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How to cite:

Chakrabarty, N.; Dey, A.; Krishnamurthy, S. and Chakraborty, Amit K. (2021). CeO₂/Ce₂O₃ quantum dot decorated reduced graphene oxide nanohybrid as electrode for supercapacitor. Applied Surface Science, 536, article no. 147960.

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Version: Accepted Manuscript

Link(s) to article on publisher's website:

<http://dx.doi.org/doi:10.1016/j.apsusc.2020.147960>

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CeO₂/Ce₂O₃ quantum dot decorated reduced graphene oxide nanohybrid as electrode for supercapacitor

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Abstract :

Herein, we report a simple hydrothermal method to synthesize CeO₂/Ce₂O₃ quantum dots anchored on reduced graphene oxide (RGO) sheets of different weight fractions for application as supercapacitor electrode. Of all the tested samples, the one containing 7 wt% RGO (CRGO3) as measured by thermogravimetry, exhibited the highest specific capacitance of 1027 F/g at 1 A/g along with good cycling stability. At current density of 4A/g, the CRGO3 sample showed charge retention of 79% after 5000 cycles, whereas at 20A/g, it showed 85% charge retention after 3000 cycles. The values obtained for CRGO3 electrode are better than all previous ceria and RGO based electrode suggesting its potential use in supercapacitor. High resolution transmission electron microscopy (HRTEM) revealed well crystalline CeO₂ nanoparticles (~5 nm) uniformly distributed on the RGO sheets as well as few lattice planes indicative of presence of some Ce₂O₃ mixed with CeO₂. X-ray photoelectron spectroscopy (XPS) revealed presence of a mixed oxides containing mostly CeO₂ with some Ce₂O₃ phase on the surface. The enhanced performance of the CRGO3 electrode was attributed to the optimized weight fraction and large surface area of electrically conducting RGO combined with enhanced electrocatalytic activity of CeO₂/Ce₂O₃ mixed oxides.

Keywords: Ceria quantum dots; supercapacitor electrode, x-ray photoelectron spectroscopy, graphene; pseudocapacitance; electrochemical properties.

1. Introduction

Supercapacitors have generated huge research interest in the recent years owing to their increasing applications as an efficient energy storage device. Supercapacitors have emerged as a fast growing energy storage technology that can find application in niche areas where conventional capacitors and batteries fail. Supercapacitors or electrochemical capacitors are devices that store energy by transforming chemical energy into electrical energy [1-5]. Energy storage in batteries and fuel cells takes place through chemical processes, whereas the electrostatic charge separation between electrode-electrolyte is utilized for harvesting energy in supercapacitors [6-7]. Supercapacitors exhibit unique properties such as extremely high power density, reasonable energy density, longer cycle life, and minimum charge separation which make them superior to the conventional capacitors [8-10]. The combination of these features makes supercapacitor an effective energy storage device in the field of modern consumer electronics, electric vehicles, and industrial power set-ups. Based on the charge storage mechanism, supercapacitors are classified into two types: electrical double layer capacitors (EDLCs) and pseudocapacitors. EDLCs use of the electrical double layer on the electrode surface for charge storage while pseudocapacitors rely on Faradaic or redox reactions occurring on the electrode-electrolyte interface. In general, carbon nanostructures like multi-walled carbon nanotubes (MWCNT), single-walled carbon nanotube (SWCNT), graphene, graphene oxide (GO), reduced graphene oxide (RGO), etc. are used as EDLC materials [11-19] whereas transition metal oxides like nickel oxide (NiO), cobalt oxide (Co_3O_4), manganese oxide (MnO_2), copper oxide (CuO) etc. and conducting polymers like polyaniline (PANI), polypyrrole (PPy) etc. are used as pseudocapacitor materials [20-25]. However, poor electrical conductivity of these pseudocapacitive materials is often a hindrance to their high performance as supercapacitor electrode. To overcome this limitation, often these pseudocapacitive materials are combined with EDLC materials such as CNT, RGO, etc. to form nanohybrids. [26-33]

A relatively less studied metal oxide is ceria (CeO_2) in spite of its dynamic redox reaction, ecofriendly features and low cost. A major drawback of CeO_2 is its poor electrical conductivity [34] that can be tuned by changing its shape and size using controlled synthetic conditions by playing with the growth parameters. Chiang et al. showed that the electronic conductivity of CeO_2 nanocrystals can be increased by 4 orders of magnitude from its bulk value.[35] There were multiple attempts made by research groups to tune the electrochemical performance of CeO_2 based electrodes for potential use in supercapacitor both by controlling its size/shape and by combining it with RGO.[36-43] However, in

spite of using a variety of simple to complex synthesis methods and different shapes and size of CeO_2 , the values of specific capacitance reported for ceria-RGO based electrodes ranged within few hundreds of Farad/g which is much smaller than those reported for other commonly used oxides of Mn, Ni, Co which exhibited specific capacitance values in excess of 2000 F/g.[31-33] A detailed description of interactions between CeO_2 based electrode and electrolyte is missing in those reports, especially no details are available on how RGO is influencing the electrode interaction with the electrolyte at the interface. Also, we could not find any systematic investigation reporting optimization of the electrochemical performance of CeO_2 -RGO nanohybrid as a function of RGO weight fraction which is essential for designing high performance CeO_2 based supercapacitor electrodes.

In view of the above, here we present an investigation of the CeO_2 -RGO nanohybrid with a fresh outlook firstly, by simplifying the synthesis approach to have better control over the size and shape of the CeO_2 particles and secondly, by conducting a systematic investigation of the influence of RGO weight fraction on the electrochemical properties of the composite electrodes. Thus, here, we report the synthesis of a CeO_2 -RGO nanohybrid based electrode consisting of CeO_2 quantum dots of ~ 5 nm diameter uniformly distributed on RGO nanosheets via a one-step hydrothermal method. The advantage of quantum dot is essentially its small size which makes its surface to volume ratio very large and renders its surface more reactive both of which are desirable characteristics of a good electrode material. Other advantages of quantum dots in electrochemistry are the reduction of the diffusion length for both ions and electrons, and negligible volume expansion/contraction.[44] Several samples were produced by varying the relative weight fraction of RGO to find its optimized weight fraction for best electrochemical performance. Electron microscopies were used to evaluate the microstructure and morphology whereas x-ray diffraction (XRD) was used to evaluate their crystallinity. Thermogravimetric analysis (TGA) revealed the relative weight fraction of RGO in the CeO_2 -RGO nanohybrid samples. X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy were further employed to understand the chemical and oxidation states of CeO_2 . The electrochemical properties of the prepared samples were evaluated using cyclic voltammetry (CV), galvanostatic charge discharge(GCD) and electrochemical impedance spectroscopy (EIS) techniques.

2.EXPERIMENTAL

2.1 Materials Used

Natural graphite flakes were procured from Kai Yu Industries, Nanjing, China. Sulphuric acid (H_2SO_4 , 98%), sodium nitrate (NaNO_3 , 97%), potassium permanganate (KMnO_4 , 98%), hydrogen peroxide (H_2O_2 , 30%), hydrazine hydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$), sodium hydroxide pellets (NaOH , 97%), 2-propanol (IPA), were purchased from Merck India. Cerium nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 99.9%) were purchased from Alfa Aesar. Nafion (NR-50) pellets were purchased from Sigma Aldrich. All chemicals were used as received without any further purification.

