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Improved Super-capacitive Performance of Carbon Foam Supported CeO_x Nanoflowers by Selective Doping and UV Irradiation

Zhemi Xu[#], Adnan Younis[#], Haolan Xu, Sean Li and Dewei Chu^{1,2*}

¹*School of Materials Science and Engineering, University of New South Wales, Sydney, 2052, NSW, Australia*

²*School of Physics and Advanced Materials, University of Technology Sydney, Sydney, 2007, NSW, Australia*

Abstract

In this work, a facile electrochemical approach for depositing Gd-doped CeO_x nanoflowers on porous carbon foam with excellent supercapacitor characteristics has been demonstrated. Moreover, the ultraviolet illumination on the electrodeposited nanoflowers significantly enhances the device supercapacitor performances as compared to thermally treated samples. Based on the experimental results in the present study, a new process to improve surface character and electrochemical property of the electrode material via UV light irradiation has been proposed.

Introduction

Recently, supercapacitors have attracted intensive research interest as they bridge the gap between conventional capacitors and rechargeable batteries. Compared with rechargeable batteries (e.g. lithium ion batteries), supercapacitors have unique advantages of high power density, high dynamic charge propagation, long cycle life (over 10,000 cycles)^[1], smaller size and tolerance of overcharge/discharge. Such distinct merits are extremely desirable in consumer electronics^[2], heavy electric vehicles^[3], renewable energy technology^[4] and industrial power management^[5], etc.

[#] Authors have equal contribution as first author.

*Corresponding Author, Tel.: +61 (0)2 9385 5386; Fax: +61 (0)2 9385 6565

E-mail address: D.Chu@unsw.edu.au, Dewei.Chu@uts.edu.au

Over the past few years, carbon-based materials for supercapacitor applications have been widely studied, owing to their low cost, light weight and good resistance to corrosion^[6]. However, their applications on vast scale were limited due to deficiency of high energy storage capacity and inferior rate capability^[7]. To overcome these challenges, activated carbon^[6], one-dimensional carbon nanostructures such as carbon nanotubes^[8], two-dimensional carbon materials, such as graphene^[9] and three-dimensional porous carbon foams^[10] have been studied as alternative materials for supercapacitors. Among them, 3-D porous carbon could be a promising supporting material that can ensure good ion transport properties owing to its high surface area, high porosity and three dimensional pore connectivity^[11].

Transition metal oxides are widely studied electrode materials that demonstrated outstanding pseudo-capacitance performances, due to their weakly attached surface ions^[1b, 11]. Specifically, the single and bimetallic transition metal oxides such as MnO₂^[12], NiO^[13], Co₃O₄^[14] and RuO₂^[15] etc. exhibited high specific power and specific capacitance. However, the high cost and pollution to environment shrink the boundaries of their applications. Hence, it is desirable to explore the eco-friendly alternative electrode materials for supercapacitors at low cost.

More recently, CeO_x has attracted much attention among metal oxides for supercapacitors, being environmental friendly and possessing excellent electrochemical redox characteristics^[16]. There are a few reports that described the fabrication of CeO_x based electrodes materials with the combination of graphene or metal substrates which demand complex synthesis procedures, corrosion issues and high costs^{[17],[18]}.

Herein, we report a facile one step electrochemical synthesis of Gd doped CeO_x (GDC) nanoflowers on porous carbon as an electrode material with excellent supercapacitor characteristics. Furthermore the devices were treated under UV irradiation for comparison. The enhanced super capacitive performance of novel CeO_x nanoflowers under UV irradiation at room temperature could be an alternate to thermal treatment which may avoid unnecessary contaminations and unwanted reactions occur at high temperatures.

Experimental

All chemicals were purchased from Sigma without further purification. The growth of GDC nanoflowers was carried out using electrochemical deposition process, using an aqueous solution containing 0.01M $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 0.01M $\text{Gd}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 0.05M NH_4Cl and 0.05M KCl with a current density of 0.5 mA/cm^2 for 2 hours at 70°C by using an Autolab 302N Potentiostat. A standard three-electrode setup in an undivided cell was used. Carbon foam (Duocel 90 PPI) was used as the working electrode while platinum foil ($0.2\text{mm} \times 10 \text{ mm} \times 20 \text{ mm}$) was used as the counter electrode. The distance between the two electrodes was 30 mm. The reference electrode was an Ag/AgCl electrode in 4 M KCl solution, against which all the potentials reported herein were measured.

