.1. Synthesis methods

2.1.1. Thermal Oxidation (Vapor-Liquid-Solid and Vapor-Solid Mechanisms):

Vapor-liquid-solid (VLS) and vapor-solid (VS) mechanisms promote one-dimensional (1D) metal oxides (MO) growth structures like nano-rods, nano-whiskers, and nanowires. Generally, VLS mechanism in MO (such as Titanium Oxide, TiO$_2$) is assisted by a metal catalyst (such as Gold, Au), which forms liquid alloy droplets on the substrate at high temperature. These liquid alloy droplets adsorb the vapor precursors (Oxygen) and attain supersaturated state, which drives the precipitation/reaction growth of 1D structures. Since the whole process involves vapor (precursor), liquid (metal catalyst alloy droplets) and solid (precipitation/reaction growth), this mechanism is referred to as VLS [1-3]. For the growth of TiO$_2$ 1D/2D nano-structures, gold is coated directly on Ti substrates and then heat treated at a high temperature, during which oxygen is adsorbed at the vapor-liquid interface and then diffuses into metal alloy (Au-Ti) liquid phase. At supersaturation stage, Ti & O crystallize to TiO$_2$ nucleation which leads to the formation of TiO$_2$ nanostructures – see Figure 2.1.

Figure 2.1. Schematic diagram of the growth mechanism of 1D TiO$_2$ structures over Au coated Ti substrate by VLS growth mechanism.
In this thesis work, titanium (Ti) substrates (wire mesh) are heat treated in an atmospheric furnace at a temperature of 800°C and 900°C with a heating rate of 15 °C/min for a time period of 4 hours and then allowed for natural cooling. A set of samples were sputtered with Gold (5 and 20nm thick) before the heat treatment process. Growth of TiO$_2$ nanostructures (nanoneedle) on Ti mesh are seen only above 800°C of atmospheric heating temperature. Ti substrates sputtered with 5nm thick of Gold (Au) shows less density of TiO$_2$ nanoneedle structures compared to substrates sputtered with 20nm. An increase in temperature from 800°C to 900°C changes the TiO$_2$ nanostructure from nanoneedle (1D) to nanoblade (2D) structure. During the initial phase of the reaction, Oxygen diffuses into the island of metal alloy Ti - Au and reacts with Titanium to form TiO$_2$. This reaction leads to the growth process in both axial and lateral direction. At lower temperature (800°C) the growth rate is fast in axial direction compared to lateral and the condition is reversed in high temperature (900°C). At higher temperature nanoneedle (1D) structure is initially formed and as the length increases the diffusion Ti to needle tip decreases, which increases the lateral growth to form nanoblade (2D) structure. Different morphology of TiO$_2$ can be obtained by controlling the parameters like ramping rate, cooling rate, soaking period and soaking temperature.

Whereas in VS mechanism the growth of a certain metal oxide (such as Copper Oxide, CuO/Cu$_2$O) nanowires are attained without the assist of a metal catalyst (Au) [4]. The precursor metal (Copper) act as a self-catalyst in which the gas molecules (Oxygen) surrounding the heated samples get dissociates on the surface of the sample and the adsorbed & diffuse into the metal, forming oxidized layer Cu$_2$O. When the oxygen diffusion is supersaturated on the sample surface nucleation of CuO is occurred and then strain is created within the sample surface due to lattice mismatch and difference in molecular volume of the two different oxide species (Cu$_2$O & CuO). These above factors influence the growth of CuO nanowires [5, 6] since this process does not involve any liquid droplets it is referred to as a vapor-solid mechanism.
In this work, Copper substrates (foil and grid) are heat treated in an atmospheric furnace at a temperature of 450˚C for a time period of 4 hours and undergoes natural cooling. Unlike Titanium, Copper does not require any metal catalyst for the growth of 1D metal oxide nanostructures. In Copper the surface oxidation starts only at the temperature 300˚C and 1D (nanowhiskers) structure is formed only after 400˚C. The synthesized nanostructure is the combination of both bottom seed layered Cu$_2$O and top grown CuO whiskers. Copper substrates heated at 450˚C for different soaking time (1, 2, 3 and 4 hours) showed an increase in nanowire length with respect to increasing in soaking time.

**2.1.2. Atmospheric Pressure Plasma Jet (APPJ) assisted VS Mechanism:**

Ionized gas plasma is characterized by a mixture of charged particles (negative electrons & positive ions) and neutral particles (atoms, molecules & radicals). Plasma is electrically quasi-neutral, which means in a macroscopic volume the count of negatively charged particles is very nearly equal to the count of positively charged particles. In a laboratory/industrial scale, gas discharged plasma is produced by applying a potential difference between two electrodes that are inserted in a reactor which is filled with inert or reactive gas, at a pressure ranging from few mTorr (low pressure) to atmospheric pressure. Low-Pressure Plasma (LPP) and Atmospheric pressure plasma (APP) have their own advantages & disadvantages with respect to the applications. For the current project work...
APPJ is more flexible to handle and avoids the complexity of vacuum connections which is required in LPP.

The in-house APPJ, the plasma discharge is ignited by applying radio frequency power through a series LC circuit between two stainless steel electrodes covered with quartz which function as a dielectric barrier discharge. The frequency used to drive the LC circuit has been chosen to be 13.56 MHz. The LC circuit consists of a tunable capacitor ($C_{ext} = 2 - 22 \text{ pF}$) and an inductor ($L = 16.5 \mu\text{H}$, Micrometals T68-6 core). When the applied frequency matches that of the LC circuit, the voltage drop across the electrodes gets amplified (resonance) to initiate a plasma discharge. At resonance, the voltage between the electrodes is measured to be 100 times that of the input voltage. In practise, when the plasma is ignited, the discharge gap also needs to be considered and added to the series LC circuit and has been optimised in the set-up. To account for any shift in the resonance frequency, the drive frequency of the signal generator is tuned accordingly to achieve the desired resonance.

In this work, copper foils are placed on a hot plate (pre-heated to 375°C) and simultaneously exposed to the APPJ for a time period of 5 minutes. This process results in growth of CuO nanowires on top Cu$_2$O seeded layer. The average length and diameter of CuO nanowires are 300nm and 50nm respectively. The growth mechanism of CuO nanowires are combination effect of thermal and plasma oxidation.

2.1.3. Hydrothermal Method:

Hydrothermal synthesis is a method to produce metal oxide nanoparticles/crystals from metal salt solutions (aqueous or non-aqueous) under high temperature and high-pressure conditions in a closed system [1] – see Figure 2.3. The synthesized particles, which are relatively insoluble under the ambient condition is collected, centrifuged, washed and calcinated. Hydrothermal reactor (Autoclave) mainly made up of two parts; outer high-quality stainless-steel jacket and inner Teflon liner or Teflon chamber. Generally, for metal oxide synthesis the reaction is carried out at a temperature between 100 - 220°C, though the autoclave can be heat treated to a maximum temperature of 250°C.
2.2. Synthesis of materials

2.2.1. Synthesis of Cupric Oxide (CuO) Thin Films:

CuO thin films were deposited on fluorine doped tin oxide (FTO) glass substrates using magnetron sputtering. All substrates were initially cleaned by ultrasonication in isopropanol (IPA) for 10 mins followed by drying in a nitrogen gas flow. Subsequently, the substrates were transferred to the sputtering chamber where CuO thin films were deposited in argon ambient at room temperature using a stoichiometric CuO target. Prior to deposition the chamber was pumped to high vacuum ($6 \times 10^{-4}$ mTorr) and then operated at 3 mTorr working pressure. The sputtering rate was optimized to achieve CuO films of average thickness $300 \pm 30$ nm.

The sputtered CuO films (surface area $\sim 150$ mm$^2$) were annealed at 375 °C on a hot plate and simultaneously exposed to an APPJ for 5 minutes. The films were kept at a distance of 5 mm from the electrodes to avoid arcing between the sample and electrodes surface. The plasma jet was operated with an input power of 10 watt at a frequency of 13.56 MHz and 12 dBm Radio frequency (RF) level. With helium as the carrier gas, flowing at 3 standard liters per minute (slpm) mixed with oxygen (1% of helium). The photocatalytic properties were then compared between as deposited copper oxide (CuO), copper oxide annealed at 375 °C for 5 mins [CuO(A)] and plasma functionalized CuO with simultaneous annealing for 5 mins [CuO(P)].
2.2.2. Synthesis of Copper Oxide Nanowires by Thermal Oxidation (VS Mechanism):

Copper substrates (foil surface area ~ 150 mm²) are heat treated in an atmospheric furnace at a temperature of 300, 375 & 450 °C for a time period of 4 hours. Copper substrates (wire mesh) are heat treated in an atmospheric furnace at a temperature of 450 °C for different soaking time (60/120/180/240 minutes).

2.2.3. Synthesis of Copper Oxide Nanowires by APPJ assisted VS Mechanism:

To grow nanowires, the copper foil (surface area ~ 150 mm²) was placed on a hot plate, pre-heated to 375 ± 10 °C and simultaneously exposed to the plasma jet for time varying from 1 min to 5 mins, with an interval of 1 min. The plasma was ignited using a gas mixture of helium and oxygen, corresponding flow rates of 3 slm and 30 sccm, respectively, with an input power of 10 watts. Distance between the jet and the copper substrate was maintained at 5 mm for all the exposure times.

2.2.4. Synthesis of MoS₂ nanoflakes in 3D flower structure

The MoS₂ was synthesized by using a simple hydrothermal method. Sodium molybdate dihydrate (0.5g) and thiourea (0.8g) are dissolved in 30 ml of distilled water (DI), and the solution volume was increased to 60 ml by adding 30 ml DI water, before transferring it to the Teflon lined stainless steel autoclave vessel (100ml volume). The hydrothermal treatment was carried out at 210 °C for 24 h and the system was naturally cooled. The obtained product was washed with ethanol and water, three times, respectively. The washed product was dried at 60 °C for 16 h and then mechanically ground to get fine powder particles. Even after multiple there are chance for the presence of trace amount of sodium and carbon.

2.2.5. Preparation of TiO₂ nanopowder solution

MPT-20 Titania paste 10g was dispersed in 30 ml of ethanol and stirred for one hour to form a homogenous solution (solution A). The volume of the solution was increased to 60 ml by adding DI water and then transferred to the autoclave vessel. The other treatment and washing cycle were the same as the MoS₂ synthesis process.
2.2.6. Synthesis of MoS$_2$/TiO$_2$ nanocomposites

The MoS$_2$/TiO$_2$ nanocomposites with different weight % of MoS$_2$ (such as 2.5, 5, 10, 20, 30, and 50 wt%) were synthesized by the hydrothermal method. These nanocomposites are coined as TM 2.5%, TM 5%, TM 10%, TM 20%, TM 30% and TM 50%, respectively. Sodium molybdate and thiourea weight was varied in 30 ml DI water to form a homogenous aqueous solution. This solution was added dropwise to the TiO$_2$ solution (solution A), which forms a 60 ml solution volume, and the final solution was stirred for one hour. The hydrothermal treatment condition was maintained the same as the synthesis of MoS$_2$ and TiO$_2$. All powder samples, including MoS$_2$, TiO$_2$, and MoS$_2$/TiO$_2$ nanocomposites, were annealed 150 °C for one hour under preheated atmospheric conditions.

2.3. Characterization:

2.3.1. Electron Microscope Techniques:

An electron microscope uses a beam of high-energy electrons and electromagnetic lenses to illuminate and magnify an image of the specimen, Whereas conventional optical microscope use light and optical lenses. The electron microscope can achieve a maximum magnification level of about 1 million times and for the optical microscope is just 2000 times. The resolution and magnification level of microscopes imposed by the wavelength of their source. Since electrons possess much smaller wavelength (2.5 – 12 picometer) than the visible light (400 – 700 nanometer), greater resolution and magnification is achieved in electron microscopes. There are 2 major types of electron microscopes are used in this thesis work, Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM).

2.3.1.1. Scanning Electron Microscope (SEM):

Scanning electron microscopy (SEM) can be harnessed to understand the surface morphology and elemental analysis of samples. In SEM, a focused beam of electron from electron gun interact with the sample which in turn induces the generation of secondary electron, back scattered electron, auger electron, characteristics x-rays and so on as shown in Figure 2.4 (a). The exact focus of beam of electron on the sample can be achieved only if beam of electrons pass through the various components as shown in Figure 2.4 (b). After the interaction of electron beam with the sample, generated electrons and X-rays are detected.
by multiple detectors which gives surface morphology and elemental compositions of the sample. The sample should possess an electrical conductivity property for SEM and if surface of the sample is not conductive, charge accumulation takes place on the sample surface which brings distortion in sample images. So, deposition of thin layer of gold (~10-20nm) is required to perform the analysis for nonconductive sample. Here, electrons are used as probe to evaluate the morphology of sample so its resolution can go up to 0.4nm. In our present work, we have employed M/s. ZEISS make SEM (Model: Supra 55VP) to examine the surface morphology of the samples.

![Figure 2.4](image)

Figure 2.4. Schematic of (a) electron beam interaction with the sample surface and (b) scanning electron microscope [16].

2.3.1.2. Transmission Electron Microscope (TEM):

High Voltage Electron Beam (40 – 400 keV) is transmitted through a specimen, in which part of electrons is transmitted and the other part is scattered. These transmitted electrons carry structural information about the specimen. Morphology and aspect ratio of 1D/2D structured nanomaterials makes a great impact on photocatalytic properties. TEM and SEM will help us to measure the diameter & length of metal oxide (MO) nanowires and analyze the morphology (sphere, cube, sheet etc) of MO nanoparticles & MoS$_2$. Since the
different phase/crystallographic structure of MO have different influence over the photocatalytic property, it is very important to identify the phase & crystal structure of the synthesized particles. Literature reports show that in the Copper oxide, Cu$_2$O has high photocatalytic property than CuO; in Titanium oxide anatase crystal structures shows better efficiency, and in MoS$_2$ the phase structure 2H with partial ratio 1T phase structure has better efficiency. SAED pattern and lattice spacing measurement from TEM provides the crystallographic information about the samples. Elemental mapping and composition analysis helps us to relate the photocatalytic efficiency with respect to increase or decrease in material composition. All the above information will support in tuning the particle size & shape, material composition, and selection of phase & crystal structure in order to achieve the better efficiency. The morphology of our samples were studied by high-resolution transmission electron microscopy (HRTEM, M/s. JEOL JEM 2100), operated at 200 kV.