2.2 Synthesis of $\text{CeO}_2/\text{Ce}_2\text{O}_3$ -RGO composites

GO was prepared from natural graphite flakes using a modified Hummer's method according to our previous study [45]. To synthesize the composites, 10 mg of GO was dissolved in 50 mL of deionized water and stirred for 30 min. Cerium Nitrate hexahydrate (0.1M) was added to the GO suspension followed by stirring for 30 min. Subsequently 35 ml of 1M NaOH solution (1.4 gm in 35 ml DI water) was added to the suspension and the pH of the solution was around 10.0. Next, 10 ml of N_2H_4 solution (0.1 M) was added to reduce the GO to RGO which led to the increase in the pH value of the resulting mixture to 12. The reaction mixture was then stirred vigorously for 1 h to mix homogeneously and transferred into a 100 mL teflon lined steel autoclave for heating at 140 °C for 6 h in an oven. After the autoclave cooled down to room temperature, the reaction mixture containing $\text{Ce}(\text{OH})_3$ -RGO was collected by filtering and washing with IPA and DI water until pH neutral. Finally the dried $\text{Ce}(\text{OH})_3$ -RGO material was calcined in air for 4 h at 300 °C in a muffle furnace to obtain CeO_2 -RGO nanohybrid. Similarly three more samples were prepared using the above synthesis route for different weights of GO (10 mg, 25 mg, 50 mg and 100 mg) which were labelled as CRGO1, CRGO2, CRGO3 and CRGO4, respectively.

2.3 Characterization Techniques

XRD was carried out for powder samples using PANALYTICAL X Pert Pro diffractometer and Cu $K\alpha$ radiation (1.5414 Å) was employed as X-ray source. TGA curves were obtained over the temperature range of 35-800 °C at a heating rate of 10 °C/min under nitrogen atmosphere using STA 6000 thermal analyser (Perkin Elmer, USA). HRTEM images were obtained using a JEOL 2100 transmission electron microscope. The HRTEM samples were prepared by depositing a few drops of a very dilute solution of the sample in isopropyl alcohol (IPA) on a 300 mesh holey carbon grid followed by drying overnight in air at room temperature. The analyses of TEM images were done by using ImageJ software. Raman spectra were recorded by a Raman Spectrometer (LabRAM HR JobinYvon) with an argon ion laser radiating wavelength of 514.5 nm (green) with a 10% filter and 50X objective. All Raman spectra were

calibrated with respect to the position of the Si peak at 520 cm^{-1} originating from the Si wafer on which the sample was deposited by drop casting of its dilute solution in IPA.[46] XPS measurements were carried out at a base pressure of $\sim 6 \times 10^{-8}$ mbar using an unmonochromated Mg K α radiation giving an overall energy resolution of 1 eV. All spectra were calibrated by the position of the Au 4f peak originating from a gold foil in direct contact with the samples. The XPS peaks were fitted using CASA XPS software with a Shirley type background subtraction and Gaussian/Lorentzian peak shapes. The binding energies were corrected by setting the C 1s peak of adventitious carbon at 284.7 eV in accordance with literature.[47,48] Electrochemical measurements were conducted in an electrochemical workstation(CHI 660E, USA) using a 3 electrode cell containing 1M NaOH as electrolyte and comprising of a 3 mm dia glassy carbon electrode coated with a CeO₂-RGO film as working electrode, a Ag/AgCl reference electrode and a platinum wire counter electrode. The working electrode was prepared by dropcasting a thick slurry, containing 92 wt.% active material, i.e., CeO₂-RGO nanohybrid and 8 wt.% nafion (used as a binder) dissolved in a solution (5mg/ml) containing water and IPA in 1:1 ratio, on the glassy carbon disc in accordance with literature.[26] The loading mass of the active material on glassy carbon substrate was 0.35 mg/cm^2 .

3. Results and Discussion

3.1 TGA and XRD analyses

Figure 1: (a)TGA curves of CeO₂, CeO₂-RGO nanohybrids and RGO (inset); and (b) XRD patterns of GO, RGO, CeO₂ and CRGO3.

TGA curves were obtained for CeO₂, RGO and CRGO nanohybrids to evaluate the exact weight fraction of RGO in various nanohybrid samples which are presented in Figure 1(a). As the temperature reaches increases, the TGA curves show a gradual loss of mass between 100 and 500°C for all the samples with the highest loss recorded for CRGO4 and the lowest loss recorded for bare CeO₂. By measuring the difference in the loss of mass from that of the bare CeO₂, the weight fractions of RGO in the nanohybrid samples were estimated which are listed in Table 1.

Table 1: The details of various prepared samples.

Sample name	Bare CeO ₂	CRGO1	CRGO2	CRGO3	CRGO4
Wt% of RGO	0	3%	4.5%	7%	9%

XRD patterns of the prepared samples are shown in Fig. 1(b) in which a peak at $2\theta = 11.3^\circ$ can be observed in the pattern of GO, which corresponds to an expanded interlayer spacing of 0.77 nm between graphitic layers, owing to the chemical exfoliation by attachment of oxygen containing functional groups on the surface of graphitic sheets. The XRD pattern of RGO (blue curve) shows a small hump at 25.0° corresponding to reflections from (002) planes of graphite suggesting a complete reduction of GO because the characteristic peak of GO (at 11.3°) disappeared [49-51]. The CRGO3 nanohybrid displayed a typical cubic phase of CeO₂ (Fm3m, $a = 5.411 \text{ \AA}$, JCPDS File no.98- 001-1731) corresponding to (111), (002), (022), (113), (222), (004), (113), (024) and (224) planes. Absence of the diffraction peak due to RGO in the CRGO3 sample may be due to its small weight fraction and destruction of regular stacks of RGO sheets in the nanohybrid [29]. The average crystallite size of CeO₂ particles in CeO₂ and CRGO3 samples was estimated to be 8.4 nm and 5.6 nm respectively using Debye-Scherrer equation. XRD curve of only CRGO3 is presented in Figure 1(b) and most other characterization data shown below because this sample exhibited the best electrochemical performance as discussed in section 3.4.

3.2 HRTEM analysis

Fig. 2(a) represents a typical TEM image of the CRGO3 nanohybrid sample in which one can see well-dispersed CeO₂ nanoparticles embedded on RGO sheets. The size of the CeO₂ nanoparticles ranged between 4 and 8 nm with a mean diameter of 5 nm as estimated from log normal fit of the histogram plot (Fig. 2b). A few larger particles can also be observed which are possibly agglomeration of few particles. It is to be noted that this size of CeO₂ nanoparticles is lower than the Bohr exciton radius of CeO₂ (7-9 nm), which confirms that our prepared nanoparticles are quantum dots [52]. From the HRTEM image in Figure 2(c), (111), (022), (133) and (002) lattice planes of CeO₂ quantum dots were identified

in accordance with the JCPDS card number 98-001-1731. In addition, a few locations were identified to have (010) and (011) lattice planes corresponding to Ce_2O_3 even though these planes were not observed in the SAED pattern in Fig. 2(f). Figure 2(d) presents the HRTEM image of CRGO3 which shows that ceria quantum dots are anchored to the RGO sheets. From the well resolved HRTEM image of CRGO3 (Figure 2(e)) shows the presence of (111) cubic phase of CeO_2 and (100) hexagonal phase of Ce_2O_3 . The SAED revealed the presence of (111), (002), (222), (022) and (113) planes of CeO_2 confirming that majority of the synthesized particles were CeO_2 .

Figure 2: (a) TEM image, (b) particle size distribution, (c-e) HRTEM images, and (f) SAED pattern of CRGO3 nanohybrid.

