Synthesis of oxygen-deficient and monodispersed Pr doped CeO$_2$ nanocubes with enhanced resistive switching properties

Nan Chen* and Sean Li
School of Materials Science and Engineering, University of New South Wales, Sydney Australia

Abstract
Monodispersed praseodymium (Pr) doped cerium oxide (CeO$_2$) nanocubes (~10 nm) were successfully synthesized via a facile two-phase solvothermal method and further assembled into a dense film through a drop-coating procedure for resistive switching applications. The XRD and Raman results showed that Pr element was successfully doped into the CeO$_2$ lattice structure while maintaining the highly uniform nano-cubic structure. In addition, the concentration of oxygen vacancy in CeO$_2$ nanocubes could be effectively modulated by varying dopant concentration evidenced by XPS and Raman analysis. The two-terminal structured device of Au/Pr doped CeO$_2$/fluorine-doped tin oxide (FTO) exhibits stable resistive switching behaviour and ON/OFF endurance for more than 1000 cycles at a small operational voltage ranging from -0.6 to 1V. The present study may extend the potential of using praseodymium (Pr) doped cerium oxide nanocube in nanoscale building block for novelty 3D architectural memory and logic design in data-dependent applications such as artificial intelligence (AI) system and machine learning.

I. Introduction
Facing the extensive growth of demand for data storage in a big-data era, resistive random-access memories (RRAMs) have attracted huge attention because of its high speed, long retention time, and high density. In general, the building block for RRAM is the memory cell based on a two-terminal metal-insulator-metal (MIM) sandwich structure, where a resistive switching layer is the layer between two electrodes A wide range of metal oxides in various nanostructures have been studied for potential RRAM application, for example, simple binary oxides HfO$_2$[1] and NiO[2]; complex oxides such as perovskites SrTiO$_3$[3] and BiFeO$_3$[4]. Many theory models such as filamentary conduction, charge trapping defects states, trap-controlled space-charge-limited current and a change of a Schottky-like barrier have been proposed according to previous reports[5]. Among all the various models, the migration of oxygen vacancies and electrons under certain exerted electric voltage has been extensively studied in metal oxides based switching behaviour[6].

It is believed that the resistive switching phenomena are associated with the migration of oxygen vacancy and the accompanied oxidation state change of the cations under the external stimuli[7] which indicates that the oxygen vacancies engineering is a promising way to tune the performance of memory devices.

Among all the candidates, cerium oxide (CeO$_2$) has been extensively investigated[7] owing to its unique properties such as high dielectric constant, and excellent redox properties with various valence states of cerium atom. Specifically, the reversible transition of Ce$^{3+}$ to Ce$^{4+}$ give rise to the formation and elimination of oxygen vacancies[8]. Furthermore, it is widely accepted that doping can introduce more surface defects such as oxygen vacancies in CeO$_2$ lattice[9]. These oxygen vacancies lead to form conductive filaments which may play a vital role in tuning the resistive switching properties. Therefore, it is of great interest to investigate the resistive switching behavior in relation to the dopant level. In the meantime, the self-assembly of monodispersed nanocrystals is currently attractive for the large-scale fabrication of metal oxide thin film devices as with the advancing in the synthesis process. The highly uniform nanostructure can be employed as
building blocks to assemble a higher dimensional structure. Moreover, the morphology of nanocrystal, size effect, ionic defect tuning as well as the interfacial carrier transportation can be well studied through this chemical route. The nanocube can be arranged into a highly coordinated square array and then layer-by-layer assembled into a 3D architecture. Many other approaches have been applied to synthesize doped cerium oxides such as hydrothermal[10], solvothermal[11], and electrochemical deposition[12]. A facile two-phase solvothermal method was chosen[13] for this study because of its unique superiority of forming dense switching film by preparing the monodispersed nanocube dispersion. With the help of a capping agent such as oleic acid, the as-prepared nanocube can be easily assembled into 2D or 3D superstructure[14]. The report on resistive switching behaviours for Pr doped cerium oxide nanocube is still very limited. As rare earth elements, both cerium and praseodymium have unique 4f electronic structure. Pr possesses different valences 3+ and 4+ which leads to more surface defects such as oxygen vacancies in the oxide. Moreover, the similar ion radius makes doping feasible.