2.3.2. Spectroscopic Techniques:

Spectroscopy deals with the production, measurement, and interpretation of spectra arising from the interaction of electromagnetic radiation with matter. Spectroscopic techniques differ with respect to the type of radiation-matter interaction to be analyzed (absorption, reflection or scattering - both elastic and inelastic) of electromagnetic radiation by the matter. This project involves 3 different spectroscopic techniques which are UV-Vis spectroscopy (UVS) [12], X-ray photoelectron spectroscopy (XPS) [13], and Raman spectroscopy (RS) [14, 15].

2.3.2.1. UV-Vis spectroscopy (UVS)

UVS is the measurement of the attenuation of the photon intensity after transmission through the sample or after reflection from a sample surface. UVS use 200 – 800 nm region of electromagnetic spectrum. Photon absorption and reflection properties of the material, band gap identification. In this thesis work the samples were analyzed by using a M/s. Thermo Scientific make UV-vis spectrophotometer (Model: Evolution 220).

2.3.2.2. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is one of the photoelectron spectroscopy (PES) in which existence of photoelectric effect triggers its utilization to investigate the
different chemical state of the surface of the sample. Photoelectric effect defined as emission electron from material by incident of electromagnetic radiation onto it. Similarly, in XPS, X-rays are being used as a radiation to emit a photoelectron from the sample surface. In typical XPS, though the X-ray penetrate deeply but photoelectrons come from about 5 nm of the sample surface. So it is a surface sensitive technique. Sputtering (ion milling) combining with the XPS measurements provides information about the depth analysis of sample which has more than 5nm depth. Figure 2.5. a depicts the instrumentation of XPS in which interaction of monochromatic X-ray radiation (X-ray source used in this project is non-monochromatic) with surface of sample leads to the emission a photoelectron from it. The energy of emitted photoelectron is measured by an analyser of electron energy. The core electron of an element has a unique binding energy, which seems like a "fingerprint". Thus almost all elements except for hydrogen and helium can be identified via measuring the binding energy of its core electron. Furthermore, the binding energy of core electron is very sensitive to the chemical environment of element. The same atom is bonded to the different chemical species, leading to the change in the binding energy of its core electron. The variation of binding energy results in the shift of the corresponding XPS peak, ranging from 0.1eV to 10eV. This effect is termed as "chemical shift", which can be applied to studying the chemical status of element in the surface. Therefore, XPS is also known as electron spectroscopy for chemical analysis (ESCA). Binding is calculated by following equation, \( \text{BE} = h\nu - \text{KE} - \Phi \). Where \( \text{BE} \) = Electron Binding Energy, \( \text{KE} \) = Electron Kinetic Energy, \( \Phi \) = Spectrometer Work Function, \( h \) = Planck’s constant and \( \nu \) = Frequency of X-rays. In our present work, we have used XPS to understand the various chemical states of the samples.

The surface chemical state of our samples were investigated by M/s. Kratos make XPS (Model: XSAM800) using non-monochromatic Mg K\( \alpha \) (1253.6 eV) anode source operated at 12kV and 10mA with base pressure <10\(^{-9}\) mbar within the analyzing chamber. High magification analyzer mode was chosen to collect electrons from an area of 4.0 mm\(^2\) on the specimen with the precision was ±0.2 eV for Binding Energy. The sample spectra were analyzed using the CasaXPS software, and the peak shift due to any apparent charging was calibrated with respect to adventitious carbon C1s peak at 284.8 eV. Sample spectra are convoluted with Gaussian and Lorentzian function having Shirley background.
2.3.2.3. Raman spectroscopy (RS)

RS technique uses a monochromatic laser light source (514nm) to irradiate a sample and generates an infinitesimal amount of Raman scattered light, which is detected as a Raman spectrum. The characteristic fingerprinting pattern in a Raman spectrum gives information about the sample such as crystallinity and crystal polymorphism, chemical & defect analysis, doping effects, contamination identification etc. Raman spectra of all samples were obtained by using a M/s. Horiba Jobin-Yvon make Raman spectrometer (Model: LabRAM HR Evolution) with 514.5 nm argon-ion LASER.

2.3.4. X ray diffraction technique (XRD)

XRD provides various structural information viz. different crystal planes, crystalline nature, crystalline size, strain, texture about the sample. In this technique, X-ray, whose wavelength comparable to inter atomic planes, are incident on the sample and diffracted in the crystal lattice. And it produces the diffraction pattern from which aforementioned structural parameter can be calculated. The diffraction of X-ray from the crystal plane can be explained by Bragg law. XRD pattern for all samples were recorded by using M/s. BRUKER
make (Model: D8 Advance) diffraction unit using Cu-Kα radiation \( (\lambda = 0.154060 \text{ nm}) \) operated at 40 kV and 40 mA.

### 2.3.5. Zeta Potential (ZP):

Zeta potential is a parameter that measures the electrochemical equilibrium at the particle-liquid interface. It measures the magnitude of electrostatic repulsion/attraction between particles and thus, it has become one of the fundamental parameters known to affect stability of colloidal particles. The most important factor that affects zeta potential is the pH of the medium and other factors include ionic strength, the concentration of any additives, and temperature. Zeta potential measurement of the photocatalyst and the organic dyes were measured using M/s. ANALYTIK oscillating piston design (Model: Stabino).

### 2.3.6. Contact Angle Measurement:

Contact angle measurement is a qualitative way to evaluate whether the surface has a hydrophobic or hydrophilic characteristic. It is based on the observation of the intermolecular interactions between the surface and a small drop of water when the drop meets the surface. It is mainly used to assess the wettability of a surface. Water contact angle (CA) of our samples were measured using attention M/s. Theta Lite make optical tensiometer with high purity distilled water.

### 2.4. Photocatalytic Activity Measurement.

The photocatalytic activity of the samples was evaluated by monitoring the degradation of organic dye irradiated under xenon light source (M/s. Asahi Spectra, HAL 320). The light source \( (300W, 75mW/cm^2, 350-1100nm, \text{ AM1.5G filter}) \) illuminated from the top with a distance of 20cm from the liquid surface. The intensity of the light source was tuned to attain 1 Sun condition, and the light illuminated area was maintained about 30mm x 30mm. Under the dark condition, the solution was magnetically stirred \( (150 \text{ RPM}) \) for 30 minutes at room temperature to attain the adsorption/desorption equilibrium. During the 3 hours of light illumination, 1 mL aliquot of the dye solution were collected at a time interval of every 30 mins. The liquid samples are transferred into a quartz cuvette (M/s. Hellma) and absorption spectra were recorded by using UV-vis spectrophotometer (M/s. Thermo Scientific, Evolution 220). The dye concentration is calculated based on calibration curve
developed in the UV–Vis absorbance spectroscopy measurement. The influence of dye concentration is analysed by dye degradation efficiency and which is calculated based on the following equation, Dye degradation efficiency (%) = \( \frac{(C_0 - C_t)}{C_0} \times 100 \). where, \( C_0 \) is initial dye concentration (mg/L) and \( C_t \) is dye concentration (mg/L) at time t. In our work, the experimental kinetic data of photocatalytic degradation of dye molecules by catalyst samples were fitted using Langmuir–Hinshelwood (L-H) kinetics / Single First-Order Rate Model, \( C_t = C_0 e^{-kt} \). Where, \( C_t \) = concentration at time t, \( C_0 \) = initial concentration, e = base e, k = rate constant of decline 1/days and t = time.

2.5. References


3.1. Introduction:

Here in this chapter copper oxide thin films (CuO) are fabricated and treated with an atomespheric pressure plasma jet (APPJ). The samples are tested for photocatalytic activity by studying the degradation of methylene blue (MB) dye having H$_2$O$_2$ has a sacrificing agent.

3.2. Basic charaterizations of Cupric Oxide (CuO) Thin Films:

One of the fundamental factors that influence the electrocatalytic activity is the surface wettability of the electrode [1]. During the process of water electrolysis, both oxygen evolution at anode and hydrogen evolution at cathode, are affected by the wettability of electrodes [2,3]. As electrolyte-wetting of the electrodes is critical for faster redox electron transfer and evolution of gas during electrochemical reactions, it has been reported that a hydrophilic surface enhances the extracellular electron transfer rate between microbes and electrode in a microbial fuel cell assembly [4]. In a water electrolysis process, the cell voltage, $E$, is represented as:

$$E = E_0 + \eta_{\text{anode}} + \eta_{\text{cathode}} + iR$$

where, “$E_0$” is the theoretical thermodynamic term, “$\eta_{\text{anode}}, \eta_{\text{cathode}}$” stands for the overpotential values at anode and cathode, respectively, and “$iR$” represents the Ohmic resistance [1]. iR drop results from the interfacial contact resistance between electrode-electrolyte and gas bubbles during electrolysis. During oxygen evolution at the electrode, the nucleation and growth of oxygen bubbles is retarded for a hydrophilic surface due to lowered adhesion of the generated gas [5]. This faster mass transfer keeps the nucleation sites free for new bubbles to be produced in succession. Moreover, the lower coverage of gas molecules on the electrode reduces the surface contact resistance. In our case, the as deposited CuO demonstrated an average (CA) of ~95° while after annealing for 5 mins, the CA value dropped to ~71° as can be observed from Figure 3.1. This could be due to the reduction in surface roughness after annealing. For CuO annealed in plasma atmosphere, the CA dropped
drastically to $\sim 10^\circ$, thus, turning the surface super-hydrophilic. This could lead to a significant drop in charge transfer resistance in the impedance spectra. Surface hydroxylation is one of the effective routes to enhance the hydrophilicity of the electrode material/surface [6]. Hydroxyl radicals induce polarity to the surface and enhances the hydrogen bonding between electrode and electrolyte. As already mentioned, plasma jets are an abundant source of hydroxyl and oxygen radicals, seen in Figure 3.2(d). The exposure to plasma acted as the hydrophilic treatment resulting in the increase of electrodes surface energy.

**Figure 3.1.** Water contact angle for (a) as deposited CuO (b) air-annealed CuO (A), (c) CuO annealed in presence of plasma (P), (d) variation in contact angle for the three CuO surfaces.
Figure 3.2. Scanning electron microscope image of (a) CuO, (b) CuO(A), (c) CuO(P) thin films, (d) optical emission spectra corresponding to He + O$_2$ and He + N$_2$ plasma jet.

Electron micrographs of the as deposited CuO films reveal a very smooth surface composed of nano-sized crystallites. Thermally annealed CuO [Figure 3.2(b)] shows similar surface morphology to the as-deposited CuO thin film [Figure 3.2(a)]. Our previous study showed that grain boundaries become prominent when annealed at 550 °C. Annealing in the plasma environment increases the surface roughness and noticeable patterns are formed on the surface of the film [Figure 3.2(c)]. Increasing the surface area is one of the potent routes for enhancing the electrocatalytic and photocatalytic activity of the catalyst. By introducing nanoscale surface features the active area of the catalyst could be increased, in turn enhancing the catalytic activity [7]. The distinctive surface features observed in the plasma functionalised film could be resulting from the strain developed during grain boundary sliding.

Interestingly, Studies have shown that formation of patterned and rough surfaces increases the water contact angle [8-10]. However in contrast to these reports, the patterned CuO surface is superhydrophillic in nature. This could mostly be due to formation of surface oxygen or hydroxyl groups that promote water contact through hydrogen bonding. The evolution of microstructure is initiated when the temperature is high enough to overcome the activation energy of grain boundary motion. From the electron micrograph for CuO(A) it is clear that in
the described timescale and at 375 °C there is no observable microstrutural evolution [Figure 3.2(b)]. However, plasma accelerates the process of grain growth by decreasing the interfacial energy. Plasmas are known to increase entropy during lattice transformation by inducing deformation and defects [11]. Figure 3.2(d) shows the optical emission spectra for He + O\(_2\) and He + N\(_2\) plasma jets. The emission spectra reveal a variety of emission peaks within the wavelength range of 200 nm to 880 nm. APPJ’s are rich in neutral and charged species and radicals. Of these oxygen radicals are highly active and can diffuse into the surface resulting in unusual surface morphologies [11]. Presence of these surface features in CuO(P) could play a critical role in enhancing the catalytic properties of this electrode material.

The structural properties of the three electrode materials were studied using X-ray diffraction and Raman spectroscopy. No distinctive peak could be observed for as-deposited CuO. This is due to the lack of long-range order in the lattice of as-deposited CuO thin films due to the lack of long-range order in the lattice [Figure 3.3(a)]. Our previous study showed that post synthesis annealing is essential to enhance the crystallinity of the sputtered films. The diffractogram for CuO(A) was found to be very similar to CuO, showing 5 mins of thermal annealing is not sufficient to induce crystallinity in the lattice. [Figure 3.3(a)] However, for CuO(P) the diffractogram showed for CuO(P), shows the presence of two prominent peaks between 20 and 25°. The peak at 23.4° could be assigned to (0 2 1) lattice of Cu(OH)\(_2\) [12]. CuO(P) showed enhanced crystallinity with grain growth along the (0 0 2)/(−1 1 1) lattice orientation at 35.7° as shown in the inset of Figure 3.3(a). This observation also confirms that plasma accelerates the evolution of microstructure. The preferential growth along (0 0 2)/(−1 1 1) could be due to the low binding energy of these low index crystal planes. At high temperature, thermal energy provides the required energy to make the adatoms mobile, thus, reaching the favoured lattice positions. The increase in entropy from the presence of plasma enhances the mobility of these adatoms. Raman spectroscopy is a complementary technique to identify the structural disorder, defects, and crystallinity of thin film. Full width at half maxima (FWHM) of the Raman peaks can be used as a measure of the crystallinity of nanostructure films. For nanometre sized system, phonon confinement plays a crucial role. This phenomenon leads to the apparent shift and broadening of the Raman peak. The Raman spectra for CuO (red line) shows a broad feature at 570 cm\(^{-1}\) [Figure 3.3(b)]. The absence of any other phonon mode proves the absence of any long-range order or crystallinity in the as-synthesised thin films. After thermal treatment, characteristic modes of CuO could be
observed in the Raman Spectra. For crystalline CuO, distinct peaks are observed around 290, 340 and 620 cm\(^{-1}\) corresponding to \(A_{1g}, B_{1g}\) and \(B_{2g}\) phonon modes respectively. In Raman spectra, peaks become intense and show blue shift with increase in grain size whereas red shift is associated with lattice strain. Both of these phenomena could be observed in the Raman spectra for CuO(A) and CuO(P) [Figure 3.3(b)]. The increase in intensity for \(A_{1g}\) and \(B_{2g}\) modes with plasma functionalisation relates to the larger crystallite size for CuO(P). Moreover, the \(B_{2g}\) mode shifts to higher wave number for CuO(P) indicating the order in lattice. Interestingly, the \(A_{1g}\) mode [inset of Figure 3.3(b)] red shifts by 10 cm\(^{-1}\), revealing that plasma functionalisation introduces strain in the lattice. This could be due to lattice expansion or anisotropy caused by oxygen rich environment in the plasma. Findings from XRD and RAMAN analysis confirm that plasmas can introduce degeneracy in morphology and crystal structure which could prove advantageous for catalytic applications.