3.3 Raman Analysis:

In the Raman spectra (Fig. 3), the most intense peak is observed at 460 cm^{-1} for the two ceria containing samples which originate from the F_{2g} symmetrical stretching mode ($\text{Ce}-\text{O}_8$) of CeO_2 . Two more peaks, much weaker in intensity, are also observed at 598 and 832 cm^{-1} , originating from the intrinsic oxygen vacancies (Ce_2O_3) and weaker phonon band of CeO_2 [53-56]. In fact, there is a small shift in the position of these two peaks in the Raman spectrum of CRGO3 nanohybrid compared to those for pure CeO_2 phase which suggests a good interaction (attachment) of CeO_2 nanoparticles with RGO. The Raman spectrum of GO exhibits two strong peaks assigned as G band at 1595 cm^{-1} , and D band at 1349 cm^{-1} in accordance with established literature. [57] The intensity ratio of these two peaks (I_D/I_G), which is widely used as a measure of disorder in carbonaceous materials, decreased from 0.98 for GO to 0.76 for RGO. This decrease confirmed the restoration of the sp^2 domains within GO during its reduction through removal of oxygen containing defect states.[58-61] For CRGO3 nanohybrid, I_D/I_G value increased compared to that of RGO in accordance with partial destruction of symmetry due to attachment of CeO_2 nanoparticles on RGO sheets.

Figure 3: Raman spectra of CeO_2 , GO, RGO, and CRGO3 nanohybrid

3.4 XPS analysis

The $3d$ XPS spectrum of Ce (Figure 4(a)) shows three distinct peaks making it quite complicated compared to that of other $3d$ transition metals as one would normally expect this to resemble $\text{Ce}^{5+}(3d^1)$ ionised state [62-64]. However, for crystalline cerium compounds the $\text{Ce}^{4+}(3d^14f^1)$ state is distinctly

more stable than the predicted Koopmans' state of $\text{Ce}^{5+}(3d^1)$ leading to its valence state to be essentially a two electron transition state through electron transfer from the valence O $2p$ orbitals to the Ce $4f$ orbitals. Previous studies have described the complex Ce $3d$ spectrum with ten components – three for tetravalent cerium states and two for trivalent states thus making a total of ten for the doublet of $3d_{3/2}$ and $3d_{5/2}$. [62] To understand the contributions from various states of Ce on the spectrum in Fig. 4(a), curve fitting was performed using CASAXPS. In accordance with the original assignment by Burroughs et al, [62] the positions of the ten components are listed in Table 2. The 18.6 eV binding energy difference between U and V states is in line with the multiplet splitting of Ce $3d$ peak and the presence of the V' , V_0 and U' , U_0 states confirm the presence of Ce (III) state, i.e., Ce_2O_3 in the sample.

Table 2: Components of Ce $3d$ in CRGO3 nanohybrid

Cerium State	Final state	Binding Energy (eV) (± 0.1 eV)	Component
Ce(IV)	$3d^9 4f^0$ O $2p^6$	898.2	V'''
		916.5	U'''
Ce(IV)	$3d^9 4f^1$ O $2p^5$	889.2	V''
		907.5	U''
Ce(IV)	$3d^9 4f^2$ O $2p^4$	882.1	V
		900.8	U
Ce(III)	$3d^9 4f^2$ O $2p^4$	885.4	V'
		903.7	U'
Ce(III)	$3d^9 4f^1$ O $2p^5$	880.2	V_0
		899.2	U_0

Fig. 4(b) and (c) depict C1s and O1s spectra of CRGO3 sample along with various components obtained by curve fitting. In photoelectron spectroscopy the binding energy values are strongly dependent on the electronegativity of the ligand attached to a given element that is being probed. The intense peak at 284.7 eV in the C1s spectrum corresponds to the carbon backbone of the graphitic RGO although the contribution from both sp^2 and sp^3 hybridized carbon species cannot be ruled out due to limited resolution of the spectrometer (1 eV). According to the Lerf-Klinowski model, GO sheets are decorated with epoxide and hydroxyl groups, whereas carbonyl or carboxylic acid groups are located at the edge sites [65]. Due to stronger electronegativity of C=O species, these carbon atoms result in a peak at higher binding energies than that of the singly bonded oxygen moieties (hydroxyl, epoxide). Hence, the peak centred at 286.5 eV represents the contributions from all C–O groups (hydroxyl, epoxide) while

the peak at 288 eV shows the contribution of C=O groups (ketone, aldehyde, carbonyl and carboxylic acid)[66]. The lattice oxygen species at 529.7 eV in the O1s spectrum (Figure 4(c)) is noticeably broad with a FWHM of 2.2 eV due to the coexistence of peaks due to CeO₂ and Ce₂O₃. Stetsovych et al.[63] reported that the transformation of CeO₂ into Ce₂O₃ can cause a shift of O 1s binding energy from 529.25 eV to 530.20 eV. In our case both the red shift and the increased FWHM of this peak corroborates to the fact that oxygen vacancies exist in the CeO₂ lattice in the form of Ce₂O₃. The higher binding energy component at 532 eV comes from the various C=O and C–O moieties of RGO. The quantitative estimates were also made for each of the fitted components using CASAXPS and the data are plotted as a column graph in Fig. 4(d) which shows that nearly 28 at. % Ce exists as Ce (III), i.e., 28% of the ceria is actually Ce₂O₃ whereas 72 at.% is CeO₂.

The existence of such large fraction of Ce₂O₃ in XPS is somewhat surprising since XRD and Raman analyses did not detect its strong presence. However, it must be noted that XPS being a surface sensitive technique, it overestimates the elements which are present only on the surface and hence it is possible that Ce₂O₃ is present only at the surface and that the overall weight fraction of Ce₂O₃ in the bulk of CRGO3 sample is much less than 28 at.% in accordance with observations from other non-surface sensitive techniques. To support this claim, we further note that some of the Ce₂O₃ could even have been produced at the surface of the sample under UHV condition of the XPS chamber through creation of oxygen vacancies.[67] Fig. 4(d) also shows that about 68 at% of carbon is present as elemental carbon, while the rest (~32%) is bound with oxygen and that the oxygen estimate fully supports this observation as one can see that ~29 at% oxygen is bound with carbon while the remaining 71% is bound with Ce.

3.5 CV Analysis

The CV curves of bare CeO₂ electrode within the voltage window of 0-0.65 V measured at different scan rates (5-200 mV/s) are shown in Figure 5(a). For CeO₂ quantum dots, the redox current peaks were observed in the potential range of 0.3–0.4 V and 0.4–0.5 V corresponding to the reversible reaction of Ce³⁺ to Ce⁴⁺ states [42,68]. Since XPS and HRTEM analysis indicated coexistence of both Ce³⁺ and Ce⁴⁺ states, the CV curves showed only one redox pair possibly because of the dynamic redox behaviour of CeO₂ and Ce₂O₃ occurring at the same redox potential. The redox peaks of Ce₂O₃, corresponding to the reversible reaction of Ce³⁺ to Ce⁴⁺ states, for the electrolytic conditions used in this work, are expected to appear (at 0.2 V and 0.45 V) within the vicinity of those of CeO₂ making it difficult to resolve. [69]

Figure 4: (a) Ce 3d, (b) C 1s, and (c) O 1s XPS spectra of CRGO3 nanohybrid. (d) Atomic fractions of different chemical states of Ce, C and O out of their total weight in CRGO3.

The overall redox reactions may be described [68, 69] as,

Figure 5(b) compares the CV curves of bare CeO₂, RGO and CRGO nanohybrids (with different wt % of RGO) at 5 mV/s scan rate. As evident from Figure 5(b), with increasing content of RGO, the prominence of redox peaks of ceria quantum dots gets reduced as the EDLC behaviour is increased. The reduction and oxidation peak currents also significantly increased with increasing RGO content from

bare CeO_2 to CRGO3 sample. This is not surprising since RGO not only provides conducting pathways for the charges to flow easily within the electrode but also facilitates larger number of ceria quantum dots to be exposed to participate in the redox reaction by preventing them from aggregation, and by dispersing them on its large surface area. As a consequence, ceria quantum dots are more accessible by the electrolyte ions in the CRGO framework than bare CeO_2 quantum dots and thus give better material utilization for charge storage. The redox reaction represented by eq. (2) exhibited by Ce_2O_3 also contributes to the total pseudocapacitance.