Different samples by having different atomic percentage of Gd in CeO_x (5 at%, 10 at%, 20 at%, 30 at%, 40 at% and 50 at%) were prepared and tested. The as-deposited films were treated under Ultraviolet light (wavelength: 254 nm) for 1 hour (30 min for each side). The as-prepared films were also dried in vacuum oven at 200°C for 1 hour for comparison with irradiated samples. The schematic procedure for synthesis and performance testing of GDC nanoflowers is shown in Figure 1.

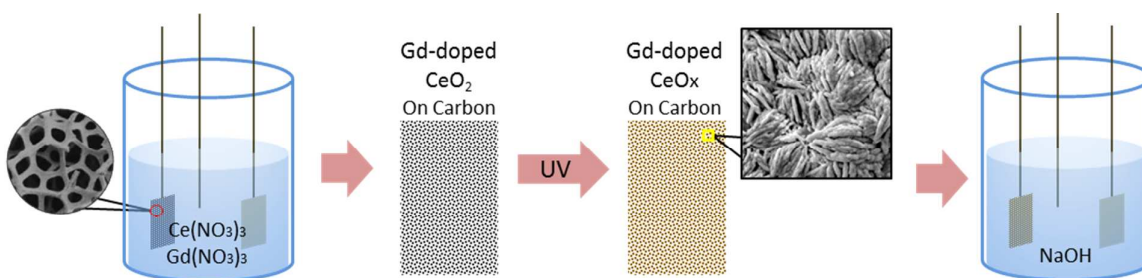


Figure 1: Schematic procedure for preparation and testing of GDC nanoflowers.

The phase composition of the as prepared and treated samples was studied by X-ray powder diffraction (PANalytical Empyrean with $\text{Cu K}\alpha$). As the diffraction peaks of the samples on carbon foam are very weak, GDC nanoflowers on F- SnO_2 glass substrate (FTO) have been prepared for XRD. The morphologies and microstructure of the samples were studied by using scanning electron microscopy (Nova Nano SEM 230) and transmission electron microscopy (Philips CM200). X-ray photoelectron

spectroscopy (XPS) was performed in ESCALAB250Xi spectrometer using a monochromatized Al K alpha X-ray source ($h\nu$) 1486.6 eV with 20 eV pass energy.

The electrochemical properties including cyclic voltammetry (CV) and Galvanostatic charge-discharge measurements were performed by electrochemical work station (Autolab 302N).

Results and discussion

The XRD patterns of as-prepared and UV treated 30 at% GDC samples on F-SnO₂ conductive glass are shown in Figure 2. All the samples exhibited peaks consistent with the face-centered cubic (FCC) fluorite structure of CeO_x in the standard data from JCPDS 34-0394. The XRD patterns indicate that Gd doped samples keep the fluorite structure, as no diffraction peaks corresponding to Gd-related impurity phases. After UV treatment the peak intensities increased, indicating higher crystallinity with UV treatment.

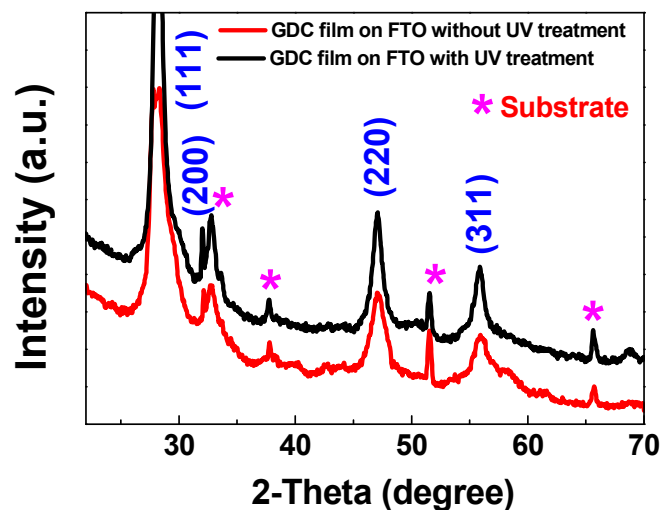


Figure 2: X-ray diffraction pattern of 30 at% Gd-doped as prepared and UV treated samples on F-SnO₂ glass substrate.