![Figure 3.3. (a) X-ray diffractogram and (b) Raman spectra comparing CuO, CuO(A), and CuO(P) thin films.](image)

X-ray photoelectron spectroscopy (XPS) was used to understand the variation in surface chemical and electronic properties of CuO, CuO(A) and CuO(P) thin films. APPJ consists of abundant oxygen, hydroxyl radicals and excited molecules that can induce disorder in the chemical, electronic and crystal structure of the surface being treated. XPS is a highly surface-sensitive technique with the signal originating from a thin layer at the surface (<5 nm). Any changes in the surface electronic and chemical environment would induce shifts in the core and valence energy levels. Figure 3.4 shows the corresponding Cu2p, Cu Auger, O1s core level and valence band spectra of the copper oxide samples. Figure 3.4(a) shows the characteristic Cu2p core level spectra of the copper oxide films, characterized by a doublet
feature at around 934.3 eV and 954.1 eV corresponding to Cu2p3/2 and Cu2p1/2 states, respectively, with a splitting of 19.8 eV. The Cu2p spectrum also shows a characteristic ‘shake-up’ satellite at 943.0 eV, which is ~8.7 eV separated from the primary Cu2p3/2 peak. Satellites are typical for copper oxides and occur due to multi-electron transitions between unoccupied Cu3d orbitals and O2p orbitals and confirm the Cu²⁺ state of the films [13-14]. For all samples, the presence of a series of shake-up satellite peaks observed at 941.5 ± 0.2 eV, 944.1 ± 0.2 eV and 962.6 ± 0.2 eV can be assigned to the unfilled Cu3d9 shell and corroborates to the +2 oxidation state of Cu [13]. Figure 3.4(a) illustrates the Cu 2p3/2 spectrum of CuO, CuO(A) and CuO(P) could be deconvoluted into two components around 933.7 ± 0.1 eV and 935.4 ± 0.2 eV to gain deeper understanding of the oxidation state of copper under different treatment conditions. The lower binding energy (BE) component for all the samples at ~933.7 eV was assigned to Cu²⁺ [15]. The higher energy component at ~935.4 eV is believed to have a contribution from Cu(OH)₂ as well as the other species adsorbed on the copper oxide films. This plasma-surface interaction to produce surface adsorbed species would validate the ~0.7 eV shift in the BE position of Cu(OH)₂ reported elsewhere in literature [16-17]. In addition, FWHM of the Cu²⁺ 2p3/2 decreases from 3.1 eV for as-prepared samples to 2.7 eV for CuO (A) and 2.9 eV for CuO(P) This would suggest an enhancement in the crystallinity of the samples after heat treatment. The disordered structure of CuO(P) could have resulted in relatively higher FWHM with respect to CuO(A). The Cu2p1/2 peak has also been fitted with two components at 953.2 and 955.1 eV keeping the parameters same as the 2p3/2 state. The oxidation state of Cu was further probed by investigating the Cu LMM region using X-ray induced Auger electron spectroscopy (AES) as shown in Figure 3.4(b). A sharp peak is observed at about 918.7 ± 0.2 eV (kinetic energy) corresponding to the Cu LMM Auger feature. Observed reduction in FWHM of the Cu LMM feature of the CuO films signifies rearrangement of surface chemical structure upon heat and plasma treatment.
The O1s spectra of as-prepared CuO sample was deconvoluted into two components corresponding to the lattice oxygen and a broad component with contribution from hydroxyl groups and/or surface-adsorbed oxygen, at ~529.5 ± 0.2 eV and ~531.3 ± 0.2 eV, respectively, as shown in Figure 3.4(c). The peak positions of the different O1s components are within ±0.2 eV of previously published reports [16]. The spectra of CuO(A) and CuO(P) shows significant variation in spectral feature. As Figure 3.4(c) illustrates, the lattice oxygen content of the films show an increase, both upon heat and plasma treatment, from 27.2% (as-deposited) to 53.4% (annealed) and 36.4% (plasma). This is proposed to result from the desorption of the hydroxyl groups from the surface upon thermal treatment along with crystallization of the lattice. In addition, a 0.2 eV reduction in the FWHM of the lattice oxygen also suggests the decrease in mixed ionic states of Cu at the surface of films. This enhancement in crystallinity of the samples post annealing can be corroborated from the reduction in the FWHM of the Cu$^{2+}$ main line as observed earlier. A considerable decrease in higher energy component is
observed for CuO(A), due to the temperature induced desorption of molecules. Interestingly, for CuO(P) this component presents a strong spectral signature along with a shift towards higher binding energy. Also, a 0.4 eV increase in FWHM of the higher BE component at ~531.3 eV of CuO(P) maybe assigned to the adsorption of different species from the APPJ which consists of abundant electronegative species including NO\textsubscript{x} and oxygen radicals (O\textsubscript{2}, radical *O2* or radical *O*). Exposure to plasma may result in the chemisorption of one or more of these species at the very surface of the films, thus resulting in shift of the electron cloud from the hydroxyl core. The positive shift in the O1s spectra maybe assigned to this charge separation. The valence band (VB) region of the samples was also probed as shown in Figure 3.4(d). Limited variation is observed in the line shape and position of the VB spectra of CuO and CuO(A) films. The Cu3d region is detectable around 3.0 eV below the Fermi level, as well as the O2p region, centred at around 5.0 eV. A significant shift of ~0.6 eV and enhancement in the partial density of states at ~5.0 eV is observed in the VB spectrum of CuO(P) films. This is most likely due to the enhanced contribution to the O2p states from the chemisorbed oxygen species or due to the quenching of lattice hydroxyl groups within the lattice. The 0.6 eV shift in the VB maxima (VBM) could be assigned to the formation of CuO(OH) due to the interaction of the OH\textsuperscript{−} and other radical groups in the plasma with the CuO film. The increase in density of states (DOS) around 5.0 eV also signifies the addition of hydroxyl groups into the CuO lattice. The peak intensity around below 0 eV in the VB is due to X-ray satellite artefact arised from non-chromatic X-ray source. The formation of additional features due to OH\textsuperscript{−} groups can be corroborated from the O1s spectra (Figure 3.4c).

To get insight into the variation in electronic and local structural properties with plasma functionalisation of the CuO catalysts, Cu K-edge X-ray absorption fine structure (XAFS) spectra including X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) was aquired. In contrast to XPS, XAFS probes the local electronic and structural details of a specific atomic species in the material [18]. Careful analysis of the EXAFS spectra provides information about the short-range order, atomic distances and coordination number with high accuracy and sensitivity. Figure 3.5(a) shows the normalized Cu K-edge spectra of the CuO catalysts. For comparison, a CuO reference has been presented simultaneously. The pre-edge region consists of three distinctive features: an intense peak at 8997.0 eV, a shakedown feature between 8980 and 8990 eV and a weak absorption pre-edge feature at 8977.0 eV. The intense edge feature corresponds to the
dipole-allowed transitions from $1s \rightarrow 4p$ (continuum) states. The weak pre-edge peak at 8977.0 eV results from the quadrapule allowed $1s \rightarrow 3d$ transitions. This feature is a signature of the Cu$^{2+}$ state stemming from its 3d9 configuration. For Cu$^{1+}$ because of the closed shell d10 configuration, these $1s \rightarrow 3d$ transitions cannot exist. Although, this $1s \rightarrow 3d$ transition is forbidden under the dipole selection rules, it could be detected due to the 3d + 4p orbital mixing along with vibronic and direct quadrupole coupling. Here, the quadrupole transitions can be neglected due to the much lower transition probability with respect to the dipole transitions. The shake-down feature corresponds to $1s \rightarrow 4pz$ transitions concurrent with ligand to metal charge transfer character. For Cu$^{2+}$ it can be observed as an intense peak at $\approx$8986 eV and shifts to lower energies for CuO (8980 eV) and Cu$^{1+}$ (8982 eV) [19]. It is to be noted that the features corresponding to CuO, but a small contribution from Cu$^{1+}$ could not be disregarded as well. However, there are signatures in the XANES region for both Cu$^{2+}$ and Cu$^{1+}$, this could be due to the distortion in the lattice symmetry of CuO. First derivative of the XANES spectra have been shown to make the pre-edge features more distinctive. Figure 3.5(b) indicates that there is significant variation in the local environment of copper between the samples. The as-deposited is partially in the Cu$_2$O type structure, as noted by the intensity of the feature at 8982 eV. After annealing for 5 mins, the structure reforms towards the characteristic CuO symmetry. Interestingly, the plasma functionalised sample showed a mixed phase of the Cu$_2$O-type and CuO-type structures, plasma treatment appears to partially restore some Cu$^{1+}$ species. The thin film annealed in the plasma atmosphere attains a superlattice structure due to the pseudo presence of Cu$_2$O like symmetry [20]. This could be due to the increase in entropy caused by the various energetic species in the plasma. Another reason could be the formation of bonds between Cu$^{2+}$ and OH$^-$ groups, which causes the formation of a distorted octahedron around Cu$^{2+}$ during the crystal growth. This observation can be corroborated to the distortion in the lattice in the form of red shift of the A$_{1g}$ mode in Raman spectra. XRD data also supports the formation of crystalline Cu(OH)$_2$ along with the growth of CuO grains.
Figure 3.5. (a) Cu K-edge XANES spectra of CuO thin films. The spectra are compared with standard CuO, Cu2O and Cu samples. (b) first derivatives of the Cu K-edge spectra, (c) EXAFS oscillations in k-space, (d) Fourier transforms (FTs) of the EXAFS oscillations. [Ex-situ X-ray absorption spectroscopy measurements were carried out at the SuperXAS beamline of the Swiss Light Source and the data was analyzed by Dr. Adam Hugh Clark, Paul Scherrer Institut (PSI), Switzerland]

To further understand the structural evolution, the post-edge features of the absorption spectra were analyzed. Figure 3.5 (c,d) shows the EXAFS spectra of the CuO catalysts in k-space and the Fourier transformed (FT) EXAFS spectra in R-space, respectively. For the k-space transformation the data range was taken from 2 to 12 Å−1 and fitted in the R-space in the range of 1–3.2 Å to obtain the structural parameters. In the (unphase corrected) R-space spectra, the peak between 1 and 2 Å arises from scattering due the Cu and first coordinate O while the second peak at 2–3 Å is associated with the Cu-Cu coordination [19]. Table 1 presents the calculated shell parameters i.e. bond-distance (R), coordination number (N) and Debye–Waller factor (σ2). From the XANES analysis, the chemical environment of the catalysts were found to be similar to CuO. Thus, we considered CuO as the primary model for fitting of all the catalysts. The FT oscillations reveals the difference in
The structural evolution of CuO annealed in two different environments. Though the first Cu2+-O2+ (~1.9 Å) and second Cu2+-Cu2+ (~2.9 Å) shells have similar structural parameters, the coordination numbers are distinctly different between CuO(A) and CuO(P) [20]. The slight decrease in the Cu-O and Cu-Cu coordination numbers suggests increased deformation in the local atomic arrangement of CuO(P) with respect to CuO(A) [21].

<table>
<thead>
<tr>
<th>Sample</th>
<th>Scattering Path</th>
<th>Radial Distance (Å)</th>
<th>Coordination Number</th>
<th>Debye Waller Factor (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO</td>
<td>Cu-O</td>
<td>1.93 ± 0.02</td>
<td>3.4 ± 0.3</td>
<td>0.005 ± 0.002</td>
</tr>
<tr>
<td></td>
<td>Cu-O</td>
<td>2.78 ± 0.04</td>
<td>0.8 ± 0.2</td>
<td>0.005 ± 0.002</td>
</tr>
<tr>
<td></td>
<td>Cu-Cu</td>
<td>2.86 ± 0.04</td>
<td>1.6 ± 0.2</td>
<td>0.010*</td>
</tr>
<tr>
<td>CuO(A)</td>
<td>Cu-O</td>
<td>1.95 ± 0.02</td>
<td>3.8 ± 0.3</td>
<td>0.003 ± 0.001</td>
</tr>
<tr>
<td></td>
<td>Cu-O</td>
<td>2.82 ± 0.02</td>
<td>1.1 ± 0.2</td>
<td>0.003 ± 0.001</td>
</tr>
<tr>
<td></td>
<td>Cu-Cu</td>
<td>2.92 ± 0.04</td>
<td>3.0 ± 0.4</td>
<td>0.010*</td>
</tr>
<tr>
<td>CuO(P)</td>
<td>Cu-O</td>
<td>1.94 ± 0.02</td>
<td>3.6 ± 0.3</td>
<td>0.004 ± 0.002</td>
</tr>
<tr>
<td></td>
<td>Cu-O</td>
<td>2.82 ± 0.02</td>
<td>1.0 ± 0.2</td>
<td>0.004 ± 0.002</td>
</tr>
<tr>
<td></td>
<td>Cu-Cu</td>
<td>2.91 ± 0.04</td>
<td>2.7 ± 0.3</td>
<td>0.010*</td>
</tr>
</tbody>
</table>

Table 3.1. Structural parameters of CuO, CuO(A) and CuO(P) determined from EXAFS measurement.