Figure 5: CV curves of CeO_2 at different scan rates (a); CV curves of CeO_2 , RGO and CRGO nanohybrids (with different wt% of RGO) (b); CV curves of CRGO3 at different scan rates (c); $\log(I_{pa})$ vs $\log(v)$ plot for CeO_2 and CRGO3 (d); I_p vs $v^{1/2}$ plot for CeO_2 and CRGO3 (inset of d).

For CRGO4 sample, the pseudocapacitance behaviour of CeO_2 is totally lost (cyan curve in Fig 5b) as we do not see any redox peaks. It shows an EDLC behaviour of RGO along with much reduced peak

current values. *Therefore, it can be concluded that too much of RGO has a deleterious influence on the overall charge storage capacity of the CRGO nanohybrid electrode due to lowering of the rate of redox reaction and associated pseudocapacitance caused by a relative reduction in the weight fraction of CeO₂ quantum dots in the nanohybrid CRGO4 compared to other nanohybrids.* The specific capacitance of the nanohybrids was calculated from the CV curves recorded at 5 mV/s (Figure 5(b)). The calculated specific capacitances were 135 F/g, 99 F/g, 339 F/g, 438 F/g, 697 F/g and 412 F/g for CeO₂, RGO, CRGO1, CRGO2, CRGO3 and CRGO4 samples, respectively, which clearly identifies CRGO3 nanohybrid as the best material. Figure 5(c) plots the CV curves of the best performing CRGO3 sample at different scan rates of voltage and it shows a continuous shift and rise in both the anodic and cathodic peaks with increase in scan rate suggesting a diffusion controlled charge storage mechanism. In general, the changes in the current density with respect to scan rates in the CV curves obey the following power law:

$$i = av^b \quad (3)$$

where i and v represent the anodic and cathodic current and scan rate while a and b represents arbitrary coefficients. When the value of b is 0.5 the charge storage mechanism is governed by diffusion whereas the value of $b=1$, indicates that current is dominated at the surface of the electrode i.e., charge storage takes place is governed by capacitive process [70-72]. The linear plots of the $\log(I_{pa})$ versus $\log(v)$ graphs (Figure 5(d)) for anodic peaks for CeO₂ and CRGO3 within the scan range 5 mV/s to 200 mV/s confirms that the charge storage mechanism is governed by diffusion mechanism as the 'b'-value varied from 0.56 to 0.73 for CeO₂ and CRGO3 nanohybrid, respectively. The deviation observed in the b values for both the cathodic and anodic current from the theoretical b value is due to the ohmic contribution coming from electrode/electrolyte interface [73].

The ratio of the anodic to cathodic peak currents (I_a/I_c) for all scan rates was found to be greater than unity indicating a quasi-reversible redox reaction [26]. Both the anodic and cathodic peak currents (I_a and I_c respectively) show a linear dependence with the square root of scan rates as shown in the inset of figure 5(d), a behaviour which is usually a signature of the rate determining step of diffusion of ions in the vicinity of the electrode surface [28]. The diffusion coefficients have been calculated using modified Randle-Sevcik's equation [74-75] for quasi-reversible systems as below:

$$I_p^{quasi} = 2.65 \times 10^5 ACn^{3/2} D^{1/2} v^{1/2} \quad (4)$$

where, the symbols bear their usual meaning. The diffusion coefficient was found to be higher ($7.5 \times 10^{-10} \text{ cm}^2/\text{s}$) for the CRGO3 electrode compared to that for the bare CeO₂ ($D = 1.1 \times 10^{-11} \text{ cm}^2/\text{s}$) which also confirms that presence of RGO improves the mobility of electrolyte ions into the electrode material.

3.6 GCD Analysis

Figure 6(a) shows the GCD plots of CeO₂ recorded at different fixed current densities from 1 A/g to 4 A/g. From the shape of the charge discharge profiles, dominance of a pseudocapacitive behaviour can be clearly observed for CeO₂ quantum dots. However on increasing RGO content, the charge discharge profiles show an increased EDLC behaviour. This change from pseudocapacitance to EDLC behaviour is in good agreement with the CV data. The specific capacitance (C) of the electrodes has been evaluated using the following equation (5)[26]

$$C = \frac{I\Delta t}{\Delta V} \quad (5)$$

where C (F/g) is the specific capacitance of the electrode based on the mass of active materials, I (A/g) is the constant current density applied during the charge- discharge process, Δt (s) is the discharge time, ΔV is the potential window (here $\Delta V = 0.45$ V).

For CeO₂ quantum dot sample (Figure 6(a)) the specific capacitance calculated from the discharging region was found to be 173 F/g at 1 A/g which decreased with increase in current density which can be understood from the observed decrease in the discharge time. Figure 6(b) compares the GCD profiles of CeO₂, RGO, CRGO nanohybrids with different RGO content at constant current density of 1 A/g. An increase in the charging-discharging times was observed with the increase in RGO content of upto 7 weight % (CRGO3 sample) after which it decreased resulting in the reduction of the specific capacitance. Thus the highest value of specific capacitance of 1027 F/g was obtained for CRGO3 nanohybrid. Figure 6(c) plots the charge discharge profiles for CRGO3 nanohybrid at different current densities showing the highest discharge time for 1 A/g with the estimated specific capacitance of 1027 F/g and the lowest specific capacitance of 444 F/g for 4A/g. The specific capacitance for CRGO3 nanohybrid at 3A/g was found to be 707 F/g which is comparable with that estimated from CV (697 F/g). Thus, we see a good correlation of the specific capacitance data obtained from CV and GCD. For convenience, the specific capacitances as calculated from GCD recorded at 1 A/g current density is separately plotted against RGO weight fraction in Figure 6(d).

In order to evaluate the cycling stability of the optimized electrode, GCD data were recorded for a continuous charging-discharging cycle of 5000 times at current density of 4 A/g and the charge retention with respect to initial value as a function of cycle number is plotted in Fig. 6(e). The CRGO3 sample clearly shows a better capacitance retention of 79% as compared to that of CeO₂ sample (63%) after 5000 cycles.

Figure 6: GCD profiles of CeO_2 at different constant current densities (a); GCD profiles of CeO_2 , RGO and CRGO nanohybrids (with different wt% of RGO) at 1 A/g (b); GCD profiles of CRGO3 at different current densities (c); Specific capacitance of CeO_2 , RGO and CRGO nanohybrids at 1 A/g (d); Capacity retention against cycle number at 4 A/g for CeO_2 and CRGO3 (e); GCD profiles (1st and 3000th cycles) of CRGO3 at high current densities of 10 A/g and 20 A/g (f).