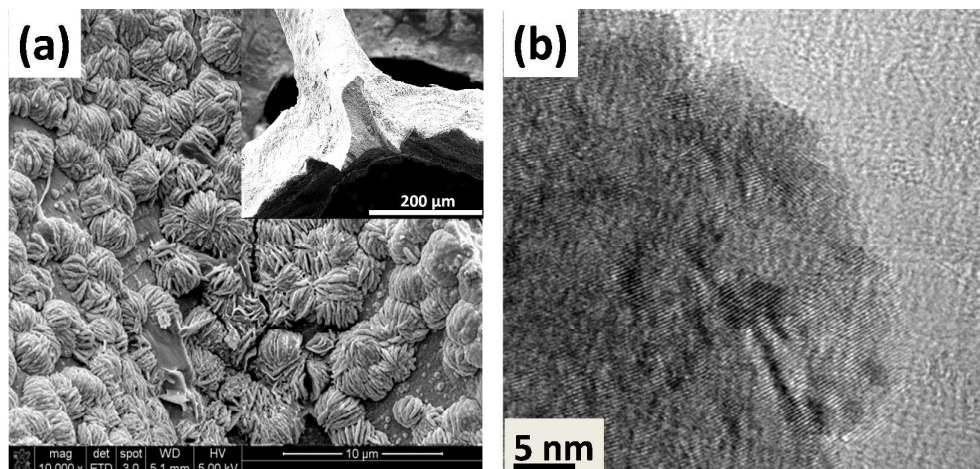


Figure 3: (a) SEM images on carbon foam, inset is a low magnification SEM image
(b) HRTEM of 30 at% GDC nanoflowers

The morphology of Gd-doped CeO_x on porous carbon substrate is illustrated in Figure 3. As can be seen from Figure 3a, homogeneous nanoflower structures are formed on the surface of carbon foam. HRTEM images of 30% Gd-doped CeO_x nanoflower is shown in Figure 3 b, where it shows clear crystalline structure and no trace of second phase was found. The lattice spacing is measured to be about 0.309 nm, referring to (111) plane, and is slightly less than (111) plane of the un-doped FCC CeO_x (0.31nm). The decreasing of lattice spacing with Gd doping may be attributed to difference in ionic radius of Gd³⁺ and Ce⁴⁺, which may induce some defects.

To investigate the electrochemical performance of the CeO_x nanoflowers with various Gd- doping levels, cyclic voltammetry and galvanostatic charge/discharge at a constant current density were tested in 1M NaOH solution as shown in Figure 4 and 5.

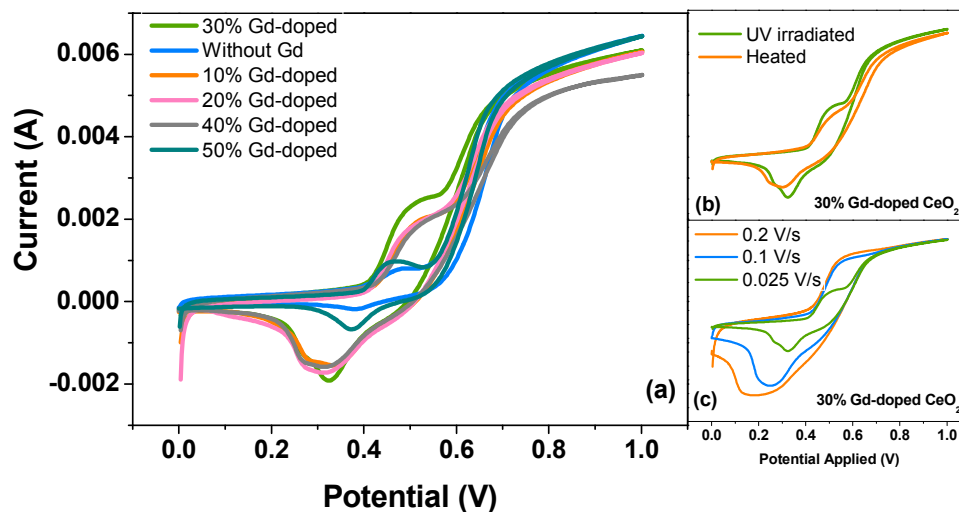


Figure 4: Cyclic voltametric response of GDC/carbon foam obtained in 1 M NaOH solution

