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Highly porous CeO₂ nanostructures prepared via combustion synthesis for supercapacitor applications

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Abstract

We report highly porous CeO₂ nanostructures (CeO₂ NSs) suitable for supercapacitor applications, synthesized using a fast and cost effective combustion approach. Due to its prominent valence states of Ce³⁺/Ce⁴⁺, CeO₂ has emerged as a promising pseudocapacitive material. The drawback of using CeO₂ as a supercapacitor electrode is its poor electrical conductivity. We overcame this drawback of CeO₂ by creating oxygen vacancies on its surface, which act to enhance its electrical conductivity. The physical interpretation of the as-synthesized CeO₂ NSs shows that they have dense active sites and diffusion pathways that enhance the performance of the electrode in a supercapacitor. Electrodes prepared using the synthesized CeO₂ NSs exhibited the initial specific capacitance of 134.6 F g⁻¹ and superior cycling stability of 92.5% after 1000 cycles at a constant current density of 1 A g⁻¹, indicating their potential suitability for use as efficient electrode for supercapacitor devices. The facile synthesis method used herein would help to reduce the cost and time required to synthesize CeO₂ particles and also would avoid the need to research and/or synthesize beneficial composite structures for enhancing the electrochemical properties of CeO₂ based electrodes.

Keywords: Combustion; Supercapacitor; Capacitance; CeO₂; Nanostructure

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1. Introduction

For the wellbeing of the future modern society intense research is carried on the energy storage devices to overcome the issues such as increasing cost of fuels, pollution, and global warming [1, 2]. Supercapacitor is one such attractive energy storage device for applications ranging from mobile electronic devices to electric vehicles [3-5]. Supercapacitors are also known as ultracapacitors or in general electrochemical capacitors [6]. The performance of a supercapacitor is reported to be intermediate to those of traditional capacitors and batteries. Batteries have high energy density and slow kinetics due to their storage of energy in the electrode by redox reactions, whereas supercapacitors have high power density due to their storage of energy at the electrode/electrolyte interface [7]. Supercapacitors have longer cycle life than batteries because batteries' electrochemical charge/discharge process includes phase change in the electrode. Supercapacitors are classified into two types, namely electric double layer capacitors (EDLCs) and pseudocapacitors, based on the energy storage mechanism [8]. In the EDLC, energy is stored by means of an electrostatic mechanism, whereas in the pseudocapacitor, a faradic redox reaction is used. The redox reaction used in the pseudocapacitor enables greater storage of charge compared to that of the EDLC and thus higher specific capacitance [9]. To further enhance the specific power and capacitance of the pseudocapacitor, several attempts have been made to find appropriate active materials. So far, active materials such as RuO_2 [10], MnO_2 [11], NiCo_2O_4 [12], NiO [13], and Co_3O_4 [14] are preferred for supercapacitors due to their high power and high specific capacitance. However, these materials also are expensive, toxic, and require complex synthesis processes; thus, despite their superlative electrochemical performances, researchers continue to search for alternative active materials [15]. Apart from the single and bimetallic transition metal oxides, conductive polymers have also attracted research interest, but their low cycling stabilities represent a considerable barrier to commercialization [16, 17]. In this research, we investigated the low cost, ecofriendly, and abundant material CeO_2 as an efficient supercapacitor electrode. CeO_2 has been coupled with various metal oxides and carbonaceous materials to enhance its properties as an active electrode during the electrochemical process. For example, for supercapacitor applications, a CeO_2 /graphene nanocomposite has been reported by Wang *et al.* [18], a graphene oxide/ CeO_2 nanocomposite has been reported by Ji *et al.* [19], a NiO-CeO_2 binary oxide has been reported by

Padmanathan *et al.* [20], and a CeO₂@MnO₂ core-shell heterostructure has been reported by Zhu *et al.* [21]. The major drawback of CeO₂ relative to other metal oxides used in supercapacitors is its low electronic conductivity. Fortunately, however, the electronic conductivity of CeO₂ can be improved simply by modifying its shape and size [22], whereas other metal oxides must be coupled with conductive elements.