The stability of the CRGO3 electrode was also tested at high current densities of 10 A/g and 20 A/g for upto 3000 cycles which are shown in Figure 6(f). The specific capacitances measured from the first cycle of GCD at 10 A/g and 20 A/g were 175 F/g and 77 F/g, respectively. These values, although much lower than that at 1A/g, but are expected due to less time available for the electrolyte ions to diffuse into the active sites at such high current densities and are quite comparable with reports on other electrode materials at such high currents.[76-78] The specific capacitance obtained from GCD plots after 3000 cycle further revealed charge retention of more than 82% at 10 A/g and 85% at 20 A/g which clearly establishes the high stability of the CRGO3 electrode even at high current densities. Loss of charge by about 20% is quite common after 5 to 10 thousands cycles of charging and discharging, since some mechanical corrosion (if not chemical) is unavoidable due to diffusion of ions into the porous nanostructured film immersed in an alkaline liquid electrolyte for prolonged duration.[79]

4. Discussion

As surface area of the nanostructures and pore size play critical role in facilitating the number of active catalytic sites for redox reactions to take place (which in turn controls the overall pseudocapacitance of the electrode), the specific surface areas and average pore sizes of various nanohybrid electrodes were measured from their sorption isotherms for N₂ using BET theory. The sorption isotherms are shown in Figure 7(a) whereas the measured values of specific surface areas and average pore sizes are compared in Figure 7(b). It is evident that in Figure 7(b) that the surface area showed a monotonous increase with RGO weight fraction in accordance with expectation due to the influence of RGO which has much larger intrinsic surface area of 106 m²/g [26]. The specific surface area of bare CeO₂ was estimated to be 48 m²/g which increased to 76 m²/g for CRGO3 and to 98 m²/g due to the influence of RGO. To understand why CRGO4 does not exhibit higher charge storage, we note that the overall charge storage of an electrode not only depends on the surface area but also on other competing factors such as yield of redox reaction, efficiency of charge transport, etc. What this means is that larger surface area although facilitates larger adsorption of ions, but it cannot alone guarantee a higher charge storage since a higher RGO weight fraction results in a lower weight fraction of ceria which can lead to a reduction in the redox reaction of ceria thus lowering the pseudocapacitance. The CV curve of CRGO4 justifies this hypothesis. Fig. 7(b) also shows that the pore size almost monotonously decreases with increasing RGO content although the difference is very small between samples CRGO2 and CRGO3. Too small a size can also hinder ion diffusion which may in turn reduce the charge storage capacity and may as well contribute to the poor performance of CRGO4 sample for which the pore size is the smallest (4.4 nm).

Figure 7: (a) N₂ sorption isotherms for different samples, (b) specific surface area and average pore sizes as estimated from the isotherms in (a).

Nyquist plots were recorded, as shown in Fig. 8, using EIS for understanding the electrochemical transport properties of all the electrode materials synthesized in this work. Fig. 8 shows that all the graphs begin with a semicircle within the high frequency range and then they follow a linear rising curve in the mid to low frequency range. The diameter of these semicircles are known to represent the charge transfer resistance (R_{ct}) of the electrodes which clearly shows a rapid and monotonous decrease in magnitude as the weight fraction of RGO is increased except for CRGO4. The R_{ct} value of CeO₂ is the largest (22.8 Ω) in accordance with its poor electrical conductivity whereas it is almost half (13.6 Ω) for RGO due to its good electrical conductivity. Addition of RGO enhances the charge transfer rate of ions in the CRGO nanohybrid samples due to synergistic influence of large surface area and efficient charge transport properties of RGO and efficient catalytic action of CeO₂ nanoparticles as evident from their much lower R_{ct} values as listed in table 3. The intercepts of the Nyquist plot on x-axis define the electrochemical series resistance (ESR) of the corresponding electrode which are also listed in Table 3. The ESR values in Table 3 reveal a monotonous decrease influenced by the presence of RGO except for CRGO4 sample which is very much in agreement with the trend observed in Fig.7(b). Since RGO is a much better electrical conductor than Ceria, it is no surprise that its presence lowers the ESR value. For CRGO4 sample, due to higher weight fraction of RGO, it is possible that aggregates of RGO forms causing a slight increase in ESR from that of CRGO3. In the inset of Fig. 8, an equivalent circuit is shown to represent the EIS plot and the error estimates in fitting are listed in Table 3.

Figure 8: Nyquist plots for RGO, CeO₂ and CRGO nanohybrids. Equivalent circuit for the plots are shown in inset.

Table 3: Different resistance values for various samples as obtained from the Nyquist plots.

Electrode Material	ESR in Ω	R_{ct} in Ω	Error in fitting
CeO ₂	7.69	22.8	1.8%
RGO	7.47	13.6	1.1 %
CRGO1	7.66	9.7	1.4%
CRGO2	6.83	8.6	1.5%
CRGO3	6.69	6.1	0.8%
CRGO4	7.1	7.6	1.4%

For better understanding of the reader of the importance of this work, we have compared the results of this work with previously published reports on ceria based electrodes in Table 4. It is evident that the nanohybrid synthesized in this work shows better performance in terms of specific capacitance and cycle stability as compared to the previous reports. The table 4 also shows that previous studies have used stronger alkaline electrolyte than that used by us (except for Ref. 42) which are likely to have poor cycle

stability over large number of cycles. Interestingly, except Ref. 42, the other studies did not show cycle stability beyond 1000 cycles whereas we have shown 90% retention of charge after 5000 cycles indicating its superior stability over previously studied materials. The enhanced performance of our CRGO3 electrode could be due to a number of reasons such as use of an optimized weight fraction of RGO, good attachment of ceria with RGO, positive catalytic influence of Ce_2O_3 mixed with CeO_2 (as reported by some literature [66]), etc.

Table 4: Comparison of the specific capacitance of the electrode prepared in this work with that of similar electrodes reported by other researchers.

CeO₂/RGO Electrode Material	CeO₂ particle Size(nm)	Electrolyte type & molarity	Specific Capacitance (F/g)	Capacity retention	Reference number
Graphene-CeO ₂	10-12	3M KOH	191 F/g at 5 mV/s 208 F/g at 1 A/g	98% @ 1000 cycles	36
Graphene-CeO ₂	10-50	1M H ₂ SO ₄	110 F/g at 10 mV/s	No data	37
CeO ₂ -RGO	25	0.5M Na ₂ SO ₄	211 F/g at 2 mV/s 185 F/g at 2A/g	105%@ 4000 cycles	38
Graphene-CeO ₂	100	2M KOH	89 F/g at 1 A/g	No data	39
CeO ₂ -RGO	3	3M KOH	265 F/g at 5 mV/s	96% @ 1000 cycles	40
CeO ₂ -graphene	2-3	6M KOH	383 F/g at 3A/g	86% @ 1000 cycles	42
CeO ₂ -RGO	14	3M KOH	282 F/g at 2 A/g	86% @1000 cycles	43
CeO ₂ -RGO-MnO ₂	10	2M KOH	648 F/g at 5 mV/s	90% @ 1000 cycles	80
CeO ₂ -graphene-Ag	20	3M KOH	710 F/g at 0.2 A/g	99 % @ 1000 cycles	81
CeO₂/Ce₂O₃-RGO	5	1M NaOH	697 F/g at 5 mV/s 1027 F/g at 1 A/g	79% @ 5000 cycles 90% @1000 cycles	This work

5. Conclusions

To conclude, CeO₂-Ce₂O₃ quantum dots (~5 nm in size) were uniformly anchored on RGO sheets to form nanohybrids containing different weight fractions of RGO via a simple in situ hydrothermal method. CRGO3 nanohybrid containing 7 wt% RGO emerged as the best performing material when tested as electrode for supercapacitor since it exhibited specific capacitance of ~1027 F/gm at 1 A/g current density which was not only higher than those of other samples tested here but also higher than all previous reports on CeO₂-RGO based electrode material tested for this purpose. The CRGO3 electrode also showed good cycle stability with 90% of charge retention after 1000 cycles and 79% retention after 5000 cycles. The charge transfer resistance for the CRGO3 sample was found to be the lowest among all the tested samples which was assigned as the reason for its highest charge storage capacity. A

synergistic influence of the optimized weight fraction of RGO nanosheets leading to largest surface area and the enhanced pseudocapacitive behaviour due to mixed phase of CeO_2 - Ce_2O_3 quantum dots is believed to be responsible for the improved charge transfer properties of the CRGO3 electrode. Thus, this work shows a facile, low-cost method to use ceria quantum dots as electrode material for supercapacitor application.