Figure 4 (a) shows typical CVs for GDC films prepared with different doping levels of Gd (0 at % to 50 at %) at the scan rate as high as 250mV/S indicated good capacitive behavior. Two redox peaks appeared in all CVs which are attributed to the faradaic redox reaction of $\text{Ce}^{3+}/\text{Ce}^{4+}$. By the increase of Gd content, the redox peaks ascend towards maxima at 30 at% Gd content. In order to explore the UV irradiation effect on GDC nanoflowers films, a comparison between irradiated and thermally treated films is presented for 30 at% GDC film in Figure 4 (b). The larger area of CVs for UV irradiated samples as compared to thermal treated sample demonstrated enhanced super capacitive capability of irradiated films. Also, the CVs for UV irradiated samples were plotted at different scan rates in figure 4c. By increasing scan rates, the redox peaks were found to shift towards higher current region, which further enlarges the CV area, thus higher indicates mass loading capacity with higher capacitance. Such extension in CV curve area may be due to the higher redox processes of the electrode^[18b].

Figure 5 (a) illustrates typical galvanostatic charge-discharge curves of UV irradiated GDC (0 at% to 50 at% Gd) at a constant current density in the potential range from 0.6 to -0.6V. The charging and discharging curves were nearly linear and symmetrical, indicating good capacitive performance. The charge and discharge duration of GDC films increases first by the increase of Gd content in GDC films and maximum charge and discharge capacity was observed in 30 at% GDC films. The specific capacitance of all samples (0 at %Gd to 50 at % Gd) GDC under both thermally treated and UV irradiated conditions were calculated by using equation $C_s = I\Delta t/m\Delta V$.^[18b], where I is the constant discharge current, m is the mass of the GDC films, t is discharge time and V is the potential.

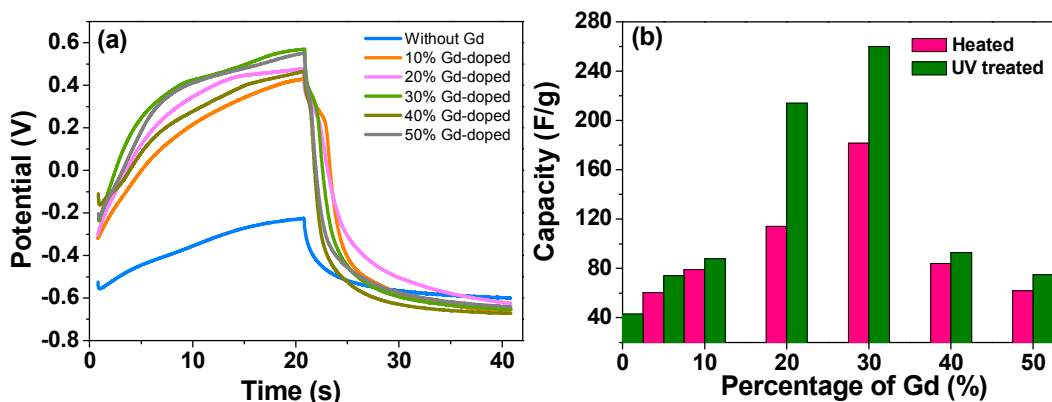


Figure 5: (a) galvanostatic charge-discharge curve of UV irradiated Gd-doped CeO_x/carbon foam obtained in 1 M NaOH solution (b) specific capacities of Gd-doped CeO_x/carbon foams with varying Gd at % in GDC films.