In this study, we synthesized highly porous CeO₂ nanostructures (CeO₂ NSs) for application in supercapacitors by means of solution combustion synthesis. We investigated its chemical and physical properties are investigated using X-ray diffraction analysis (XRD), X-ray photoelectron spectroscopy (XPS), field emission scanning electron microscopy (FE-SEM), high-resolution transmission electron microscopy (HR-TEM), and Brunauer-Emmett-Teller (BET) surface area analysis. When applied as a supercapacitor active material, the porous CeO₂ was observed to deliver high specific capacitance and excellent rate capability behavior. Thus, we confirmed that merely altering the morphology of the CeO₂, rather than coupling it with a conductive element, was suitable for enhancing its electrochemical properties.

2. Experimental

2.1. Materials

The chemicals used during the synthesis process were of analytical grade. Chemicals like cerium nitrate hexahydrate (Ce(NO₃)₃·6H₂O) and glycine nitrate (C₂H₅NO₂) were purchased from Sigma Aldrich and were used without any further refinement. Distilled water was used during the experimental process.

2.2. Preparation of porous CeO₂

During the combustion process, Ce(NO₃)₃·6H₂O and C₂H₅NO₂ were used as the oxidizer and the fuel, respectively. In a typical synthesis, 5 mmol of Ce(NO₃)₃·6H₂O and 2.5 mmol of C₂H₅NO₂ were dissolved in 30 mL of deionized (DI) water under continuous magnetic stirring at room temperature to form a homogeneous solution. The prepared mixture was placed in a preheated muffle furnace at 300 °C to allow combustion to take place. During the combustion process, the solution boiled and eventually self-ignited; the entire reaction was completed within 5 min. The powdered product was collected and washed with absolute ethanol and DI water several times to remove impurities and then dried in a vacuum oven at 80 °C

for 2 h. The dried CeO₂ powders were further calcined at 600 °C in air for 4 h to remove traces of unburnt fuel. The synthesis process is schematically illustrated in Fig. 1.

2.3. Material characterizations

The structure and chemical state of the prepared sample were respectively analyzed using X-ray diffraction analysis (M18XHF-SRA, Mac Science Ltd.) with a Cu K α (λ = 0.15406 nm) radiation source and using X-ray photoelectron spectroscopy (Thermo Multi-Lab 2000 System). The morphology of the prepared sample was depicted by field emission scanning electron microscopy (Carl Zeiss, LEO SUPRA 55, Germany) and high-resolution transmission electron microscopy (JEM 200CX, JEOL, Japan) coupled with energy-dispersive X-ray spectrometry (EDX) to measure the intrinsic microstructure, intrinsic crystallographic properties, and elemental composition. Specific surface area and pore size distributions were calculated using analysis Brunauer-Emmett-Teller and Barrett-Joyner-Halenda, respectively.

2.4. Electrochemical characterizations

The electrochemical properties of the as-synthesized CeO₂ NSs were characterized using an IVIUMSTAT electrochemical workstation (IVIUM Technologies) in a three-electrode system at room temperature. Cyclic voltammetry (CV), galvanic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS) analyses were conducted using nickel foam coated with the CeO₂ nanoparticles as a working electrode, platinum wire as a counter electrode, and Ag/AgCl as a reference electrode in a freshly prepared 1 M potassium hydroxide (KOH) electrolyte solution. The obtained EIS spectra were fitted with Z-View software in terms of appropriate circuit. To prepare the working electrode, a slurry was made by mixing 80 wt% of CeO₂ nanoparticles, 10 wt% of Super P carbon black, and 10 wt% of PVdF in the solvent *N*-methyl-2-pyrrolidone (NMP). The prepared slurry was uniformly coated on the surface of a 1 cm² piece of nickel foam. The coated nickel foam was dried at room temperature and subsequently dried in an oven for 3 h at 120 °C.