Acknowledgements

The authors acknowledge the MHRD, Govt. of India for the “Centre of Excellence in Advanced Materials” grant of April 2013 under the Technical Education Quality Improvement Programme (TEQIP) phase II for funding this research.

References:

1. A. Balducci, R. Dugas, P.L. Taberna, P. Simon, D. Plée, M. Mastragostino, S. Passerini, High temperature carbon–carbon supercapacitor using ionic liquid as electrolyte, *J. Power Sources*. 2007, 165, 922–927.
2. Y. Gogotsi, P. Simon, True Performance Metrics in Electrochemical Energy Storage, *Science* (80-.). 2011, 334, 917 LP – 918.
3. A. González, E. Goikolea, J.A. Barrena, R. Mysyk, Review on supercapacitors: Technologies and materials, *Renew. Sustain. Energy Rev.* 2016, 58, 1189–1206.
4. C. Largeot, C. Portet, J. Chmiola, P.-L. Taberna, Y. Gogotsi, P. Simon, Relation between the Ion Size and Pore Size for an Electric Double-Layer Capacitor, *J. Am. Chem. Soc.* 2008, 130, 2730–2731.
5. P. Sharma, T.S. Bhatti, A review on electrochemical double-layer capacitors, *Energy Convers. Manag.* 2010, 51, 2901–2912.
6. A. Noori, M.F. El-Kady, M.S. Rahmanifar, R.B. Kaner, M.F. Mousavi, Towards establishing standard performance metrics for batteries, supercapacitors and beyond, *Chem. Soc. Rev.* 2019, 48, 1272–1341.
7. P. Simon, Y. Gogotsi, Materials for electrochemical capacitors, *Nat. Mater.* 2008, 7, 845.
8. J. Libich, J. Máca, J. Vondrák, O. Čech, M. Sedlaříková, Supercapacitors: Properties and applications, *J. Energy Storage*. 2018, 17, 224–227.

9. S.S. Zhang, Eliminating pre-lithiation step for making high energy density hybrid Li-ion capacitor, *J. Power Sources*. 2017, 343, 322–328.
10. A.K. Shukla, A. Banerjee, M.K. Ravikumar, A. Jalajakshi, Electrochemical capacitors: Technical challenges and prognosis for future markets, *Electrochim. Acta*. 2012, 84, 165–173.
11. R.A. Susantyoko, F. Parveen, I. Mustafa, S. Almheiri, MWCNT/activated-carbon freestanding sheets: a different approach to fabricate flexible electrodes for supercapacitors, *Ionics (Kiel)*. 2019, 25, 265–273.
12. E.P. Gilshteyn, D. Amanbayev, A.S. Anisimov, T. Kallio, A.G. Nasibulin, All-nanotube stretchable supercapacitor with low equivalent series resistance, *Sci. Rep.* 2017, 7, 17449.
13. A. Bakandritsos, P. Jakubec, M. Pykal, M. Otyepka, Covalently functionalized graphene as a supercapacitor electrode material, *FlatChem*. 2019, 13, 25–33.
14. M.F. Iqbal, M.N. Ashiq, A. Razaq, M. Saleem, B. Parveen, M.-U. Hassan, Excellent electrochemical performance of graphene oxide based strontium sulfidenanorods for supercapacitor applications, *Electrochim. Acta*. 2018, 273, 136–144.
15. B. Xu, H. Wang, Q. Zhu, N. Sun, B. Anasori, L. Hu, F. Wang, Y. Guan, Y. Gogotsi, Reduced graphene oxide as a multi-functional conductive binder for supercapacitor electrodes, *Energy Storage Mater.* 2018, 12, 128–136.
16. R. Kumar, E. Joanni, R.K. Singh, D.P. Singh, S.A. Moshkalev, Recent advances in the synthesis and modification of carbon-based 2D materials for application in energy conversion and storage, *Prog. Energy Combust. Sci.* 2018, 67, 115–157.
17. R. Kumar, E. Joanni, R. Savu, M.S. Pereira, R.K. Singh, C.J.L. Constantino, L.T. Kubota, A. Matsuda, S.A. Moshkalev, Fabrication and electrochemical evaluation of micro-supercapacitors prepared by direct laser writing on free-standing graphite oxide paper, *Energy*. 2019, 179, 676–684.
18. R. Kumar, R.K. Singh, A.R. Vaz, R. Savu, S.A. Moshkalev, Self-Assembled and One-Step Synthesis of Interconnected 3D Network of Fe₃O₄/Reduced Graphene Oxide Nanosheets Hybrid for High-Performance Supercapacitor Electrode, *ACS Appl. Mater. Interfaces*. 2017, 9, 8880–8890.
19. R. Kumar, S. Sahoo, E. Joanni, R.K. Singh, R.M. Yadav, R.K. Verma, D.P. Singh, W.K. Tan, A. Pérez del Pino, S.A. Moshkalev, A. Matsuda, A review on synthesis of graphene, h-BN and

- MoS₂ for energy storage applications: Recent progress and perspectives, *Nano Res.* 2019,12, 2655–2694.
20. X. Ren, C. Guo, L. Xu, T. Li, L. Hou, Y. Wei, Facile Synthesis of Hierarchical Mesoporous Honeycomb-like NiO for Aqueous Asymmetric Supercapacitors, *ACS Appl. Mater. Interfaces.* 2015, 7, 19930–19940.
  21. G.-S. Jang, S. Ameen, M.S. Akhtar, H.-S. Shin, Cobalt oxide nanocubes as electrode material for the performance evaluation of electrochemical supercapacitor, *Ceram. Int.* 2018, 44, 588–595.
  22. X. Su, L. Yu, G. Cheng, H. Zhang, M. Sun, X. Zhang, High-performance α -MnO₂ nanowire electrode for supercapacitors, *Appl. Energy.* 2015, 153, 94–100.
  23. R. K. Agrawalla, V. Meriga, R. Paul, A. K. Chakraborty, A. K., Mitra, Solvothermal synthesis of a polyaniline nanocomposite-a prospective biosensor electrode material. *Express. Polym. Lett.* 2016. **10**, 780–787.
  24. Y.Y. Smolin, K.L. Van Aken, M. Boota, M. Soroush, Y. Gogotsi, K.K.S. Lau, Engineering Ultrathin Polyaniline in Micro/Mesoporous Carbon Supercapacitor Electrodes Using Oxidative Chemical Vapor Deposition, *Adv. Mater. Interfaces.* 2017, 4, 1601201.
  25. Y. Huang, H. Li, Z. Wang, M. Zhu, Z. Pei, Q. Xue, Y. Huang, C. Zhi, Nanostructured Polypyrrole as a flexible electrode material of supercapacitor, *Nano Energy.* 2016, 22, 422–438.
  26. N. Chakrabarty, A.K. Chakraborty, Controlling the electrochemical performance of β -Ni(OH)₂/carbon nanotube hybrid electrodes for supercapacitor applications by La doping: A systematic investigation, *Electrochim. Acta.* 2019, 297, 173–187.
  27. I.Chakraborty, N. Chakrabarty, A. Senapati, A.K. Chakraborty, CuO@NiO/Polyaniline/MWCNT nanocomposite as high-performance electrode for supercapacitor, *J. Phys. Chem. C.* 2018, 122, 27180-27190.
  28. A. Sarkar, A.K. Chakraborty, S. Bera, S. Krishnamurthy, Novel hydrothermal synthesis of CoS₂/MWCNT nanohybrid electrode for supercapacitor : a systematic investigation on the influence of MWCNT, *J. Phys. Chem. C.* 2018, 122, 18237-18246.
  29. N. Chakrabarty, A.K. Chakraborty, H. Kumar, Nickel-Hydroxide-Nanohexagon-Based High-Performance Electrodes for Supercapacitors: A Systematic Investigation on the Influence of Six Different Carbon Nanostructures, *J. Phys. Chem. C.*, 2019, 123, 29104–29115.
  30. N. Chakrabarty, S. Sivaprakash, A.K. Chakraborty, Electrochemical properties of CNT/NiO composite, *AIP Conf. Proc.* 2015, 1665, 50072.