It can be seen from Figure 5 (a), with the increase of Gd-doping percentage till 30%, the potential while charging ascended significantly, whereas Gd-doping continually increase to 40% or 50%, potential fallen accordingly. For the UV irradiated group, capacity of Gd-doped CeO_x climbed from 43 F/g of none Gd-doped sample to 260 F/g at a 30% Gd-doped CeO_x as shown in Figure 5 (b), while, for those heated instead of UV treated, the capacity was raised from 33 F/g to 181 F/g. Hence, it can be known

that 30% Gd-doped CeO_x/carbon foam has the idealist capacitive characteristics and an excellent electrochemical reversibility. Meanwhile, UV irradiation at room temperature effectively reduced the possibility of contaminate produced during the procedure. One thing is clear from figure 5 a, that every sample including undoped and doped with different Gd concentration, demonstrate supercapictor capability. However, the most profound results were achieved with 30% Gd doped CeO_x nanoflowers grown on carbon foam. Also, from figure 5b, it was quite clear that UV treated samples were far better in terms of performances than thermally treated samples. So, the supercapacitor performances of the UV treated 30 % Gd doped CeO_x nanoflower films were further explored and shown in figure 6a. Figure 6a, shows the galvanostatic charge-discharge behavior of 30 at % Gd-doped CeO_x nanoflowers UV treated samples at different current densities. The charging and discharging curves were nearly linear and symmetrical, indicating excellent capacitive performances of UV treated 30 % Gd doped CeO_x nanoflower films.

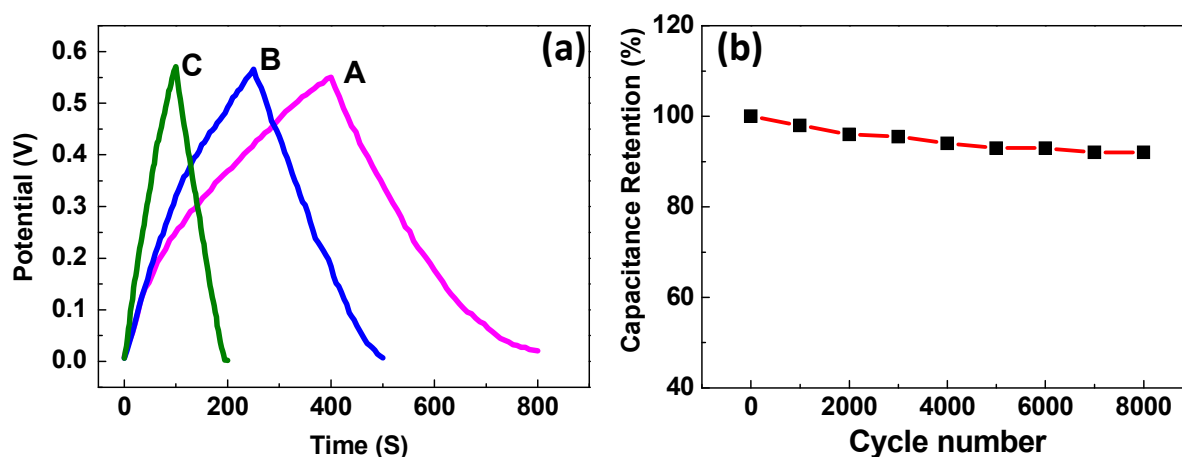


Figure 6: (a) Galvanostatic charge-discharge curves at current densities of (A) 0.33A/g (B) 0.67A/g and (C) 1.01 A/g for electrodes with mass loading of 14 mg/cm² (b) Cycling test of UV irradiated 30 at% Gd-doped CeO_x/carbon foam.

The excellent long-term stability of the GDC films is also demonstrated by charge-discharge test up to 8000 cycles and shown in figure 6b. The GDC films present unique capacitance retention with a ratio near 98% of initial capacitance after about

8000 cycles. The possible reason for that may be the poor cyclability of oxide materials in the electrolyte. Therefore, carbon foam being possessing good electrical conductivity and excellent ion transportation capability may offer the electrode material to sustain its cyclic capability for 8000 cycles.