### 3.3. Photocatalytic Activity

CuO has been widely used as photocatalyst for degradation of organic pollutants. In this section, we intend to demonstrate that the activity of CuO photocatalysts could be boosted with plasma functionalisation and understand the possible underlying mechanism. The photocatalytic activity of CuO thin films (as-deposited, annealed, and plasma-treated) was investigated by using them to degrade Methylene Blue (MB) under visible light matching solar spectra, and the performance is compared in Figure 3.6. It is to be noted, all the photodegradation measurements were carried out in the presence of H₂O₂. Hydrogen peroxide (H₂O₂) accelerates the photocatalytic activity of CuO photocatalysts by acting as an electron scavenger and in releasing high energy radical .OH species which degrades the organic dye molecules. Two batches of CuO, CuO(A), and CuO(P) were used to study their
photocatalytic activity. In batch-I [Figure 3.6(a)], the photocatalyst thin films were immersed in the MB dye solution and stored in dark condition for 30 min at room temperature to attain the adsorption/desorption equilibrium. After the dark mode, the photocatalysts immersed in dye solution were irradiated with visible light. But in batch-II [Figure 3.6(c)], the photo-degradation test was undertaken directly under light mode without involving dark mode adsorption/desorption equilibrium. Photocatalytic degradation of dye molecules by catalyst samples were fitted using Langmuir–Hinshelwood (L-H) kinetics / Single First-Order Rate Model, \( C_t = C_0 e^{-kt} \). Where, \( C_t \) = concentration at time t, \( C_0 \) = initial concentration, e = base e, \( k \) = rate constant of decline 1/days and \( t \) = time. Figure 3.6(b) and (d) show the degradation kinetics of MB for the CuO films, and the rate constant (k) of degradation for each is obtained by calculating the slope of the plot ln\((C/C_0)\) vs. time where \( C_0 \) and \( C \) represent the concentrations of MB before and after light irradiation, respectively. In both the batches, the photocatalysts have the following order of photo-degradation efficiency and kinetic rate constant (k): CuO(P) > CuO > CuO(A).
It is reported that amorphous CuO has larger bandgap (2.3 eV) compared to annealed crystalline CuO (1.7 eV), which might favour the optical absorption property of visible spectra in amorphous CuO [22]. XRD and Raman results (Figure 3.3) indicate the amorphous nature of the as-deposited CuO. Annealing at 375 °C (5 min), improves the crystallinity of the CuO(A). Hence, the as-deposited CuO shows a higher MB degradation efficiency and rate constant (k) compared to CuO(A). However, (Figure 3.2) of as-deposited CuO and CuO(A) does not show any characteristic difference in morphology. SEM image (Figure 3.2) of CuO(P) showed the formation of nanodots on the surface. XRD and Raman spectra show further improvement in crystallinity for CuO(P) sample compared to CuO(A). Increase in crystallinity and grain size is one of the key factors which enhances the photocurrent generation or photocatalytic degradation in CuO. Also, these nanostructures could act as plasmonic centres to trap the light and enhance the optical absorption [23]. Thus, CuO(P) with higher surface area shows the degradation rate (k) of 0.0283 min$^{-1}$ (batch-I) and 0.0227 min$^{-1}$ (batch-II) which is higher than CuO (0.0173 min$^{-1}$) and CuO(A) (0.0139 min$^{-1}$). The average degradation efficiency of CuO(P) photocatalysts from the two batches was around 93% after 90 min of visible light irradiation, which is higher than CuO (80%) and CuO(A) (70%). This also proves the effectiveness of the proposed process; a higher degradation rate could be achieved with just 5 min of plasma treatment. Adsorption is another key factor that accelerates the degradation and plays a major role in the photocatalysis process. An increase in surface area and enhanced hydrophilic nature of CuO(P) promotes surface adsorption of dye molecules. The surface hydroxyl groups on CuO(P) surface, changes the surface potential to negative, which in turn shows greater adsorption affinity towards cationic MB dye molecules [24]. Upon solar light irradiation, the photo-excited holes (h$^+$) from the CuO(P) photocatalyst are captured by surface hydroxyl groups and then oxidize the organic dye molecules, which are adsorbed on
the photocatalyst surface [equation (2)]. The trapped holes within the hydroxyl groups also
activates the water oxidation process to release high energy hydroxyl radicals, which further
degradates the organic dye molecules in the aqueous medium [equation (3a), (3b)] [22]. CuO
gets etched during the photocatalysis and the copper ions leaches into the solution. So there
may be some homogeneous catalytic Cu$^{2+}$/Cu$^{+}$ with H$_2$O$_2$ leading to hydroxyl radical and
degradation of the dye.

\[ \text{h}^+ + \text{organic pollutant} \rightarrow \text{organic pollutant degradation} \]

\[ \text{h}^+ + \text{H}_2\text{O} \rightarrow \text{OH}^+ + \text{H}^+ \]  \hspace{1cm} (3a)

\[ \text{OH}^+ + \text{organic pollutant} \rightarrow \text{organic pollutant degradation} \]

Methylene Blue is used here as the model pollutant because its concentration can be
easily monitored using a UV–Vis Spectroscopy. However, as MB absorbs light in the visible
range the influence of this photo-absorption cannot be excluded while evaluating the real
photocatalytic activity of CuO thin film photocatalyst. To address this issue, we studied the
photocatalytic degradation of phenol, which absorbs in the UV region around 270 nm. Phenol
is routinely found in industrial wastewaters, mostly chemical and petrochemical industries
[25]. Figure 3.6(e) shows the UV–Vis absorption spectra of phenol taken at different intervals
of time. The spectral features show drastic changes when CuO(P) is used as the photocatalyst.
During photo degradation, phenol changes to p-benzoquinone (~240 nm) by the superoxide
radical and hydroquinone (~240 nm) by the hydroxyl radicals (radical OH$^*$) as shown in the
inset of Figure 3.6(e). Hydroquinone and benzoquinone represent the first step in oxidative
degradation of phenol. Previous reports have suggested that, these entities degrade further
via ring opening reactions [25]. The spontaneous decay of H$_2$O$_2$ to O$_2^-$ led to the formation
of benzoquinone even in the dark conditions, here H$_2$O$_2$ is used as the hole scavenger.
Comparing the UV–Vis spectra after 180 mins of light, plasma treated CuO shows faster
oxidative decay of phenol with respect to annealed CuO. Mainly due to the faster photo-
induced charge transfer accelerates the proposed reactions at the catalyst surface. These
photo-generated charge carriers react with H$_2$O$_2$ producing hydroxyl and superoxide radicals,
which breakdown phenol via multi step ring opening reactions. The results resented here
proves the efficacy of CuO(P) towards photodegradation of a range of organic pollutants. It is
understood that the formation of surface nanodots and surface hydroxyl groups on CuO(P)
are two main aspects that determine both adsorption and photocatalytic degradation of MB
represented schematically in Figure 3.7.
Figure 3.7. (a) Schematic illustration of CuO (or) CuO(A) with no characteristic surface morphology showing low MB dye adsorption and photocatalytic degradation; (b) CuO(P) with surface nanodots showing enhanced MB dye adsorption and enhanced photo degradation.

To further investigate the enhanced photocatalytic activity after plasma functionalisation Scanning Kelvin probe microscopy (SKPM) was carried out on these CuO thin films. In SKPM, a conducting tip with an applied bias is made to raster the sample surface and the feedback loop detects the surface potential (SP) as the difference in work function between the tip and the sample surface, i.e. $SP = \Phi_{\text{tip}} - \Phi_{\text{sample}}$. Hence the surface potential value can indicate toward the relative increase or decrease in work function of the sample being measured. It has been reported, that work function of the electrode material influence the electron and proton transfer at the double layer region eventually effecting the rate of catalysis [26]. In our case a considerable drop by 80 mV in surface potential is observed with plasma functionalisation as shown in Figure 3.8. This could be due to the formation of crystalline hydroxide. The presence of OH group lowers the energy level of the unoccupied states. The drop is also supported by the 0.6 eV shift towards higher BE the in the valence band emanating form the increased density of O 2p states. This also indicates that, with plasma functionalisation the Fermi level is positively shifted towards the water redox potential favouring the electron transfer processes require for catalysis. The defects in the crystal structure as seen in EXAFS can introduce additional states near the unoccupied region causing the shift of the Fermi level. Also the large space charge region caused by the surface
polar groups significantly enhances the electron-hole separation efficiency which in turn results in higher photocatalytic activity of the CuO [27].

**Figure 3.8.** Surface potential map for (a) CuO, (b) CuO(A) (c) CuO(P) (d) Average surface potential value for the three CuO films. With plasma functionalisation the work function dropped by 80 mV.

### 3.4. Summary

The present study demonstrates an innovative route to enhance the catalytic properties of CuO thin films using a low power atmospheric pressure plasma jet. The process involves annealing and simultaneously treating the CuO films with a helium-oxygen plasma jet. CuO films functionalized with APPJ demonstrated significantly higher electrocatalytic oxygen evolution and photocatalytic dye degradation activities. XRD and RAMAN studies revealed that plasma accelerated the crystallization of CuO domains and induced high degree of strain in the lattice. XANES and EXAFS techniques were applied to probe the local electronic/atomic structure of the CuO thin films. The spectral features revealed that for CuO(P) the atomic structure deviated from typical CuO structure. Additionally, with plasma functionalization CuO surface became highly hydrophilic and was attributed to the formation of polar surface groups. From XPS it was found that the polar nature of the CuO surface stem
from the electrostatically bonded hydroxyl radicals. The enhance density of states at O2p region of the valence band indicating the probable formation of CuOOH at near surface region. This unique surface chemistry significantly reduces the onset potential for oxygen evolution reaction by 130 mV. Moreover, these plasma treated electrodes achieved 3 times the current density compared to standard annealed electrodes, 10 mA cm\(^{-2}\) against 3 mA cm\(^{-2}\) respectively at 1 V vs SCE in 0.1 M KOH. It was demonstrated that the presence of oxygen in the plasma is necessary for the enhanced activities. The treated films also exhibited higher degree of dye adsorption and faster degradation of Methylene Blue and Phenol under simulated solar light. This work presents potential opportunities to develop highly active catalysts for water splitting and organic pollutant degradation applications using atmospheric pressure functionalized thin films.

**3.5. References:**


Chapter 4
Foil based copper oxide nanowires with enhanced stability for photocatalytic degradation of organic pollutants.

4.1. Abstract
In previous chapter the photocatalytic activity of sputtered copper oxide thin films was studied with and without plasma treatment. Though the thin film samples showed enhanced photocatalytic activity after the plasma treatment, the stability of the samples were very poor for the consecutive cycle. Here in this chapter copper oxide nanowires are grown directly on copper foils by thermal and plasma treatment. The samples were tested for photocatalytic performance and stability for multiple cycles.

4.2. Basic characterization of Copper Oxide Nanowires
From SEM the oxidation at temperature 300 °C and 375 °C shows a thin layer of CuO with a surface morphology like cabbage (Figure 4.1.a1 and 4.1.a2) and rice grain (Figure 4.1.b1 and 4.1.b2) respectively. And there was no formation of 1D nanostructures (nanowires) on the copper foil substrates at an oxidation temperature below 375 °C. Nanowire structures (Figure 4.1.c1 and 4.1.c2) formed around the temperature 450 °C and unlike Titanium, Copper does not require any metal catalyst for the growth of 1D metal oxide nanostructures.
Figure 4.1. SEM image of copper foil substrates with different oxidation temperature 300 °C, 375 °C and 450 °C showing the surface morphology cabbage (a1 and a2), rice grain (b1 and b2) and nanowire (c1 and c2) respectively.

Copper substrates (wire mesh) heat treated in an atmospheric furnace at 450 °C for different soaking time (60/120/180/240 minutes) to understand the growth of nanowires with respect to the increase in soaking time. The graph (Figure 4.2) shows the temperature profile used for the heat treatment cycle and then the samples undergone natural cooling.

Figure 4.2. Graph showing the temperature profile used to heat treat the copper substrates (wire mesh) for different soaking time.
Image J software tool is used to process the SEM images (Figure 4.3) and to measure the length of CuO Nanowires. Copper substrates heat treated at 450 °C for different soaking time (60/120/180/240 minutes) showed an increase in nanowire length with respect to increasing in soaking time. The average diameter of the nanowire remained the same (50nm) for all samples.

<table>
<thead>
<tr>
<th>Soaking Time</th>
<th>CuO Nanowire Length</th>
</tr>
</thead>
<tbody>
<tr>
<td>60 min (1 hr)</td>
<td>5 - 11μm</td>
</tr>
<tr>
<td>120 min (2 hr)</td>
<td>8 - 13μm</td>
</tr>
<tr>
<td>180 min (3 hr)</td>
<td>10 - 20μm</td>
</tr>
<tr>
<td>180 min (3 hr)</td>
<td>18 - 25 μm</td>
</tr>
</tbody>
</table>

**Table 4.1.** Tabulation showing the length of the nanowires with respect to different soaking period.
Figure 4.3. TEM images of copper wire mesh heat treated at 450 °C for 1 hr (a), 2 hr (b), 3 hr (c) and 4 hr (d) showing copper oxide nanowires on the surface of the copper mesh.

Literature review showed that the growth mechanism involves the formation of seeded thin layer Cu$_2$O bottom layer and then CuO nanowire top layer (Figure 4.4a). Copper oxide nanowires (nano-whiskers) grown by thermal oxidation on copper substrates were very fragile and showed poor adherence. Both Cu$_2$O seed layer and CuO nanowires are easily exfoliated by ultrasonication of the oxidized foil samples for 30 minutes in a propanol solution (Figure 4.4b). The obtained solution mixture was centrifuged at 2000 RPM, and the supernatant with CuO nano-whiskers were collected leaving behind the Cu$_2$O flakes. This was confirmed by dropcasting the solution mixture on silicon wafers and holey carbon support grids for SEM (Figure 4.4c & d) and TEM (Figure 4.5) characterization respectively.
Figure 4.4. Schematic diagram copper foil showing bottom seeded Cu$_2$O nanoflake layer and top CuO nanowire structures (a); IPA solution mixture of highly dispersed CuO nanowires/nanowhiskers with sedemented Cu$_2$O nanoflakes which are extracted from ultrasonication of oxidized copper foil sample (b); SEM image of CuO nanowires/nanowhiskers (c) and Cu$_2$O nanoflakes dropcasted on silicon wafer (d).

Figure 4.5. TEM images of copper oxide nanowires which got exfoliated from oxidized copper substrates and drop casted on holey carbon TEM grids.