31. P. Sivakumar, M. Jana, M. Kota, H.S. Lee, H.S. Park, Porous interconnected NiCo₂O₄ nanosheets and nitrogen- and sulfur-codoped reduced graphene oxides for high-performance hybrid supercapacitors, *J. Alloys Compd.* 2019, 781, 515–523.
32. R. K. Agrawalla, S. Paul, P. K. Sahoo, A. K. Chakraborty, A. K. Mitra, A facile synthesis of a novel three-phase nanocomposite: Single-wall carbon nanotube/silver nanohybrid fibers embedded in sulfonated polyaniline, *J. Appl. Polym. Sci.* 2015, 132, 41692.
33. H. Chen, S. Zhou, L. Wu, Porous Nickel Hydroxide–Manganese Dioxide–Reduced Graphene Oxide Ternary Hybrid Spheres as Excellent Supercapacitor Electrode Materials, *ACS Appl. Mater. Interfaces.* 2014, 6, 8621–8630.
34. R. Chiba, T. Komatsu, H. Orui, H. Taguchi, K. Nozawa, H. Arai, SOFC Cathodes Composed of LaNi_{0.6}Fe_{0.4}O₃ and Pr-Doped CeO₂, *Electrochem. Solid-State Lett.*, 2009, 12, B69–B72.
35. Y. M. Chiang, E.B. Lavik, I. Kosacki, H.L. Tuller, J.Y. Ying, Defect and transport properties of nanocrystalline CeO_{2-x}, *Appl. Phys. Lett.* 1996, 69, 185–187.
36. Y. Wang, C.X. Guo, J. Liu, T. Chen, H. Yang, C.M. Li, CeO₂ nanoparticles/graphene nanocomposite-based high performance supercapacitor, *Dalt. Trans.* 2011, 40, 6388–6391.
37. T. Saravanan, M. Shanmugam, P. Anandan, M. Azhagurajan, K. Pazhanivel, M. Arivanandhan, Y. Hayakawa, R. Jayavel, Facile synthesis of graphene-CeO₂ nanocomposites with enhanced electrochemical properties for supercapacitors, *Dalt. Trans.* 2015, 44, 9901–9908.
38. A.S. Dezfouli, M.R. Ganjali, H.R. Naderi, P. Norouzi, A high performance supercapacitor based on a ceria/graphene nanocomposite synthesized by a facile sonochemical method, *RSC Adv.* 2015, 5, 46050–46058.
39. K. Chen, D. Xue, *Journal of Colloid and Interface Science* In-situ electrochemical route to aerogel electrode materials of graphene and hexagonal CeO₂, *J. Colloid Interface Sci.* 2015, 446, 77–83.
40. Z. Ji, X. Shen, H. Zhou, K. Chen, Facile synthesis of reduced graphene oxide/CeO₂ nanocomposites and their application in supercapacitors, *Ceram. Int.* 2015, 41, 8710–8716.
41. R. Kumar, A. Agrawal, R.K. Nagarale, A. Sharma, High Performance Supercapacitors from Novel Metal-Doped Ceria-Decorated Aminated Graphene, *J. Phys. Chem. C.* 2016, 120, 3107–3116.

42. D. Deng, N. Chen, X. Xiao, S. Du, Y. Wang, Electrochemical performance of CeO₂ nanoparticle-decorated graphene oxide as an electrode material for supercapacitor, *Ionics* (Kiel). 2017, 23, 121–129.
43. T. Li, H. Liu, A simple synthesis method of nanocrystals CeO₂ modified rGO composites as electrode materials for supercapacitors with long time cycling stability, *Powder Technol.* 2018, 327, 275–281.
44. X. Hu, W. Zhang, X. Liu, Y. Mei, Y. Huang, Nanostructured Mo-based electrode materials for electrochemical energy storage, *Chem. Soc. Rev.* 2015, 44, 2376–2404.
45. S. Chakraborty, S. Saha, V.R. Dhanak, K. Biswas, M. Barbezat, G.P. Terrasi, A.K. Chakraborty, High yield synthesis of amine functionalized graphene oxide and its surface properties, *RSC Adv.* 2016, 6, 67916–67924.
46. A.K. Chakraborty, and K.S. Coleman, Poly(ethylene) Glycol/Single-Walled Carbon Nanotube Composites, *J. Nanosci. Nanotechnol.* 2008, 8, 4013–4016.
47. S.M.D. Watson, K.S. Coleman, A.K. Chakraborty, A New Route to the Production and Nanoscale Patterning of Highly Smooth, Ultrathin Zirconium Oxide Films, *ACS Nano.* 2008, 2, 643–650.
48. S.P. Mondal, A. Dhar, S.K. Ray, A.K. Chakraborty, Bonding, vibrational, and electrical characteristics of CdS nanostructures embedded in polyvinyl alcohol matrix, *J. Appl. Phys.* 2009, 105(8), 084309.
49. V. Meriga, S. Valligatla, S. Sundaresan, C. Cahill, V.R. Dhanak, A.K. Chakraborty, Optical, electrical, and electrochemical properties of graphene based water soluble polyaniline composites, *J. Appl. Polym. Sci.* 2015, 132 (45), 42766 (1–9).
50. L. Jiang, M. Yao, B. Liu, Q. Li, R. Liu, H. Lv, S. Lu, C. Gong, B. Zou, T. Cui, B. Liu, G. Hu, T. Wågberg, Controlled Synthesis of CeO₂/Graphene Nanocomposites with Highly Enhanced Optical and Catalytic Properties, *J. Phys. Chem. C.* 2012, 116, 11741–11745.
51. Q. Ling, M. Yang, R. Rao, H. Yang, Q. Zhang, H. Liu, A. Zhang, Simple synthesis of layered CeO₂–graphene hybrid and their superior catalytic performance in dehydrogenation of ethylbenzene, *Appl. Surf. Sci.* 2013, 274, 131–137.
52. Z. Wang, Z. Quan, J. Lin, Remarkable Changes in the Optical Properties of CeO₂ Nanocrystals Induced by Lanthanide Ions Doping, *Inorg. Chem.* 2007, 46, 5237–5242.