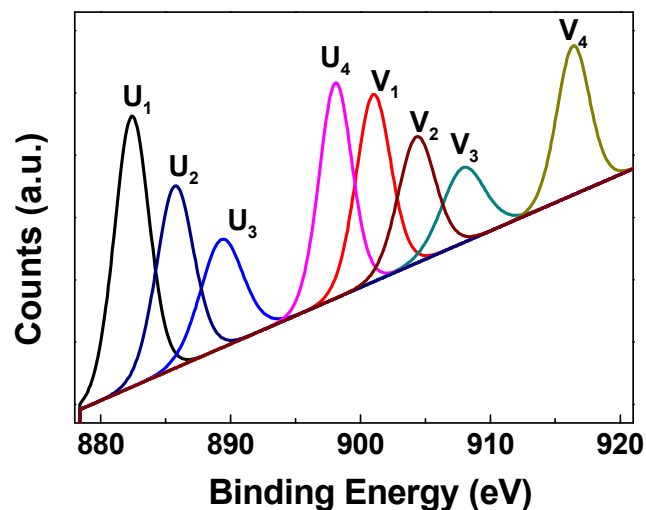


Figure 7: XPS Ce3d level spectra of UV treated Gd- doped CeOx film.

The XPS measurements were carried out to investigate the surface chemical compositions and bonding states of the UV treated Gd- doped CeOx films. To examine the oxidation state of cerium ions in 30 at% Gd doped CeOx films, cerium 3d spectra were measured (as shown in Fig. 7), where the binding energies were calibrated using the C 1s peak as a reference.

The XPS spectra of Ce 3d level can be deconvoluted into eight characteristic peaks in the spectra. The peaks at 882.4, 885.8, 889.40, and 898.10 eV are corresponding to the components of the Ce 3d_{5/2}^[19], while the peaks at 901, 904.40, 908.10 and 916.40 eV are attributed to the components of the Ce 3d_{3/2}. The peaks of 898.10 eV and 916.40 eV represent the 3d¹⁰4f⁰ initial electronic state corresponding to the Ce⁴⁺ ion, and the peak of 885.8eV is the 3d¹⁰4f¹ initial electronic state corresponding to the Ce³⁺ ion. The results indicate the coexistence of Ce³⁺ and Ce⁴⁺ in the Gd at 30at% CeOx porous film^[19a], which further clued towards critical role of redox reaction during capacitive measurements in these films.

Conclusion

In summary, Gd-doped CeO_x nanoflowers for supercapacitor electrodes have been successfully prepared for the first time by a low-cost, simple and environmental friendly electrochemical approach. The coexistence of Ce³⁺ and Ce⁴⁺ ions in the UV treated samples were confirmed by XPS studies. Furthermore, the GDC nanoflowers based electrodes materials were found to exhibit excellent capacitive behavior with maximum specific capacitance of 280 F/g in 1 M NaOH solution. The present work demonstrates that GDC nanoflowers could be a potential material for next generation energy efficient devices.

Acknowledgement

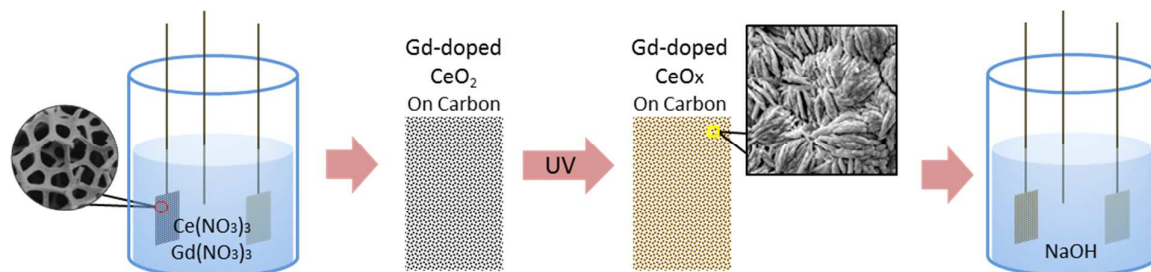
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Table of Content



In this work, we developed a facile electrochemical deposition approach to prepare Gd-doped CeO_x nanoflowers on porous carbon foam with improved supercapacitor characteristics by UV irradiation.