In this work, oxygen-deficient Praseodymium (Pr) doped cerium oxide (Pr$_x$Ce$_{1-x}$O$_2$-$\delta$, $x$=0-0.2) nanocubes with the size of around 10 nm were synthesized via a facile two-phase solvothermal method and then self-assembled to a dense film on fluorine-doped tin oxide (FTO) coated glass substrate simply by drop-coating. 10 at. % Pr doped CeO$_2$ with adequate oxygen vacancy concentration exhibited a high resistance difference and optimal stability in the voltage ranging from -0.6 to 1V. The underlining mechanism for resistive switching process is claimed to be the result of the migration of oxygen vacancies inside the nanoparticles.

2. Experimental section

All chemicals were purchased from Sigma without further purification. Pr doped CeO$_2$ nanocubes were prepared by using a solvothermal process as shown in Figure 1(a). In a typical reaction, a certain amount of cerium (III) nitrate and praseodymium (III) nitrate (0,5,10,15,20 at. % of cerium) was dissolved in15 mL of DI water then transferred into a 50 mL autoclave. Meanwhile, a miscible solution of 0.56ml oleic acid (OLA) and 14ml of toluene was prepared separately until they are fully mixed. The ratio of OLA to the metal ions is fixed to be 8:1. Afterward, 0.15 ml of tert-butylamine was added into the mixture and then the organic solution was carefully transferred into the previous autoclave upon the aqueous solution to maintain the two-phase state. The sealed autoclave was heated at 180 °C for 24 h and then cooled to room temperature. The upper organic solution was centrifuged to separate the nanocrystals. The separated CeO$_2$ nanocrystals were redispersed into 4 mL of toluene. Subsequently, the suspension solution was drop-coated on an FTO coated glass substrate to obtain a thin film with self-assembled Pr doped CeO$_2$ nanocube. To assemble a device, the round gold top electrode (diameter 250 μm) was sputtered on the surface of the thin film. The schematic illustration of the obtained device was shown in Figure 1(b).

![Figure 1](image1.png)

Figure 1. (a)Schematic illustration of solvothermal synthesis and (b)

Structural analysis of the as-prepared Pr doped CeO$_2$ film was carried out using an X-ray diffractometer (XRD; PANalytical Empyrean 1) with Cu Kα radiation. The accurate chemical composition was studied by inductively coupled plasma mass spectrometry (ICPMS; PerkinElmer Nexion). Raman Microscope (Renishaw inVia) was employed to determine the chemical bond of the as-prepared sample with a 514 nm laser beam. The microstructures of the as-prepared materials were studied by transmission electron microscopy (TEM; Phillips CM200) and field-emission scanning electron microscope (FE-SEM; FEI Nova NanoSEM 450).
TEM with the focused ion beam (FIB; FEI Nova Nanolab 200) was used to observe the cross-section of the thin film to determine the thickness of thin film. X-ray photoelectron spectroscopy (XPS; ESCALAB 250Xi spectrometer) was employed to analyse the chemical composition. The I-V curves were measured by Autolab 302N electrochemical workstation connected to Nova software.

3. Results and Discussion

3.1. Phase and Chemical composition

The XRD patterns shown in Figure 2a demonstrated that all diffracted peaks can be indexed as the face-centered-cubic pure phase with space group $Fm\overline{3}m$ of cerium oxide (JCPDS 34-0394). No impurity peaks were detected which indicates that no Pr-related oxide was formed during synthesis. To verify the absence of dopant Pr, an ICP measurement was examined, shown in Figure 2(b). It can be seen the actual dopant concentration is close to the nominal dopant concentration. Combining with the XRD result, it’s suggested the Pr element is successfully doped into the cerium oxide lattice.

The chemical bonding of as-prepared samples was investigated by Raman spectroscopy, as shown in Figure 2(c). A dominant peak of all samples is located at $\sim$461 cm$^{-1}$, which refers to active F2g mode originating from a symmetrical stretch of the eight surrounding O$^{2-}$ ions with respect to the central stationary Ce ion in the fluorite structure[9].