53. C. Zhang, J. Lin, Visible-light induced oxo-bridged Zr^{IV}–O–Ce^{III} redox centre in tetragonal ZrO₂–CeO₂ solid solution for degradation of organic pollutants, *Phys. Chem. Chem. Phys.* 2011, 13, 3896–3905.
54. F. Vindigni, M. Manzoli, A. Damin, T. Tabakova, A. Zecchina, Surface and Inner Defects in Au/CeO₂ WGS Catalysts: Relation between Raman Properties, Reactivity and Morphology, *Chem. – A Eur. J.* 2011, 17, 4356–4361.
55. M. Srivastava, A.K. Das, P. Khanra, M.E. Uddin, N.H. Kim, J.H. Lee, Characterizations of in situ grown ceria nanoparticles on reduced graphene oxide as a catalyst for the electrooxidation of hydrazine, *J. Mater. Chem. A* 2013, 1, 9792–9801.
56. L. Jiang, M. Yao, B. Liu, Q. Li, R. Liu, Z. Yao, S. Lu, W. Cui, X. Hua, B. Zou, T. Cui, B. Liu, Shape-selective synthesis and optical performance of ceria nanocrystal/graphene hybrid composites, *CrystEngComm* 2013, 15, 3739–3743.
57. A.A. Dubale, W.-N. Su, A.G. Tamirat, C.-J. Pan, B.A. Aragaw, H.-M. Chen, C.-H. Chen, B.-J. Hwang, The synergetic effect of graphene on Cu₂O nanowire arrays as a highly efficient hydrogen evolution photocathode in water splitting, *J. Mater. Chem. A* 2014, 2 18383–18397.
58. A.A. Ibrahim, A. Lin, F. Zhang, K.M. AbouZeid, M.S. El-Shall, Palladium Nanoparticles Supported on a Metal–Organic Framework-Partially Reduced Graphene Oxide Hybrid for the Catalytic Hydrodeoxygenation of Vanillin as a Model for Biofuel Upgrade Reactions, *ChemCatChem* 2017, 9, 469–480..
59. N. Mohanty, A. Nagaraja, J. Armesto, V. Berry, High-Throughput, Ultrafast Synthesis of Solution- Dispersed Graphene via a Facile Hydride Chemistry, *Small*, 2010, 6, 226–231..
60. V.G. Sreeja, G. Vinitha, R. Reshmi, E.I. Anila, M.K. Jayaraj, Effect of reduction time on third order optical nonlinearity of reduced graphene oxide, *Opt. Mater. (Amst)*, 2017, 66, 460–468. .
61. F. Ghasemi, M. Jalali, A. Abdollahi, S. Mohammadi, Z. Sanaee, S. Mohajerzadeh, A high performance supercapacitor based on decoration of MoS₂/reduced graphene oxide with NiO nanoparticles, *RSC Adv* 2017, 7, 52772–52781.
62. P. Burroughs, A. Hamnett, A.F. Orchard, G. Thornton, Satellite structure in the X-ray photoelectron spectra of some binary and mixed oxides of lanthanum and cerium, *J. Chem. Soc. Dalt. Trans.* 1976, 17, 1686–1698.
63. V. Stetsovych, F. Pagliuca, F. Dvořák, T. Duchoň, M. Vorokhta, M. Aulická, J. Lachnitt, S. Schernich, I. Matolínová, K. Veltruská, T. Skála, D. Mazur, J. Mysliveček, J. Libuda, V.

- Matolín, Epitaxial Cubic Ce₂O₃ Films via Ce–CeO₂ Interfacial Reaction, *J. Phys. Chem. Lett.* 2013, 4, 866–871.
64. T. Ghoshal, P.G. Fleming, J.D. Holmes, M.A. Morris, The stability of “Ce₂O₃” nanodots in ambient conditions: a study using block copolymer templated structures, *J. Mater. Chem.* 2012, 22, 22949–22957.
65. H. He, J. Klinowski, M. Forster, A. Lerf, A new structural model for graphite oxide, *Chem. Phys. Lett.* 1998, 287, 53–56.
66. A. Dey, S. Krishnamurthy, J. Bowen, D. Nordlund, M. Meyyappan, R.P. Gandhiraman, Plasma Jet Printing and in Situ Reduction of Highly Acidic Graphene Oxide, *ACS Nano.* 2018, 12, 5473–5481.
67. R. Verma, S.K.Samdarshi, S. Bojja, S. Paul, B. Choudhury, A novel thermophotocatalyst of mixed-phase cerium oxide (CeO₂/Ce₂O₃) homocomposite nanostructure: Role of interface and oxygen vacancies, *Solar Energy Materials Solar Cells* 2015, 141, 414–422.
68. D. Deng, N. Chen, Y. Li, X. Xing, X. Liu, X. Xiao, Y. Wang, Cerium oxide nanoparticles/multi-wall carbon nanotubes composites: Facile synthesis and electrochemical performances as supercapacitor electrode materials, *Phys. E Low-Dimensional Syst. Nanostructures.* 2017, 86, 284–291.
69. Y. Yue, K. S. V. Santhanam, K Reed, T.Allston, Redox Behavior of Dicerium Trioxide and the Possible Formation of Sesquioxide- C for Fuel Cells. *MRS Proceedings* 2015, 1735, mrsf14–1735-s05–36.
70. M. Sathiya, A.S. Prakash, K. Ramesha, J. Tarascon, A.K. Shukla, V₂O₅-Anchored Carbon Nanotubes for Enhanced Electrochemical Energy Storage, *J. Am. Chem. Soc.* 2011, 133, 16291–16299.
71. J. Duay, S.A. Sherrill, Z. Gui, E. Gillette, S.B. Lee, Self-Limiting Electrodeposition of Hierarchical MnO₂ and M(OH)₂/MnO₂ Nanofibril/Nanowires: Mechanism and Supercapacitor Properties, *ACS Nano.* 2013, 7, 1200–1214.
72. H. Yin, C. Song, Y. Wang, S. Li, M. Zeng, Z. Zhang, Z. Zhu, K. Yu, Influence of morphologies and pseudocapacitive contributions for charge storage in V₂O₅ micro/nano-structures, *Electrochim. Acta.* 2013, 111, 762–770.

73. M. Zhu, W. Meng, Y. Huang, Y. Huang, C. Zhi, Proton-Insertion-Enhanced Pseudocapacitance Based on the Assembly Structure of Tungsten Oxide, *ACS Appl. Mater. Interfaces*. 2014, 6, 18901–18910.
74. D.A.C. Brownson and C.E. Banks, *The Handbook of Graphene Electrochemistry*, Springer-Verlag, London, 2014.
75. A. Sarkar, A.K. Chakraborty, S. Bera, NiS/rGO nanohybrid: An excellent counter electrode for dye sensitized solar cell, *Sol. Energy Mater. Sol. Cells*. 2018, 182, 314–320.
76. S. Teng, G. Siegel, W. Wang, A. Tiwari, Carbonized Wood for Supercapacitor Electrodes, *ECS Solid State Lett.* 2014, 3, M25–M28.
77. K. Xu, X. Zhu, P. She, Y. Shang, H. Sun, Z. Liu, Macroscopic porous MnO₂ aerogels for supercapacitor electrodes, *Inorg. Chem. Front.* 2016, 3, 1043–1047.
78. K.S. Ranjith, G.S.R. Raju, N. R. Chodankar, S.M. Ghoreishian, C.H. Kwak, Y.S. Huh, Y.-K. Han, Electroactive Ultra-Thin rGO-Enriched FeMoO₄ Nanotubes and MnO₂ Nanorods as Electrodes for High-Performance All-Solid-State Asymmetric Supercapacitors, *Nanomaterials*. 2020, 10. doi:10.3390/nano10020289.
79. T. Nguyen, M. de F. Montemor, Metal Oxide and Hydroxide–Based Aqueous Supercapacitors: From Charge Storage Mechanisms and Functional Electrode Engineering to Need-Tailored Devices, *Adv. Sci.* 2019, 6, 1801797.
80. G.P. Ojha, B. Pant, S.J. Park, M. Park, H.Y. Kim, Synthesis and characterization of reduced graphene oxide decorated with CeO₂-doped MnO₂ nanorods for supercapacitor applications, *J. Colloid Interface Sci.* 2017, 494, 338–344.
81. M. Vanitha, Keerthi, P. Cao, N. Balasubramanian, Ag nanocrystals anchored CeO₂/graphene nanocomposite for enhanced supercapacitor applications, *J. Alloys Compd.* 2015, 644, 534–544.

CRedit author statement

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Highlights

- We report a systematic investigation of influence of RGO on electrochemical properties of CeO_2/Ce_2O_3 quantum dots.
- The optimized electrode containing 7 wt% RGO exhibited specific capacitance of 1027 F/g at 1 A/g with 79% cycling stability @5000 cycles.
- The above performance parameters are better than all previous reports of CeO_2 and RGO based electrode.
- High surface area of electrically conducting RGO and highly catalytic mixed phase of CeO_2/Ce_2O_3 resulted in the improvement.