XRD pattern of copper foil oxidized at 450 °C for 4 hour is shown in Figure 4.6. The sample shows the peak finger prints (2θ) confirming the presence of two oxide layers: Cu$_2$O (29.5, 36.4, 45.7, 61.3, and 74.4°) and CuO (32.1, 39.1, and 43.3°). The sharp and high intense Cu peaks (2θ = 50.9 and 44.1°) shows that the foil samples are majorly composed by metallic copper crystals than the mixed oxide composition, even exposing the metal foils to larger oxidation time period.
Figure 4.6. XRD pattern of copper foil oxidized at 450 °C for 4 hr showing the peaks for metallic copper, Cu$_2$O and CuO.

Copper foil substrate with CuO nano-whiskers showed (Figure 4.7) increase in contact angle (140°) compared to pure copper foil (65°).

Figure 4.7. Copper foil substrate with CuO nano-whiskers showed increase in contact angle (140°) compared to pure copper foil (65°).
Nanowire (NW) structured copper oxide layer grown on copper foil showed poor adherence on copper surface irrespective to the soaking period (oxidation period) and nanowires with micrometer length shows poor wettability (hydrophobic) which would result in low photocatalytic performance. And thus a different mode of synthesis process assisted with atmospheric pressure plasma was approached to increase the oxide layer adherence and also to get control over the oxidized nanowire length to achieve high photocatalytic performance.

CuO NWs were grown using atmospheric pressure plasma functionalisation of Cu substrates placed on a hot plate fixed at 375 °C ± 10 °C named CuOp. The processes were performed simultaneously to control the grain boundary diffusion in the plasma environment. The morphology of the copper foil, after heat treatment with simultaneous plasma-exposure was studied using SEM shown in Figure 4.8. The substrates were subjected to the He + O2 plasma jet for 1, 2, 3, 4, and 5 mins to inspect the growth dynamics of CuO NWs. From Figure 4.8a, it could be observed that after plasma-exposure, the copper foil gets oxidized forming a thin oxide film but there is no observable growth of nanowires till after 2 minutes of exposure time (Figure 4.8b). However, the grains of CuO could be distinctively observed. The nucleation sites or the seeding of the nanowires is observed after 3 minutes of plasma exposure as in Figure 4.8c. This shows that an optimal CuO film thickness is necessary to initiate the NW growth. The growth of nanowires becomes observable with the increase in treatment time from 3 to 5 minutes. The average length of the NWs after 5 minutes of plasma treatment were measured to be 300 ± 30 nm. Interestingly, no NWs were observed on the Cu substrates in the absence of the plasma jet (Figure 4.9). Here the substrates were exposed to the gas flow placed on a hot plate. This shows the efficacy of the atmospheric pressure plasma jet as a facile technique to grow copper oxide nanowires.
Figure 4.8. SEM image of copper foil after 1 min (a), 2 min (b), 3 min (c), 4 min (d), 5 min (e) of plasma assisted oxidation. SEM image of TEM grid after 5 mins of plasma oxidation (f).
During thermal oxidation atmospheric oxygen dissociates on the surface of the copper substrates causing a slow growth of the oxide layer. The formation of nanowires is preceded by the formation of Cu$_2$O followed by the gradual oxidation to CuO. (1) Unlike the thermal process, the plasma jet-induced oxidation is a thermodynamically non-equilibrium process. Here the reaction kinetics are accelerated by the energised species present in the plasma. Optical emission spectra (Figure 4.10a) of the plasma jet shows the presence of excited atomic oxygen (O*) lines at 616 nm, 777nm, 844 nm and molecular oxygen ion (O$_2^+$) lines at 526nm, 560 nm. (2) Here, nucleation of the nanowires is initiated by diffusion processes followed by growth due to recombination of the excited oxygen atoms at the surface. We have observed that the exposure of the substrates only to plasma is not sufficient to oxidise the surface. As diffusion of oxygen is favoured at higher temperatures (>300 °C) and occurs through the grain boundaries, an external source of energy was required. The electron backscatter diffraction (EBSD) images in Figure 4.11, shows the drastic increase in grain size of the copper foil after NW growth. During the oxidation process metal ions moves from the core to the surface and the oxygen ions diffuse to the bulk. This diffusion slows down with the increase in oxide thickness. With the oxide layer on top of Cu foil, strain is developed at the interface. These internal stresses in the Cu foil is released as protuberance from the foil, this is the stage when nucleation or seeding of the NWs starts as shown in Figure 4.10b. (3) Now the NW grows from the diffusion of Cu ions along bi-crystalline grain boundary from root to tip, where they react with adsorbed oxygen followed by surface diffusion towards the sidewall. There are two main factors which influences the effective growth of NWs: (i) increase in rate of oxygen species
adsorbed on the surface and (ii) low resident time of adsorbed oxygen species. APPJs are known to enhance the surface adsorption and stabilisation of oxygen radicals. (4, 5) High pressure gas flow from APPJs also lowers the resident time of oxygen species, which allows more oxygen species to get adsorbed on the surface and this relatively increases the amount of oxygen diffusing through the top layer. (6) The abundance of oxygen radicals as observed in the OES spectra is crucial for the rapid growth of NWs at high pressure. Also, the electrons in the plasma jet have enough energy to catalyse the dissociation or recombination of the oxygen molecules/ions on the NW surface. This results in oxidation of yet non-reacted copper ions. Heat released from the recombination to molecular oxygen can create a high temperature gradient at the NW tip, driving the accelerated surface diffusion of the adsorbed species. Thus, the plethora of electrically charged particles, neutrals and radicals in APPJ provides a considerable advantage since they open a multitude of possibilities within a single environment, enabling higher efficiency to the NW growth process. Moreover, the ballistic effects of high energy ions at the surface generates a large number of defects such as vacancies, interstitial atoms and lattice distortions.(7) These defects are known to increase the activity of the photocatalyst and will be discussed in the following sections. The activities of these plasma grown nanowires (CuOp) are compared with NWs grown through thermal annealing at 400 °C for 4 hour named CuOa.

**Figure 4.10.** Optical emission spectra of the atmospheric pressure plasma jet taken on the sample surface (a). Schematic representation of the NW growth in the plasma atmosphere (b). Recombination, dissociation and adsorption of various oxygen species drives the growth.
Figure 4.11. EBSD inverse pole Figures of as received copper foil (a) after 5 mins of plasma oxidation (b). Showing the increase in grain size due to the heat treatment.

The crystal structure and phases of these nanostructures were investigated using X-ray diffraction (XRD) and Raman spectroscopy. Figure 4.12a shows the comparative XRD patterns of CuOa and CuOp. For CuOa there is a distinctive sharp peak at 38.5° corresponding to the (111) lattice of CuO (JCPDS No. 045-0937), while the other intense peaks at 43.5, 50.7 and 74.3° corresponds to copper from the copper foil (JCPDS No. 04-0836). For the plasma treated sample two additional peaks could be observed at 36.4 and 61.1° corresponding to the cubic Cu$_2$O phase (JCPDS No. 05-0667). On comparing the two diffractograms no shift or broadening of the CuO features were observed between CuOa and CuOp, revealing the monoclinic structure of CuO is preserved in the bulk. For CuOp, Cu$_2$O contribution could be from the remnant partially oxidized layer which acts as the building block for CuO NWs. Maybe, 5 mins is not enough time to convert all Cu$_2$O to the CuO. As the vibrational properties of these materials are dependent on their crystal symmetry. Hence Raman spectroscopy a very sensitive to the phase of the material being studied. Raman Spectra for the CuOp and CuOa electrodes as shown in Figure 4.2b correlates well with the XRD results. Thermally grown NW electrodes (CuOa) shows the presence of CuO phase only, characterized by the peaks at 297, 345, and 632 cm$^{-1}$. The peak at 297 cm$^{-1}$ attributed or assigned to the $A_g$ mode, while the other two peaks correspond to the $B_g$ phonon modes of the CuO crystal. Whereas the APPJ assisted NW grown electrodes (CuOp) shows the presence of the Cu$_2$O phase (148, 216 and 650 cm$^{-1}$) in addition to CuO phase.
related to the Cu$_2$O phase are noticeably sharper, this is due to the relative larger size of Cu$_2$O grains. (9, 10) This also indicates the initially Cu oxidizes to Cu$_2$O, before eventually oxidizing to CuO.

Figure 4.12. X-ray diffractogram (a) and Raman spectra (b) of the copper foil annealed at 400 °C for 4 hours (CuOa) and copper foil plasma functionalised at 375 °C for 5 mins (CuOp).

In order to understand the surface chemistry of growth formation, X-ray photoelectron spectroscopy (XPS) was carried out on the treated and untreated copper foils. XPS is a powerful surface sensitive tool to probe the chemical and electronic properties at the very surface of the material, typically up to 5nm. Figure 4.13a shows the copper 2p core level spectra for the oxidized and pristine copper foils. Cu 2p core level spectra of the as received copper substrate shows two sharp peaks around 932.5 ± 0.1 eV and 952.4 ± 0.1 eV corresponding to Cu 2p$_{3/2}$ and Cu 2p$_{1/2}$ peaks of metallic copper (Cu$^0$) with a negligible satellite peak between 940.0 to 945.0 eV. On the other hand, the oxidized foils show considerable broadening of the core levels and a prominent satellite feature. The broadening occurs due to the presence of multiple oxidation states of copper (Cu$^{2+}$, Cu$^{1+}$, Cu$^0$) after copper oxide formation. [13] Satellite peaks are the signature of ground state 3$d^9$ configuration of divalent copper (Cu$^{2+}$). These satellite peaks originate due to the transfer of electrons from the O 2p to the Cu 3d orbital to screen the electric field of the core holes in the Cu 2p orbital created during the photoelectron emission process. The satellite feature for CuOp is weaker than CuOa, indicating to the lower O 2p to 3d charge transfer. This is attributed to the mixed valency of d orbitals (d$^9$ /d$^{10}$) or perturbations at O 2p density of states caused by oxygen vacancy. The deconvoluted Cu 2p$_{3/2}$ and O 1s spectra is shown in Figure 4.14. CuOp shows
the presence of three oxidation states at 932.4 ± 0.2 eV, 933.6 ± 0.2 eV and 935.1 ± 0.2 eV corresponding to Cu$_2$O, CuO and Cu(OH)$_2$ respectively. [11] While CuOa is predominantly in the Cu$^{2+}$ state, as would be expected after 4 hours of annealing in ambient and a high energy component around 935 ± 0.2 eV due to formation of surface copper hydroxide. [11] The presence of Cu$^+$ along with Cu$^{2+}$ partially screens the Auger transitions shifting the auger peak to lower kinetic energies and shift the valence levels to higher binding energy (Figure 4.13b and 4.13c). Considerable variation is observed in the O1s line shapes between the CuOp and CuOa. The O 1s spectrum for CuOp can be deconvoluted into lattice oxygen (529.6 ± 0.2 eV), oxygen defects or vacancies (530.7± 0.2 eV) and contribution from hydroxyl groups (531.8 ± 0.2 eV) [12]. The presence of an oxygen vacancy can affect the surrounding shell of the oxygen atoms by effectively altering their 1s binding energies and subsequent shells surrounding the vacancy. For CuOa the characteristic contribution from lattice oxygen dominates with lowered contribution from hydroxyl (531.8± 0.2 eV) and adsorbed molecular components (534.2 ± 0.2 eV). Oxygen vacancies in metal oxides induce increased doping density and also enhanced band bending towards the semiconductor interface. Higher doping density in metal oxides moves the Fermi energy towards the conduction band exhibiting metallic characteristic favouring the charge conductivity which lowers the electron-hole recombination rate and the band bending in heterostructured metal oxides favours the absorption of high energy photons. And thus the CuO with oxygen vacancies might exhibit enhanced photocatalytic activity. However, high concentrated oxygen vacancies in the photocatalyst can act as a charge-recombination centre promoting low photocatalytic performance.

**Figure 4.13.** (a) Cu 2p spectra of as received, plasma oxidized (5 mins) and annealed (400 °C 4hour) copper substrates.(b) Cu LMM auger spectra of plasma oxidized (5 mins) and annealed (400 °C 4hour) copper substrates.(c) Valence band spectra for plasma oxidized (5 mins) and annealed (400 °C 4hour) copper substrates.
Figure 4.14. Comparison between (a) Cu 2p$_{3/2}$ and (b) O 1s deconvoluted spectra for CuOp and CuOa NW electrode.

Transmission electron microscopy (TEM) was used to analyse the crystal structure and composition of the plasma synthesized nanowires. Figure 4.5(a) shows the TEM image of an individual plasma-grown nanowires with length > 400nm. Unlike thermally grown nanowires which tend to be tapered at the tip (Figure 4.15), plasma grown nanowires were observed to have a uniform cross section throughout their length with diameter ranging from 10 to 20 nm. Interestingly, some of the nanowires are highly oriented and single crystalline in nature (Figure 4.16). The single crystalline NWs followed the \( \langle 111 \rangle \) lattice planes of the base CuO. This could be due to the thermal recrystallisation of the NWs caused by the high temperature gradient from ion bombardment or oxygen recombination. For CuO, the surface with \( (111) \) plane has lowest specific surface energy, which is the energetically favourable surface for nucleation and growth. It has been reported that depending on the oxygen partial pressure and temperature, oxygen vacancies can be incorporated during the ordering
of the lattice. [18] Sun et al. determined that the CuO surface is not atomically flat but consists of high density of surface defects such as atomic steps, kinks, ledges, and vacancies resulting from the surface growth of the CuO NWs both along the length and width of the nanowire. [13] The high-resolution images in Figure 4.16 (b-d) highlights some of the defects in the lattice of CuO NWs. The inset of Figure 4.16 (b) shows the diffuse streak diffraction patterns from the single crystal CuO NW. Four-fold diffraction spot streaks are observed along the \( \langle 111 \rangle \) directions, which is an indication of the high defect densities in these nanowires on the \( \langle 111 \rangle \) planes. [14] Voids in the lattice highlighted in yellow circle showing the presence of vacancies. Figure 4.5 (c) shows the steps at the edge of the nanowires, emanating from the ion induced etching. Additionally, twining defects are also observable in the NWs. The electron diffraction pattern obtained from twin domains can be seen as spot splitting along the \( \langle 111 \rangle \) direction, as shown in Figure 4.16 (d).