The substitution of Pr$^{4+}$/Pr$^{3+}$ contributes to a local disorder in the sublattice since the radius of Ce$^{3+}$ (0.103 nm), Ce$^{4+}$ (0.970 nm) and Pr$^{3+}$ (0.113 nm), Pr$^{4+}$ (0.960 nm) are different. In addition, the introduction of Pr$^{3+}$ resulted in oxygen defects to maintain the electronic natural state. In addition, the peak shifts of Ce-O bond can be attributed to the replacement of Ce$^{4+}$ ions with Pr$^{4+}$/Pr$^{3+}$ after doping. As the dopant concentration increased, the degree of shifts increased because more Ce-oxygen bond was replaced by Pr-O bond. Additional broad peaks at around $\sim$597 cm$^{-1}$ can be assigned to the second-order optical mode and to the presence of oxygen vacancies[15]. These oxygen vacancies may originate from the presence of Ce$^{3+}$ and Pr$^{3+}$ in the lattice. The ratio of the intensity of F2g peak and defect peak can be used to determine the defects level. As shown in Figure 2(d), as the dopant concentration increased, more defects were formed which indicates that the high concentration results in high degree of oxygen vacancies.

Figure 2. (a)XRD patterns; (b)dopant concentration; (c) Raman spectra; (d) Raman peak shifts of F2g peak; (e)Intensity ratio of F2g and D Raman peaks of as-prepared samples.

The chemical bonding of as-prepared samples was investigated by Raman spectroscopy, as shown in Figure 2(c). A dominant peak of all samples is located at $\sim$461 cm$^{-1}$, which refers to active F2g mode originating from a symmetrical stretch of the eight surrounding O$^{2-}$ ions with respect to the central stationary Ce ion in the fluorite structure[9].

The substitution of Pr$^{4+}$/Pr$^{3+}$ contributes to a local disorder in the sublattice since the radius of Ce$^{3+}$ (0.103 nm), Ce$^{4+}$ (0.970 nm) and Pr$^{3+}$ (0.113 nm), Pr$^{4+}$ (0.960 nm) are different. In addition, the introduction of Pr$^{3+}$ resulted in oxygen defects to maintain the electronic natural state. In addition, the peak shifts of Ce-O bond can be attributed to the replacement of Ce$^{4+}$ ions with Pr$^{4+}$/Pr$^{3+}$ after doping. As the dopant concentration increased, the degree of shifts increased because more Ce-oxygen bond was replaced by Pr-O bond. Additional broad peaks at around $\sim$597 cm$^{-1}$ can be assigned to the second-order optical mode and to the presence of oxygen vacancies[15]. These oxygen vacancies may originate from the presence of Ce$^{3+}$ and Pr$^{3+}$ in the lattice. The ratio of the intensity of F2g peak and defect peak can be used to determine the defects level. As shown in Figure 2(d), as the dopant concentration increased, more defects were formed which indicates that the high concentration results in high degree of oxygen vacancies.
3.2. Microstructure observation

The TEM images of the Pr doped CeO$_2$ nanocrystals (Figure 3(a)-(d)) exhibit well-dispersed nanocubes forming a monolayer of the self-assembly structure on a copper grid. The nanoparticles in all samples have a consistent size at around 10 nm and uniform morphology which ensures a long-range ordered structure via a simple drop-coating method. On the substrate, a dense and tightly packed self-assembly thin film can be produced owing to the distinct structure of nanocubes. By repeating dropping the solution on the substrate, multiple layers of nanocube can form into a 3D architect. The single-crystalline nature of an individual 3% Pr doped CeO$_2$ nanocube was determined by a high-resolution TEM (HRTEM) image. The lattice spacing was measured to be 0.278 nm, corresponding to the (100) planes of CeO$_2$, showing that the as-prepared doped CeO$_2$ nanocubes are exposed with (100) facets. The d-spacing of all as-prepared samples were measured and shown in Figure 3(f). The distance of each crystal plane is decreased in a subtle degree from 0.282 nm to 0.274 nm which indicates the difference of radius of Pr and Ce elements would not hinder the doping process.