3. Results and discussion

3.1. Material characterizations

XRD analysis was carried out to determine the structural phase of the synthesized CeO₂ nanoparticles. Fig. 2 shows XRD spectra collected over the 2θ range of 10-80° of the CeO₂ nanoparticles synthesized by the combustion process, followed by annealing at 600 °C. The XRD pattern showed eight major diffraction peaks from the planes (111) [$2\theta = 28.60^\circ$, $d = 3.11 \text{ \AA}$], (200) [$2\theta = 33.09^\circ$, $d = 2.70 \text{ \AA}$], (220) [$2\theta = 47.61^\circ$, $d = 1.91 \text{ \AA}$], (311) [$2\theta = 48.52^\circ$, $d = 1.69 \text{ \AA}$], (222) [$2\theta = 56.42^\circ$, $d = 1.58 \text{ \AA}$], (400) [$2\theta = 59.05^\circ$, $d = 1.34 \text{ \AA}$], (331) [$2\theta = 69.4^\circ$, $d = 1.24 \text{ \AA}$], and (420) [$2\theta = 76.70^\circ$, $d = 1.21 \text{ \AA}$], which were indexed to the face-centered cubic structure with lattice parameters $a = b = c = 5.406 \text{ \AA}$ (JCPDS card no. 34-0394) [23, 24]. The average grain size of the synthesized CeO₂ NSs is calculated using the well-known Scherrer's equation:

$$D = \frac{k\lambda}{\beta \cos \theta}$$

Where D is the crystalline size, k is the Scherrer constant, λ is the wavelength of X-ray, β is the full width half maxima, and θ is the Bragg angle. The measured peaks are fitted using the Gaussian curves to obtain the exact peak position and full width half maximum (FWHM) corresponding the monochromatic Cu K α radiation. With the increase in Bragg angle the systematic error decreases, hence the grain size of the synthesized CeO₂ NSs is measured for the reflection peak (311) which have both higher angle and equitable intensity [24]. The grain size of the CeO₂ NSs is determined to be 28 nm.

The elemental compositions and oxidation states of the combustion-synthesized CeO₂ NSs were analyzed using XPS. The Ce 3d and O 1s spectra were fitted using Gaussian fitting. The peaks observed in the Ce 3d spectra corresponded to the Ce³⁺ and Ce⁴⁺ oxidation states. The peaks observed at ~881.2 and ~897.3 eV in Fig. 3a corresponded to the 3d_{5/2} and 3d_{3/2} electron states of Ce³⁺, respectively. The representative indication of Ce⁴⁺ observed at ~915.9 eV was due to the 3d_{3/2} electron state. These peaks are denoted as V, V', V'', and V''' for the Ce 3d_{5/2} spin orbit state and as U, U', U'', U⁰, and U''' for the Ce 3d_{3/2} spin orbit state. The approximate amounts of Ce³⁺ and Ce⁴⁺ in the synthesized sample were estimated from the areas of their representative peaks

at ~881.2 and ~915.9 eV; according to this measure, Ce^{3+} was more abundant than Ce^{4+} in the sample. This observation confirmed the presence of oxygen vacancies in the synthesized CeO_2 NSs [25]. The fitted O 1s spectrum (Fig. 3b) showed two peaks: the first, observed at ~528.2 eV, indicates the lattice oxygen, and the second at ~531.7 eV corresponds to the oxygen vacancies. The intensity of the former was much higher than that of the latter, indicating high levels of surface defects caused by oxygen vacancies in the synthesized CeO_2 NSs [26]. The oxygen vacancies lead to the formation of new gap states in which the electrons previously associated with the Ce-O bonds tend to become delocalized, greatly increasing the electrical conductivity [26, 27].