![Figure 4.15](image)

**Figure 4.15.** HRTEM image of (a) CuO nanowires grown using plasma functionalisation and (b) highly magnified single crystal CuO nanowire with lattice spacing \( d=0.257\text{nm} \) which corresponds to \( \langle 111 \rangle \) crystal orientation.
4.3. Photocatalytic Activity

The photocatalytic activity of CuOP was evaluated by monitoring the degradation of Methylene Blue (MB) dye irradiated under xenon light source (M/s. Asahi Spectra, HAL 320). Foil sample of area 1.5cm² placed inside the glass vessel containing 20 mL of MB solution (10mg/L in deionized water), and the dye solution mixed with 1 ml of H₂O₂ (0.5M). The light source (300W, 75mW/cm², 350-1100nm, AM1.5G filter) illuminated from the top with a distance of 20cm from the liquid surface. The intensity of the light source was tuned to attain 1 SUN condition, and the light illuminated area was maintained about 30mm x 30mm. Under the dark condition, the solution was magnetically stirred (150 RPM) for 30 minutes at room temperature to attain the adsorption/desorption equilibrium. During the 3 hours of light illumination, 1 mL aliquot of the MB solution were collected at a time interval of every 30 mins. The liquid samples are transferred into a quartz cuvette (M/s. Hellma) and absorption spectra were recorded by using UV-vis spectrophotometer (M/s. Thermo Scientific, Evolution 220).
The photodegradation of MB by CuOp in presence of H$_2$O$_2$ is recorded by UV-Visible absorption spectra. Normalised spectra Figure 4.17(a) shows that the peak position absorbance intensity at $\approx$666nm decreases continually with an increase of light irradiation. XPS confirms the presence of surface hydroxyl groups, and the dark adsorption of MB dye molecules might be due this presence this surface hydroxyl. XPS, XRD and Raman also confirms the presence of Cu$_2$O along with CuO. Compared to CuO, Cu$_2$O is a promising photocatalytic material because it has a direct band gap structure with a favourable band gap (2.0 to 2.2 eV) showing high absorption coefficient towards visible light. In CuOp sample with CuO/Cu$_2$O heterostructure, the CuO with narrow band gap (1.3 to 1.6 eV) having the conduction band minimum (CBM) and valence band maximum (VBM) are lower than the corresponding bands of Cu$_2$O. The band edge positions CuO and Cu$_2$O forms a type II heterostructure, which enhances the charge transfer and charge separation rate resulting in improved photocatalytic activity. Hydrogen peroxide (H$_2$O$_2$) accelerates the photocatalytic activity of CuOp, by acting as a scavenger in releasing high energy OH$^*$ species which degrades the organic dye molecules. In addition to degrading the dye molecules, H$_2$O$_2$ also reacts with the sample surface hydroxyl groups (equation 1) and Cu$_2$O (equation 2a or 2b) to form CuO, and during photodegradation cycle Cu$_2$O also undergoes photo corrosion to form CuO (equation 3a and 3b). These possible two chemical reactions increase the concentration of CuO on the sample surface and hampers the sample dye removal properties (adsorption and photocatalysis).

$$2\text{Cu(OH)}_2 + \text{H}_2\text{O}_2 \rightarrow \text{Cu}_2\text{O} + 6\text{OH}^* \quad \text{(1)}$$

$$\text{Cu}_2\text{O} + \text{H}_2\text{O}_2 \rightarrow 2\text{CuO} + \text{OH}^* + \text{H}^+ \quad \text{(2a)}$$

$$\text{Cu}_2\text{O} + \text{H}_2\text{O}_2 \rightarrow 2\text{CuO} + \text{H}_2\text{O} \quad \text{(2b)}$$

$$2\text{H}_2\text{O} + 4\text{h}^+ \rightarrow \text{O}_2 + 4\text{H}^+ \quad \text{(3a)}$$

$$2\text{Cu}_2\text{O} + \text{O}_2 \rightarrow 4\text{CuO} \quad \text{(3b)}$$

Normalised spectra Figure 4.18(a) anf Figure 4.18(b) shows the repeatability cycle of photocatalytic experiments and there was no re-plasma treatment was carried out before starting the consecutive cycles. It is noticed that sample without re-plasma treatment shows decrease in dye adsorption rate with increase in number of photocatalytic cycle (Figure 4.18(c)). Which is due the surface reaction of sample with H$_2$O$_2$, modifying Cu(OH)$_2$ to CuO. Where as the sample with re-plasma treatment (5 mins) before every experimental cycle in order to restrain the multiple oxidation states / defects of CuOP showed dye adsorption
property (Figure 4.18(c)) increased by ≈30% after every plasma treatment. This increase in dye molecule adsorption is due to two reasons, (i) increase in surface area by increase in length of nano wires and (ii) restoring the surface hydroxyl group on the sample surface. Figure 4.18(d) shows the degradation rate of CuOP for all three cycles and pseudo-first order kinetics model was used to determine the rate constant (k), of photodegradation of MB with respect to light irradiation time. Dye degradation rate constant (k) for all three cycles of sample with re-plasma treatment was constant around 0.025 min$^{-1}$. But dye degradation rate constant (k) for the sample without no re-plasma treatment decreases with increase in cycle [0.023 min$^{-1}$ (1st cycle), 0.018 min$^{-1}$ (2nd cycle) and 0.018min$^{-1}$ (3rd cycle)]. This shows that the stability of the sample can be maintained just by 5 mins of plasma treatment and it is evident that plasma synthesized CuO nanowires could be a promising candidate for photocatalytic applications.

**Figure 4.17.** (a) Absorption spectra of methylene blue (MB) after photocatalytic degradation by CuOp, (b) adsorption and photocatalytic degradation of MB by the same CuOp sample for three cycle without intermediate plasma treatment; (c) dye removal (adsorption and photocatalytic) efficiency (%) of CuOp sample based on (b), (d) plot of photocatalytic degradation kinetics under light illuminated condition based on (b).
4.4. Summary:

In summary, we have successfully demonstrated a new APPJ assisted oxidation route to synthesise CuO NWs on copper substrate. The presence of ions, radicals and neutral species in the plasma are critical to the growth of these NWs. The state-of-the-art plasma jet used here operates at a minimal input power of 10W. Through this process, NWs of length 300±30 nm could be grown within 5 mins, which would require hours of thermal annealing to achieve. These NWs possess abundant defects as oxygen vacancies and lattice defects, which are introduced during the growth process and enhances the photocatalytic activity. It was also
demonstrated that a short duration plasma functionalization between cycles is an effective strategy to retain the activity and reuse the catalyst for prolonged operation.

4.5. References:


Chapter 5

Rapid removal/degradation of dye pollutants using TiO$_2$/MoS$_2$ nanocomposites

5.1. Abstract
In previous chapters we studied the photocatalytic activity and the stability of copper oxide nanowires grown on copper electrodes with H$_2$O$_2$ as sacrificing agent. This chapter investigates the adsorption and photocatalytic activity of MoS$_2$/TiO$_2$ nanocomposites with different weight percentage of MoS$_2$ (TM 2.5%, TM 5%, TM 10%, TM 20%, TM 30% and TM 50%) tested on both cationic and anionic dyes without H$_2$O$_2$ or any other sacrificing agent.

5.2. Basic characterization of TiO$_2$/MoS$_2$ nanocomposites:
As explained in the Chapter 2, MoS$_2$ was synthesized by using a simple hydrothermal method using sodium molybdate dihydrate and thiourea as precursors by dissolving them in distilled water (DI), whereas TiO$_2$ nanopowder was synthesized using MPT-20 Titania paste which was dispersed in ethanol. The MoS$_2$/TiO$_2$ nanocomposites with different weight % of MoS$_2$ were synthesized and the samples were identified as TM 2.5%, TM 5%, TM 10%, TM 20%, TM 30% and TM 50%, respectively.

The SEM image of hydrothermal synthesized MoS$_2$ powder is presented in Figure 5.1 (a1, a2 and a3). It shows a 3-D flower structure in 2 - 3 micron size. Further analyzing this sample by HRTEM (Figure 5.1.b1 and 5.2.b2), it clearly demonstrated that few-layer 2-D nanoflakes were bundled together and form a 3-D flower structure. The interspace distance of MoS$_2$ crystal lattice is estimated from the HRTEM image (Figure 5.1.b3) and found to be 0.64 nm and this corresponds to the (002) crystalline phase of MoS$_2$ (14). SEM (Figure 5.1.c1, 5.1.c2 and 5.1.c3) and TEM (Figure 5.1.d1, 5.1.d2 and 5.1.d3) image of commercially available TiO$_2$ (MPT 20) confirms the morphology of TiO$_2$ with average particle size 20nm. The interspace distance of TiO$_2$ crystal lattice is estimated from the HRTEM image (Figure 5.1.d3) and found to be 0.36 nm and this corresponds to the (101) anatase crystalline phase of TiO$_2$. 
Figure 5.1. SEM and TEM image of pure MoS$_2$ and TiO$_2$ [MoS$_2$ SEM (a1, a2, a3); MoS$_2$ TEM (b1, b2, b3); TiO$_2$ SEM (c1, c2, c3); TiO$_2$ TEM (d1, d2, d3)].

The SEM (Figure 5.3a) and HRTEM (Figure 5.3b and 5.3c) images of MoS$_2$ shows bundled and individual layer of MoS$_2$. The magnified MoS$_2$ HRTEM image showing interlayers (Figure 5.3d) and inverse FFT image of MoS$_2$ interlayers (Figure 5.3e) confirms the presence of MoS$_2$ (002) crystal phase having an interlayer spacing of ~0.64nm. In the case of 10 wt %, MoS$_2$ coated TiO$_2$ (TM 10%), the aggregated nanoflakes presence in the pristine MoS$_2$ became debundled as few-layer sheets (Figure 5.3f). These debundled few-layer MoS$_2$ nanosheets are
coated on the TiO₂ surface due to high van der Waal force during hydrothermal synthesis [1, 2] where the TiO₂ nanoparticles act as a substrate for the growth of a few-layered 2-D MoS₂ nanoflake. It was difficult to differentiate the TiO₂ and MoS₂ nanoparticles from SEM images (Figure 5.2a and 5.2b).

Figure 5.2. SEM image of MoS₂/TiO₂ nanocomposite TM 10%

But, the HRTEM image (Figure 5.3g) of TM10% illustrated a well-defined grain boundary between the MoS₂ (002) phase and the TiO₂ (101) phase, which infers the MoS₂/TiO₂ heterointerface. Interestingly, the diameter of the MoS₂ interspace layer is increased to 0.88 nm (Figure 5.3g and 5.3h) at MoS₂/TiO₂ nanocomposite compared to pristine MoS₂ (0.64 nm) in Figure 5.3d and 5.3e.
Figure 5.3. (a) SEM image of MoS$_2$. HRTEM images of MoS$_2$ measured at (b) 20 nm scale and (c) 5 nm scale. (d) High magnification TEM image of interlayers seen in Figure 2(c) at 2nm scale, and (e) respective inverse FFT image of MoS$_2$ interlayers. (f) HRTEM image of TM 10% (TiO$_2$/MoS$_2$) composite, (g) High magnification TEM image of interlayers seen at Figure 2(f) at 2nm scale, and Inverse FFT images of (h) MoS$_2$ interlayers (i) TiO$_2$ interlayers marked in Figure 2(g). (j) HRTEM image of TM 50% (TiO$_2$/MoS$_2$) composite, (k) High magnification TEM image of interlayers seen at Figure 2(j) at 2nm scale, and Inverse FFT images of (l) MoS$_2$ interlayers (m) TiO$_2$ interlayers marked in Figure 2(k).

The widening/expansion in the interlayer spacing of MoS$_2$ can be explained by the solvent effect. The ethanol is used as co-solvent in synthesis of MoS$_2$/TiO$_2$ in hydrothermal
reaction, resulting in increasing the interspace layer of MoS₂. In the hydrothermal process, Mo and S ions react to form MoS₂ nucleus, the resultant MoS₂ nucleus further accumulates and then grow interlayered nanosheets through a ripening process [3]. Here, the ethanol molecules get trapped between the layers of MoS₂, which weakens the van der Waals force and widens the interspace distance [4,5]. Also, at high temperature, weakened S-S van der Waals interactions and the reduced restacking probability of MoS₂ [6,7] may also be responsible for expanding the interspace layer. Further increasing the ratio of MoS₂ at composite TM 50% the interspace distance of MoS₂ is increased to 0.75 nm (Figure 5.3 (j-l) but this increase is lesser than TM 10%. The widening of MoS₂ interspace layer implies the transformation of 2H crystal phase towards 1T phase, resulting in partial phase conversion of MoS₂ in nanocomposites. Higher the wt% of MoS₂ lead to the increase in layer stacking and reduces the interspace distance of MoS₂. However, the interspace distance of TiO₂ remains constant in both TM 10% (Figure 5.3i) and TM 50% samples (Figure 5.3m) due to its thermal stability. Figure 5.4 shows the interlayer spacing of MoS₂ (002) crystal lattice at different position for pristine MoS₂, TM 10% and TM 50%. This again confirms the following order of lattice spacing, TM10% > TM50% > MoS₂.

Figure 5.4. Plot showing the MoS₂ (002) lattice spacing at different random location for pristine MoS₂, TM10% and TM50%
The X-ray powder diffraction (XRD) patterns of TiO$_2$, MoS$_2$ and different MoS$_2$ wt% based MoS$_2$/TiO$_2$ nanocomposites (TM 2.5%, TM 5%, TM 10%, TM 20%, TM 30% and TM 50%) are shown in Figure 5.5. The diffraction peaks of pure TiO$_2$ can be assigned to the (101), (103), (004), (200), (105), (211), (213), and (204) planes match the standard peak of anatase phase [8-10]. As for pure MoS$_2$, the detected peaks can be assigned to the (002), (100), (103), and (110) planes of the hexagonal phase [11]. It is difficult to observe MoS$_2$ reflections in the MoS$_2$/TiO$_2$ nanocomposites because MoS$_2$ is too thin to detect [12, 13]. The peak Si(002) is from silicon substrate which might be due to pin holes in the thin film samples.

![XRD pattern of MoS$_2$, TiO$_2$ and MoS$_2$/TiO$_2$ nanocomposites with different weight percentage of MoS$_2$.](image)

**Figure 5.5.** XRD pattern of MoS$_2$, TiO$_2$ and MoS$_2$/TiO$_2$ nanocomposites with different weight percentage of MoS$_2$.