Figs. 4a-c show FE-SEM images of CeO_2 nanoparticles prepared using the combustion process. The inset image in Fig. 4a shows a photograph of synthesized CeO_2 nanoparticles. From these figures, it can be observed that the synthesized sample was brown-yellow with a soapsuds-like morphology. FE-SEM images taken at the micro and nano scales also showed the pores generated during the combustion process. When the prepared colloidal solution was introduced to the high-temperature $Ce(NO_3)_3$ precursor in the colloidal solution, it burnt and decomposed under the influence of the $C_2H_5NO_2$. In addition, during the combustion process, excess amounts of gases such as CO_2 , N_2 , and H_2O were produced. Release of these gases induces the formation of porous morphology, as observed over the surfaces of the synthesized CeO_2 nanoparticles [28]. Further, the calcination process applied to the synthesized sample helps in improving the crystallization of the CeO_2 nanoparticles. The chemical reaction can be represented as follows [29]:

Figs. 4d-i show the results obtained from FE-TEM analysis. The image shown in Fig. 4d is consistent with the results of FE-SEM analysis, showing a highly porous soapsuds-like morphology. The observed morphology produces abundant canals that allow the efficient transport of electrons and ions. Fig. 4e shows the lattice spacing observed from the FE-TEM analysis; the d-spacing values of 0.31 and 0.27 nm shown in the inset images correspond to the (111) and (200) planes, respectively. The SAED patterns shown in Fig. 4f correspond to the planes (111), (200), (220), (311), (222), (400), (331), and (420), confirming the

formation of CeO₂. In addition, to visually confirm the formation of CeO₂ NSs, energy dispersive X-ray spectroscopy was carried out (Figs. 4g-i), showing the presence of Ce and O

The surface area and pore size distribution of the synthesized nanostructures were investigated using nitrogen adsorption-desorption analysis. The obtained plots depicted a type IV adsorption/desorption with an H3 hysteresis loop (Fig. 5) according to the IUPAC grouping of hysteresis loops [30, 31]. From the BET results, the specific surface area was calculated to be 181.81 m² g⁻¹. The pore size distribution calculated from the adsorption data by means of the BJH model was 9.36 nm (Fig. 5 inset). These results indicate that the synthesized CeO₂ NSs had surface area and pore size distribution that were advantageous for the diffusion of ions in the electrolyte and for increasing the contact between the electrode and electrolyte. Schematic illustration of diffusion of ions and transport of electrons is also shown in Fig. 5.

3.2. Electrochemical characterizations

To assess the potential applicability of the as-prepared sample for supercapacitor applications, electrochemical properties of porous CeO₂ NSs coated on nickel foam (*i.e.*, CeO₂ NSs/Ni foam) as an electrode were investigated *via* CV, GCD, and EIS analysis in 1 M KOH electrolyte solution using a conventional beaker-type three-electrode cell at RT. Fig. 6a demonstrates comparative CV curves of CeO₂ NSs/Ni foam and pristine Ni foam electrodes at the constant scan rate of 20 mV s⁻¹ over the potential range of -0.3 to 0.45 V (*vs.* Ag/AgCl). Because of its high surface area and porosity, the CeO₂ NSs/Ni foam electrode exhibited much higher CV enclosed area and current response compared to the pristine Ni foam, suggesting that the contribution of the Ni foam to the capacitance was negligible. Noticeably, the CV curve of CeO₂ NSs/Ni foam clearly exhibited a pseudocapacitive characteristic with faradaic redox behavior. This phenomenon of porous CeO₂ NSs in aqueous alkaline electrolyte was mainly attributed to the redox reactions between Ce³⁺ and Ce⁴⁺ ions in the material. The redox behavior of porous CeO₂ NSs can be expressed using the following reaction formulas [32]:

Fig. 6b shows CV curves of porous CeO₂ NSs/Ni foam electrode measured at various scan rates from 10 to 80 mV s⁻¹. As the scan rate increased, the enclosed areas surrounded by the CV curves were not significantly influenced, but the current responses were enhanced. Under forward and reverse sweeps, all CV curves showed almost mirror image symmetry with redox behavior, implying excellent electrochemical reversibility and good rate capability of the sample. The prominent electrochemical ability of CeO₂ NSs can be attributed to their meso/macroporous features and high surface area, which can contribute to the rapid diffusion of electrolyte ions into the material during redox reactions. Specific capacitances (C_{sp} , F g⁻¹) were estimated from the CV curves of the CeO₂ NSs using the following equation [33]:

$$C_{sp} = \frac{\int I \times dV}{2 \times v \times \Delta V \times m}, \quad (3)$$

where $\int IdV$ is the CV integral area (one complete cycle), I is the voltammetric current, v is the scan rate, ΔV is the potential window, and m is the mass of the material. The specific capacitance of CeO₂ increased with decreasing scan rate, reaching a maximum of about 114.6 F g⁻¹ at the lowest scan rate of 10 mV s⁻¹ (Fig. 6c). As the scan rate increased, the specific capacitance of the CeO₂ NSs decreased, with capacitance retention of 72.94% observed at 80 mV s⁻¹. The decreased capacitance occurring under high scan rates arose because the electrolyte ions did not have enough time to completely wet the active material to allow completion of the electrochemical reaction. Furthermore, GCD analysis was carried out under various current densities (1 to 10 A g⁻¹) to determine the energy storage capabilities of the porous CeO₂ NSs/Ni foam electrode; the corresponding plateaus are shown in Fig. 6d. Nonlinear charge-discharge shapes with pseudocapacitive characteristics were observed in each GCD cycle; these were ascribed to the rapid mutation of Ce³⁺ and Ce⁴⁺ ions with electrolyte and are in accordance with the CV curves of Fig. 6b. The specific capacitances were calculated from the GCD curves using the following equation [9]:

$$C_{sp} = \frac{I \times \Delta t}{m \times V}, \quad (4)$$

where I is the discharge current (mA), Δt is the discharge time (s), m is the mass of the electroactive material (mg), and ΔV is the potential window (V). The calculated specific capacitances of 134.6, 120.9, 117.8, 116.2, 112.5, and 109.5 F g⁻¹ were observed under the current densities of 1, 2, 3, 5, 7, and 10 A g⁻¹, respectively (Fig. 6e). The porous CeO₂ NSs sample prepared in the present work showed higher specific capacitance than that of previously reported nanomaterials based on CeO₂ and other conventional metal oxides [34-39]. The superior energy storage properties of the porous CeO₂ NSs could be attributed to the following merits: (i) the facile combustive synthesis of CeO₂ NSs enables high surface area and meso/macroporous features; (ii) the oxygen vacancies produced on the surfaces of the CeO₂ NSs enhance their electronic conductivity and thereby their electrochemical properties; (iii) the unique porous holes of high surface area in the CeO₂ NSs allow easy entry of electrolyte ions, leading to richly concentrated electrochemical active sites and thereby allowing rapid redox reaction with electrolyte ions; (iv) the rapid redox reactions within the porous CeO₂ NSs sample further shorten the distance of ion diffusion paths and improve the charge storage via quick electron transportation to the current collector. Fig. 6f schematically illustrates the charge transport paths and electrolyte diffusion of the porous CeO₂ NSs on the Ni foam current collector.

Cycling stability of the as-prepared porous CeO₂ NSs, particularly at high current rates, is of great importance to their practical applicability to supercapacitors. Fig. 7a shows the long-term cycling stability of the CeO₂ NSs/Ni foam electrode at the low and high current densities of 1 and 5 A g⁻¹, respectively. Apparently, compared to the initial cycle, the specific capacitance values decrease during continued cycling. However, the capacitance retention observed here was 92.5% of the initial cycle capacitance at the current density of 1 A g⁻¹. Of special importance, we noted that the capacitance degraded only 7.5% after 1000 cycles. Furthermore, as observed from the same figure, the capacitance retention of porous CeO₂ NSs maintained 82.4% of its initial value after 1000 continuous cycles at 5 A g⁻¹. These results indicate that the as-prepared porous CeO₂ electrode has excellent cycling stability at lower and higher current densities. EIS analysis was also carried out to investigate the mechanism of charge storage in porous CeO₂. EIS

measurements were conducted over the frequency range from 0.01 Hz to 100 kHz. Fig. 7b shows EIS plots of a porous CeO₂ NSs electrode, measured before and after cycling. Both EIS spectra consisted of a semicircle in the high-frequency region and an inclined line in the low-frequency region, which were characterized by the frequency response of the electrode/electrolyte system by examining the imaginary component ($-Z''$) of the impedance compared to the real component (Z'). The semicircle indicates the charge-transfer resistance (R_{ct}), and the sloped line is associated with the Warburg resistance (Z_w) of the porous CeO₂. From Nyquist plots, the R_{ct} values of the porous CeO₂ before and after cycling were calculated to be 2.01 and 2.86 Ω , respectively. The lower R_{ct} values of the material further indicated that it had lower resistance and aids in the maintenance of excellent stability during the electrochemical measurements. The results presented in this work show that the porous CeO₂ NSs prepared by a combustion process could be a good candidate for use as cathodes in supercapacitor applications.

4. Conclusions

A highly porous CeO₂ NS material synthesized by a combustion process was proven as an efficient electrode for use in supercapacitors. The combustion process is not only fast and cost-effective, but also aided in the creation of oxygen vacancies on the surface of CeO₂ NSs, as proven by XPS analysis. In addition to the presence of oxygen vacancies, the CeO₂ NSs also had a high surface area of 181.81 m² g⁻¹ and average pore diameter of 9.36 nm, allowing rapid diffusion of ions and electrons. The enhanced physical properties of the active material helped in achieving the high specific capacitance of 134.6 and 116.2 F g⁻¹ with a capacitance retention ratio of 92.5% and 82.4% at the constant current densities of 1 and 5 A g⁻¹, respectively. Overall, the proposed combustion process helped in producing CeO₂ NSs with favorable electrochemical properties; this research also showed that producing a CeO₂ material of advantageous size and shape overcame its disadvantage of low electrical conductivity without the addition of any conductive materials.

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Figures

Fig. 1. Schematic illustration of synthesis of CeO₂ NSs.

Fig. 2. XRD pattern of as-synthesized CeO₂ NSs.

Fig. 3. XPS spectra of as-synthesized CeO₂ NSs. Ce 3d (a) and O1s (b).

Fig. 4. FE-SEM images (a-c); FE-TEM images (d & e) and the inset images in (e) shows the d-spacing; SAED pattern (f); EDX mapping images of Ce and O (g & h); EDX spectrum (i); of the as-synthesized CeO₂ NSs.

Fig. 5. N₂ gas adsorption-desorption isotherm of CeO₂ nanoparticles (inset image: pore size distribution of CeO₂ nanoparticles) and schematic illustration of diffusion of ions and transportation of electrons.

Fig. 6. Electrochemical properties of CeO₂ NSs: Comparison of CV curves between Ni foam and CeO₂ NSs/Ni foam (a); CV curves of CeO₂ NSs/Ni foam at different scan rate (b); Specific capacitance obtained at different scan rate (c); Potential profile obtained by varying current density; (d) Specific capacitance obtained at different current density; (e) Schematic representation of diffusion of ions and transport of electrons.

Fig. 7. Cyclic performance (a); Capacitance retention (b); EIS (c) of CeO₂ NSs/Ni foam. The inset image in the left top of (c) shows the equivalent circuit.

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.