Raman spectroscopy was carried out on the MoS$_2$, TiO$_2$, and TM 50% nanocomposite samples. In the spectrum obtained for TiO$_2$ (Figure 5.6a), the Raman active modes were
observed at 143.5 cm$^{-1}$($E_g$), 198.2 cm$^{-1}$($E_g$), 398.6 cm$^{-1}$($B_{1g}$), 517.9 cm$^{-1}$ ($A_{1g} + B_{1g}$) and 639.3 cm$^{-1}$ ($E_g$), which confirms the presence of anatase phase [14].

**Figure 5.6.** (a) Raman spectrum of TiO$_2$ showing active modes of anatase phase and (b) Raman spectra comparison of TiO$_2$ and TM50% showing peak shift and peak broadening in the insert.

The spectrum obtained for pure MoS$_2$ (Figure 5.7a) shows two prominent peaks, which correspond to the in-plane vibration of Mo and S atoms ($E_{1g}$ at 381.8 cm$^{-1}$) and out-of-plane vibration of S atoms ($A_{1g}$ at 409.1 cm$^{-1}$). The Raman spectra obtained for TM 50% (Figure 5.6b), confirms the presence of TiO$_2$ anatase phase, by matching with Raman peak values of pristine TiO$_2$. However, the MoS$_2$ peaks between the region 360 cm$^{-1}$ to 410 cm$^{-1}$ are superimposed by TiO$_2$ peak $B_{1g}$ (398.6 cm$^{-1}$), which unveils peak broadening and could not differentiate MoS$_2$ and TiO$_2$ Raman active peaks. And thus MoS$_2$ Raman spectrum acquired with a reduction in the acquisition rate for the nanocomposite TM 50%, and this condition was not favorable to acquire MoS$_2$ Raman peaks for the samples having less than 50wt% of MoS$_2$. Based on the literature, the lesser the peak position difference ($\Delta k$) between $E_{1g}$ and $A_{1g}$ of MoS$_2$, the lesser is the number of MoS$_2$ layers [15]. The Raman spectrum obtained for TM 50% (Figure 5.7b) shows that the peak difference ($\Delta k$) reduced from 27.3 cm$^{-1}$ (MoS$_2$) to 24.3 cm$^{-1}$ (nanocomposite), which suggests that the number of layers has been reduced from multilayer nanoflakes in pure MoS$_2$ to few-layer nanoflakes in the TM 50% nanocomposite. This is in line with HRTEM results of 3-D flower structure (Figure 5.3c) debundled to 2-D nanoflakes (Figure 5.3f and 5.3j).
Figure 5.7. Raman spectra of MoS$_2$ vibrational peaks ($E_{2g}^1$ and $A_{1g}$) in (a) MoS$_2$ and (b) TM 50% showing $\Delta k$. 
X-ray photoelectron spectroscopy (XPS) results of MoS$_2$ and MoS$_2$/TiO$_2$ nanocomposite (TM 2.5% and TM 50%) are presented in Figure 5.8 (a-f). Irrespective of MoS$_2$ wt%, the analysis of deconvoluted Mo3d spectra (Figure 5.8 (a), (c), and (e)) in all nanocomposite samples shows two oxidation states of Molybdenum, Mo$^{4+}$ and Mo$^{6+}$. The Mo3d spectrum of TM 2.5% sample (Figure 5.7c) shows peak at 227.36eV, 230.56eV, 230.92eV and 234.12eV can be ascribed to Mo$^{4+}$ 3d$_{5/2}$ (MoS$_2$), Mo$^{4+}$ 3d$_{1/2}$ (MoS$_2$), Mo$^{6+}$ 3d$_{5/2}$ (MoSO$_4$ / MoO$_3$) and Mo$^{6+}$ 3d$_{1/2}$ (MoSO$_4$ / MoO$_3$), respectively [16]. The presence of sulfide (MoS$_2$, Mo$^{4+}$) and sulfate (MoSO$_4$, Mo$^{6+}$) also confirmed from the analysis of deconvoluted S2p spectra (Figure 5.8 (b), (d) and (f)) in all samples. The S2p spectrum of TM 2.5% (Figure 5.8b)) shows two distinct peaks having binding energy (BE) position at 161.3eV and 167.5eV, which can be assigned to sulfides and sulfates, respectively. These two major peaks are deconvoluted further which gave rise to four peaks at the BE position 160.99eV (S2p$_{3/2}$ - MoS$_2$), 162.29 eV (S2p$_{1/2}$ – MoS$_2$), 167.30eV (S2p$_{3/2}$ – MoSO$_4$) and 168.60 (S2p$_{1/2}$ – MoSO$_4$). It also noted that by increase in MoS$_2$ wt% in the MoS$_2$/TiO$_2$ composites, there was increase in Mo$^{4+}$ (MoS$_2$) and sulfide (MoS$_2$) peak area, compared to Mo$^{6+}$ (MoSO$_4$/MoO$_3$) and sulfate (MoSO$_4$). From the Table 1, it is shown that the peak positions of Mo3d and S2p shift towards higher BE level (i.e., shows redshift) with an increase in MoS$_2$ wt%. The Mo$^{6+}$ peaks of pristine MoS$_2$ (Figure 5.8a) at 232.73eV and 235.93eV can be ascribed to MoO$_3$, and from the S2p spectrum (Figure 5.8b), it was confirmed that the sulfate group was absent in pure MoS$_2$. The formation of molybdenum sulfate within MoS$_2$/ TiO$_2$ composites might be due to the presence of ethanol during the synthesis process. Ethanol was not used in pristine MoS$_2$ synthesis, and thus, this justifies the absence of sulfate group in pure MoS$_2$. 
Figure 5.8. XPS core level spectra of MoS$_2$ - Mo3d (a), MoS2 - S2p (b), TM 2.5% - Mo3d (c), TM 2.5% - S2p (d), TM 50% - Mo3d (e) and TM 50% - Mo3d (f).
Table 5.1: The fitted Mo3d and S2p peak position and atomic percentage of TM 2.5%, TM 50% and pure MoS$_2$.

<table>
<thead>
<tr>
<th>Samples</th>
<th>3d$_{5/2}$ (eV)</th>
<th>3d$_{3/2}$ (eV)</th>
<th>3s (eV)</th>
<th>S-Mo (eV)</th>
<th>S-O (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo$^{4+}$</td>
<td>227.36 (6.8)</td>
<td>230.56 (4.56)</td>
<td>230.92 (57.20)</td>
<td>230.92 (19.42)</td>
<td>234.12 (12.02)</td>
</tr>
<tr>
<td>Mo$^{6+}$</td>
<td>234.12 (19.42)</td>
<td>230.56 (12.02)</td>
<td>224.90 (35.32)</td>
<td>160.99 (31.35)</td>
<td>167.30 (15.67)</td>
</tr>
<tr>
<td>S</td>
<td>230.92 (57.20)</td>
<td>230.56 (12.02)</td>
<td>230.92 (19.42)</td>
<td>160.99 (31.35)</td>
<td>167.30 (15.67)</td>
</tr>
<tr>
<td>S-Mo</td>
<td>234.12 (19.42)</td>
<td>224.90 (35.32)</td>
<td>160.99 (31.35)</td>
<td>167.30 (15.67)</td>
<td>167.30 (15.67)</td>
</tr>
<tr>
<td>S-O</td>
<td>230.92 (57.20)</td>
<td>230.56 (12.02)</td>
<td>234.12 (19.42)</td>
<td>160.99 (31.35)</td>
<td>167.30 (15.67)</td>
</tr>
</tbody>
</table>

Figure 5.9a shows the absorbance spectra of TiO$_2$, TM 2.5%, TM 50% and MoS$_2$. The tangent drawn shows the strong cut off wavelength (λ) at 394.89 nm (TiO$_2$), 425.27 nm (TM 2.5%) and 537.72 nm (MoS$_2$), where the photon energy absorption value is minimum. Bandgap of the samples are calculated using the formula, Bandgap energy ($E_g$) = (h*c)/λ. Where h is planks constant (6.626 x 10$^{-34}$ joules sec), C is speed of light (3 x 10$^8$ meter/sec) and λ is cut off wavelength. The corresponding cut off wavelengths leads to the bandgap 3.15 eV (TiO$_2$), 2.92 eV (TM 2.5%) and 2.31 eV (MoS$_2$). Incase of TM 50% absorption spectra, there are two significant cut off wavelength at 492.89 nm and 581.65 nm, which corresponds to the bandgap energy 2.52 eV and 2.14 eV, respectively. These two bandgap energy can be assigned to TiO$_2$ (2.52 eV) and MoS$_2$ (2.14 eV) in TM 50%. The bandgap 3.15 eV of pristine TiO$_2$ matches the early reported literature, whereas pristine MoS$_2$ shows bandgap of 2.31 eV which is slightly higher than the theoretical value of monolayer MoS$_2$ = 1.9 eV [13]. The bandgap of TiO$_2$ in TM 2.5% and TM 50% got lowered by 0.23 eV and 0.63 eV respectively. MoS$_2$ bandgap in TM 50% got lowered 0.17 eV compared to pristine MoS$_2$ sample. These bandgap reduction can be due to formation of mid-gap states either below the conduction band (CB) or above the valence band (VB) which overlaps with the respective band to form band tail. The peak intensity around -4 eV in the VB (MoS$_2$) is due to X-ray satellite artefact arised from non-chromatic X-ray source.
Valence band XPS (Figure 5.9b) was performed to observe the valence band maximum (VBM) of the samples. Pristine TiO$_2$ shows VBM at 1.3 eV which got shifted to lower binding energy of about 0.9 eV for TM 2.5%. Valence band spectrum of TM 50% shows two VBM at 1.4 eV followed by a band tail at -0.82 eV, which can be associated to VBM of TiO$_2$ and MoS$_2$ respectively. Unlike in TM 2.5%, TiO$_2$ VBM in TM 50% got shifted towards higher binding energy and MoS$_2$ VBM in TM 50% shifted towards lower binding energy compared to pristine MoS$_2$ VBM 0.3 eV. Conduction band minimum (CBM) can be calculated from estimated VBM and $E_g$. A schematic illustration of the density of states (DOS) of TiO$_2$, MoS$_2$, TM 2.5%, and TM 50% is shown in Figure 5.10.
Schematic band diagram of TM 2.5% and TM 50% with predicted charge transfer mechanism is shown in Figure 5.11. VBM and CBM position of type II heterostructured TM 2.5% is maintained with low conduction band offset (CBO) and valence band offset (VBO), which favors the charge separation and fast charge transfer during photodegradation process. But whereas in TM 50%, CBO and VBO are very high, which restricts the charge transfer rate and also the possibility of charge recombination will be high due to the band edge positions. And this suppress the photocatalytic activity of TM 50% in addition to shielding effect of MoS$_2$.

5.3. Photocatalytic Activity:

The adsorption performance of the powder samples was evaluated by monitoring the adsorption level of both cationic (Methylene blue - MB and Crystal Violet - CV) and anionic
(Methyl Orange – MO and Rhodamine B – RhB) dyes. Figure 5.12. shows the molecular structure of the dyes. Under the dark condition, the powder sample (25 mg) dispersed inside the glass vessel containing 50 mL of dye solution (25mg/L of dye in 50 mL deionized water). The solution was magnetically stirred (120 RPM) for 30 minutes under dark at room temperature to attain the adsorption/desorption equilibrium. Then to study the photocatalytic activity of the sample, the light source (300 W, 75mW/cm², 350-1100nm, AM1.5G filter) illuminated from the top with a distance of 30cm from the liquid surface. The intensity of the light source was tuned to attain 1 SUN condition, and the light illuminated area was maintained about 50mm x 50mm. During the experiment cycle, 1mL aliquot of the dye solution was collected at a time interval of 30 mins. The liquid samples were centrifuged (1200 rpm, 10 minutes) and then transferred into a quartz cuvette (M/s. Hellma) to record the absorption spectra (250nm – 750nm) by using a UV-vis spectrophotometer (M/s. Thermo Scientific, Evolution 220).

(a) Methylene blue
(Molecular Weight: 319.85 g/mol)

(b) Crystal Violet
(Molecular Weight: 407.99 g/mol)

(c) Methyl Orange
(Molecular Weight: 327.33 g/mol)

(d) Rhodamine B
(Molecular Weight: 442.5 g/mol)

Figure 5.12. Molecular structure of Methylene Blue (a), Crystal Violet (b), Methyl Orange (c) and Rhodamine B (d).
The removal and photocatalytic degradation of dye pollutants by MoS$_2$ and MoS$_2$/TiO$_2$ samples were qualitatively studied using methylene blue (MB) (25 mg/L). First 30 minutes, the MoS$_2$/TiO$_2$ samples were kept at MB dye solution under the dark condition, which explores capable of dye adsorption. Then light illumination was allowed in the photocatalytic reactor for a few hr and analyzed the photocatalytic degradation process. Briefly, change in dye concentration at dark conditions infers the physical removal of dye molecules from solution to the adsorbent surface. Under light illumination, the semiconductor produces photocharge carriers (photoelectron and photohole) at the conduction band and valence band, which generate superoxide and hydroxyl radicals, respectively. Briefly, the photogenerated holes and electrons react with water and dissolved oxygen to form hydroxyl radical (•OH) and superoxide radical (•O$_2^-$). These high energy species (•OH and •O$_2^-$) undergo multiple reactions with the organic pollutants in the aqueous medium in order to degrade pollutants. Figure 5.13 (a) shows the percentage of the ratio between final dye concentration (C) and initial (C$_0$) vs. time. From Figure 5.12 (a), in the absence of adsorbent or photocatalyst materials, only light illumination (photolysis) does not change in dye concentration. After introducing the MoS$_2$, TiO$_2$, and MoS$_2$/TiO$_2$ nanocomposite samples in the dye solution, a significant change in MB dye concentration has been noticed at dark and light illumination conditions. In particular, Figure 5.13 (a) shows two types of changing behaviour in (C/C$_0$) values. Under the dark condition, the MoS$_2$, TiO$_2$, and TM 2.5% sampled showed less change in (C/C$_0$) value indicates poor dye adsorption on their surface. Under light illumination condition, the rate of change in (C/C$_0$) values are ordered as TM 2.5%>TM 5%>TM 10%>TiO-2>MoS$_2$. The higher photocatalytic dye degradation rate observed at TM 2.5% nanocomposite might be due to effective charge separation at MoS$_2$/TiO$_2$ heterointerfaces. This photoexcited charges (electrons and holes) further reacts with water molecules to produce superoxide and hydroxyl radicals, which degrade the dye molecules. However, higher loading (above 2.5 wt %) of MoS$_2$ with the nanocomposite samples reduces the photocatalytic effect. The major plausible reason is the shielding effect of MoS$_2$, which hinders the interaction of the photons with TiO$_2$. This shows that in MoS$_2$/TiO$_2$ composite, TiO$_2$ plays a predominant role as a photo-harvester, and MoS$_2$ act majorly as a co-catalyst to enhance the charge separation. Further analyzing the results in Figure 5.13 (a), the C/C$_0$ values of TM 20%, TM 30%, and TM 50% showed effective dye adsorption in dark conditions. The adsorption of MB gets saturated beyond 30wt% of MoS$_2$ in composite samples and the highest adsorption efficiency of 73% of
MB dye is noticed in TM 50 wt% sample. As observed in the HRTEM image, the increased interspace distance of MoS$_2$ lattice at higher wt % of MoS$_2$ could increase the penetration of dye molecules into the interior spaces of 2-D nanoflakes. Similarly, interspace mediated heavy metal (Hg and Pb) removal was demonstrated in 2-D MoS$_2$ adsorbents [17, 18]. The remaining 27% of dye after adsorption on TM 50% samples are degraded by the photocatalysis process. Overall, TM 2.5% results in weak dye adsorption with high photocatalytic dye degradation, and TM 50% results in high dye adsorption with less photocatalytic activity. The dye removal (%) values of different materials were estimated from Figure 5.13 (a) and summarized in Figure 5.13 (b). Figure 5.13 (b) illustrates any material such as pristine MoS$_2$, TiO$_2$, or MoS$_2$/TiO$_2$ composites couldn’t remove the dye completely, either dark or light illumination condition. It requires combinatorial action of adsorption and photocatalytic degradation for complete dye removal. However, the complete dye removal process took over around 5hr. From an industrial viewpoint, the water treatment process time is a crucial factor that decides the effective cost involved with treatment.

Figure 5.13. Photocatalytic degradation (a) & dye removal efficiency (b) of MB by TiO$_2$, MoS$_2$, TM 2.5%, TM 5%, TM 10%, TM 20%, TM 30% and TM 50%.

In order to reduce the time duration for the complete removal of dye molecules, we propose two-stage water treatment utilizing the different functional properties of MoS$_2$/TiO$_2$ composites instead of a single material. Figure 5.14 illustrates the schematic of two-stage dye pollutant removal/degradation. The high adsorption behaviour of TM 50% helps to remove
the dye quickly, and the remaining dye molecules will be degrading by TM 2.5% photocatalyst. Therefore, involving TM 50% at stage-I and TM 2.5% at stage-II could remove the dye pollutant in a short span of time.

![Diagram of two-stage rapid adsorption and photocatalysis based dye pollutant removal.](image)

**Figure 5.14.** Two-stage rapid adsorption and photocatalysis based dye pollutant removal.

Two-stage based dye degradation rate vs. time plot for MB dye pollutants are presented in **Figure 5.15 (a)**. The percentage of dye removal is estimated from **Figure 5.15 (a)** and summarized in **Figure 5.15 (b)**. From **Figure 5.15 (a)** and **5.15 (b)**, a complete 100% of MB dye degradation was achieved within 1 hr. This clearly endorses that a two-stage nanofiltration /photocatalysis integrated approach is highly effective in reducing the treatment time from 5hr to 1hr compared to a single material-based dye degradation process. The same procedure has been followed for other dyes like CV, RhB and MO. TM 50% showed very strong adsorption property towards cationic dyes (CV and MB) compared to anionic dyes (RhB and MO). This can be ascribed to the electrostatic interaction between the samples and dyes.
Figure 5.15. Dark Adsorption (stage 1) and Photocatalytic degradation (stage 2) (a) & dye removal efficiency (b) of MB, MO, RhB and CV dyes by combined effect of TM 50% and TM 2.5%.

To decipher the inter-relationship between the surface charge of the MoS$_2$ adsorbent and dye molecules, we examine the Zeta potential (ZP) value of the MoS$_2$, TiO$_2$, and MoS$_2$/TiO$_2$ nanocomposite samples (Figure 5.16 (a)). From Figure 5.16 (a), it clearly understands that MoS$_2$/TiO$_2$ samples shifts towards negative potential with an increase in MoS$_2$ wt%. Increase in MoS$_2$ wt% increases the acidic nature of the samples by lowering the pH from 4.08 (TM 2.5%) to 3.3 (TM 50%). Though TM 30% showed higher negative potential (-45.8 mV) than TM 50% (-37.9 mV), they both showed the same adsorption efficiency (73%) and pH value (3.3). Due to high negative potential value and an increase in surface area compared to MoS$_2$, TM 50% showed greater affinity towards cationic dyes like CV (+40.2 mV) and MB (+23 mV). Though RhB was reported as a cationic dye [19], the ZP measurement showed it to be anionic (Figure 5.16 b). This might be due to deprotonation of -COOH groups in RhB at the pH around 4.86 and RhB (-29.5 mV) showed more negative potential than MO (-16 mV). For ZP value, the negative potential TM 50% should exhibit less adsorption towards RhB compared to MO. But in contrast, TM 50% showed less adsorption activity towards MO rather than RhB. Generally, anionic dyes show an increase in adsorption under low pH conditions [20] and because of this condition, RhB (4.86 pH) showed a higher level of adsorption compared to MO (6.5 pH). Since TiO$_2$ showed no adsorption of dyes (cationic/anionic), and this confirms that the adsorption of dyes molecules is only due to the presence of MoS$_2$ within the nanocomposites.
Figure 5.16. pH vs Zeta Potential of TiO$_2$, TM 2.5%, TM 5%, TM 10%, TM 50% and MoS$_2$ (a). pH vs Zeta Potential of MB, MO, RhB and CV dyes (b).

We further validate the two-stage dye pollutant treatment in mixed dye solution with two different dye concentration. Anionic (RhB and MO) and cationic (MB and CV) dye solutions are mixed to attain 25mg/L and 50mg/L of 50ml mixed dye solution volume. The optical absorbance spectrum of mixed dye solution (Figure 5.17) was obtained showing the approximate spectra region of individual dyes.

Figure 5.17. Absorbance spectra of mixed dye solution showing the corresponding spectrum of MB, CV, RhB nad MO dyes.
As is expected TM 50% (Figure 5.18) removed 100% of cationic dyes and 70% of anionic dyes from the mixed dye solution having a concentration of 25mg/L under stage I - dark mode adsorption. This explains that 2D- MoS$_2$ having a high affinity towards cationic dye. The remaining 30% of anionic dyes are degraded in stage II - light mode (Figure 5.19) i.e, the photocatalytic process completely degrading 30% of anionic dye after 3.5h. To understand the saturation level of cationic dyes adsorption onto TM50% surface at stage I, the dye concentration of mixed dye solution is doubled to have the dye concentration 50mg/L. After increasing the concentration of mixed dye from 25 to 50mg/L, Figure 5.20 showed that 86% of cationic dyes and just 36% of anionic dyes were removed. It implies that dye adsorption at stage-I relies on the surface area and the number of adsorption sites of the TM50%. The remaining 14% of cationic dyes and 64% of anionic dyes are further degraded in stage II- light mode (Figure 5.21) photocatalytic degradation stage which took about 5h. Qualitatively, the adsorption of dye molecules towards the TM50% is a rapid process in which more than 60% of dye molecule adsorption occurs in a minute (Figure 5.22 and Figure 5.23). The dye adsorption activity for 50mg/L dye concentration solution gets saturated in 15 minutes, whereas in 25mg/L the adsorption activity was active throughout 30 minutes under dark mode stage. This might be due to the trade-off between the surface area of TM50% and dye molecules concentration can be overwhelmed by enhancing the quantity of TM50% in the reactor. The above results evident that two-stage dye pollutant removal process using TM50% and TM2.5% be an effective route for tackling both single as well as mixed dye compounds in the textile waste. It is worthy to implement this approach in real-time pre-treated textile dye pollutant where classical photocatalysis or filtration approach not able to resolve it completely.
Stage I:

(a)

(b)

Figure 5.18. Adsorption profile of dye (25mg/l) represented by the decrease in normalised absorbance spectra (a) and respective dye color change (b) over time in stage I using TM 50%.

Stage II:

(a)

(b)

Figure 5.19. Photocatalytic degradation profile of dye (25mg/l) represented by the decrease in normalised absorbance spectra (a) and respective dye color change (b) over time in stage II using TM 2.5%.
Stage I:

Figure 5.20. Adsorption profile of dye (50mg/l) represented by the decrease in normalised absorbance spectra over time in stage I using TM 50%.

Stage II:

Figure 5.21. Photocatalytic degradation profile of dye (50mg/l) represented by the decrease in normalised absorbance spectra over time in stage II using TM 2.5%.
Figure 5.22. Adsorption (stage I) and photocatalytic degradation (stage II) curve of mixed dye (25 mg/l and 50 mg/l) using TM 50% and TM 2.5% respectively.

Schematically (Figure 5.23.) illustrate is made based on the experimental results and it illustrate the dye adsorption in 3-D MoS$_2$ and 2-D MoS$_2$ nanoflake grown on TiO$_2$. The debundling 2-D nanoflakes assembled onto the photocatalyst surface is highly effective for accessing interior surface as well as lattice interspace mediated dye pollutant removal compared to 3-D MoS$_2$ structure.

Figure 5.23. Schematic illustration of dye adsorption in 3-D MoS$_2$ (a) and 2-D MoS$_2$ nanoflakes grown on TiO$_2$ (b)
5.4. Summary:

Ultrathin, few-layered 2-D MoS\(_2\) mediated adsorption sites are created onto light active TiO\(_2\) host nanoparticles by a single-step hydrothermal process. The TiO\(_2\) host nanoparticles served dual role in protecting 2-D MoS\(_2\) nanoflakes from undesired aggregation and widen interlayer spacing of MoS\(_2\) sheet which favourable for accessing interior surface of MoS\(_2\) in effective dye-adsorption compared to 3-D MoS\(_2\) structure. Nanocomposites with high MoS\(_2\) wt% (TM 50%) and low MoS\(_2\) wt% (TM 2.5%) showed high adsorption, and photocatalytic activity towards cationic and anionic dyes, respectively. Two-stage integrated adsorption and photodegradation dye removal process was evaluated using MoS\(_2\)/TiO\(_2\) nanocomposites. For the first time, a mixed dye (anionic and cationic) pollutant model was demonstrated as a proof-of-concept towards textile wastewater treatment. The ultrathin MoS\(_2\)/TiO\(_2\) nanocomposite developed in this work will be a futuristic candidate to enhance the filtration efficiency of nanofiltration membranes in the Zero Liquid Discharge process.

5.5. References


Chapter 6
Conclusion

6.1. Conclusion:

In conclusion, helium-oxygen atmospheric pressure plasma spray followed by calcination was used to improve the photocatalytic properties of CuO thin films for removal of pollutant dye molecules. The plasma spray induces higher degree of strain in the lattice and enhanced rate of crystallization of CuO film as confirmed from the XRD and Raman studies. Furthermore, to get insights about local structural and electronic properties due to plasma functionalisation of the CuO catalysts, XAFS investigations was carried out. In addition, the plasma functionalization results in the highly hydrophilic surface of the CuO films due to the formation of polar surface groups. The XPS investigations confirms the presence of the hydroxyl radicals on the surface of CuO film that further causes the enhanced photocatalytic activity. Plasma treated CuO thin film showed improved dye adsorption and faster rate of photocatalytic dye degradation for industrial dye MB and phenol under solar light irradiations. This work paves the way for developing the highly active plasma functionalized thin films thin films for dye pollutant removal from wastewater.

Further, we have successfully implemented the low power APPJ functionalization of the highly hydrophilic CuO nanowires onto the Cu substrate. The plasma spraying process resulted in the epitaxial growth of the CuO nanowires within 5 minutes that can be replace the conventional long time thermal annealing technique for CuO nanowire synthesis. It was found that the APPJ spray introduced the oxygen vacancies and lattice defects in the CuO nanowires that causes superior photocatalytic performance of the catalyst. The as prepared nanocomposite was thoroughly characterized by various spectroscopic techniques to understand their structural, morphological and electronic properties. Subsequently, the CuO thin film was used for the photocatalytic degradation of the organic pollutants under simulated solar light. This work could pave the way for design and development of the defect enrich, highly efficient photocatalytic material for wastewater treatment.

Finally, we have synthesized few layered ultrathin two-dimensional MoS$_2$ mediated TiO$_2$ nanoparticles using single step hydrothermal technique. The MoS$_2$-TiO$_2$ nanocomposite was utilized for the integrated adsorption-photocatalysis of the removal of cationic and anionic dyes. The decoration of the TiO$_2$ nanoparticles onto MoS$_2$ nanoflakes causes less
aggregation and more interlayer spacing of MoS$_2$ nanosheets that could result in high surface area of the photocatalyst. Further, the optimization of the photocatalyst was done by varying the weight ratio of MoS$_2$ as 2.5 wt%, 5 wt%, 10 wt%, 20 wt%, 30 wt% and 50 wt%. It was found that the nanocomposite with higher MoS$_2$ content (50 wt%) showed the highest adsorption while with lower MoS$_2$ content (2.5 wt%) is photocatalytically more active.

Overall, in this thesis work, we have rationally designed, developed and utilized three materials (CuO, TiO$_2$, and MoS$_2$) to prepare highly efficient nanocomposites using APPJ, calcination and hydrothermal routes. Subsequently, we have deployed the prepared nanocomposites as efficient catalysts for wastewater treatment. We believe that this work will pave way for the use of photocatalytic materials for several real-life applications.

6.2. List of Publications:

Publications associated with this thesis:

4. Ultrafast epitaxial growth of CuO nanowires using atmospheric pressure plasma with enhanced electrocatalytic and photocatalytic activities. Avishek Dey, Paheli Ghosh,

**Other Publications:**