3.3. Oxygen vacancies tailoring

To investigate the chemical states of as-prepared samples, the XPS was employed. The O1s curve of all samples was shown in Figure 4(a), which can be fitted into two peaks. One peak located at the higher binding
energy level at ~531.5 eV can be attributed to the oxygen ions in the oxygen-deficient region, while the other one at the lower binding energy level at ~529 eV refers to lattice oxygen bonding to cerium. The ratio of the intensity of peaks of two O1s can be viewed as an indicator of oxygen defects level as shown in Figure 4 (b). As dopant concentration increased, the ratio decreased which suggests high doping level results in a high concentration of oxygen vacancies in accordance with Raman results. To verify the valance state of Praseodymium ions, the curves of Pr 3d orbit were investigated closely. One peak located at ~933 eV attributed to Pr$^{3+}$ while the other at ~ 929 eV may originate from Pr$^{4+}$[16]. The intensity ratio of Pr$^{3+}$ and Pr$^{4+}$ was calculated and could found in Figure 4(c). It is obvious that the as the doping level increased the 3+ valence Pr accounts the larger portion of all Pr elements.

3.4. Current-voltage (I-V) response of the device

The I-V response of the sandwich-structured device with gold top electrode was tested. The display of top electrodes was shown in Figure 5(a) and the cross-section image was shown in Figure 5(b). From the top view, the drop-coating thin film is crack-free and dense. The cross-section shows that the thickness of the Pr doped CeO$_2$ film is around 300 nm and no crack can be found which indicates a higher dimensional structure could be achieved through layer-by-layer fabricating the 1D nanocube. Figure 5(c) shows the I-V characteristics of the Au/Pr doped CeO$_2$/FTO structure under voltage sweeping mode, at a speed of 1 V s$^{-1}$, in the following sequence 0 → 1 → 0 → −0.6 → 0 V. The resistance state of the device is transformed from ON (low-resistance state (LRS)) to OFF (high-resistance state (HRS)) on the first sweep from 0 V to 1 V. During the subsequent voltage sweep from 1 V to −0.6 V, the cell remained in the HRS until the next coming sweep. When switching the voltage from −0.6 V to 0 V, the current dramatically jumped to LRS level around 0.5 V. And such resistance switching behaviour is reproducible for 5 repeating IV sweepings. In order to evaluate the potential for applications in non-volatile memory devices, a cycling switching test (endurance) was implemented. The electrical pulse-induced resistance change effect in the memory device is shown in Figure 5(d).

**Figure 5.** The (a) top view (b) the cross-section of the 15% Pr-doped CeO$_2$ thin film with gold top electrodes; (c) the I-V curve response under sweeping voltage; (d) The endurance curve of device

The I-V response of the sandwich-structured device with gold top electrode was tested. The display of top electrodes was shown in Figure 5(a) and the cross-section image was shown in Figure 5(b). From the top view, the drop-coating thin film is crack-free and dense. The cross-section shows that the thickness of the Pr doped CeO$_2$ film is around 300 nm and no crack can be found which indicates a higher dimensional structure could be achieved through layer-by-layer fabricating the 1D nanocube. Figure 5(c) shows the I-V characteristics of the Au/Pr doped CeO$_2$/FTO structure under voltage sweeping mode, at a speed of 1 V s$^{-1}$, in the following sequence 0 → 1 → 0 → −0.6 → 0 V. The resistance state of the device is transformed from ON (low-resistance state (LRS)) to OFF (high-resistance state (HRS)) on the first sweep from 0 V to 1 V. During the subsequent voltage sweep from 1 V to −0.6 V, the cell remained in the HRS until the next coming sweep. When switching the voltage from −0.6 V to 0 V, the current dramatically jumped to LRS level around 0.5 V. And such resistance switching behaviour is reproducible for 5 repeating IV sweepings. In order to evaluate the potential for applications in non-volatile memory devices, a cycling switching test (endurance) was implemented. The electrical pulse-induced resistance change effect in the memory device is shown in Figure 5(d).
5(d). A positive and a negative pulse voltage were programmed and applied to the device to activate the resistance switching process, respectively. The cell was repeatedly switched between the HRS and the LRS. The endurance test indicates that the memory cell exhibits negligible degradation during 1000 ON/OFF switching cycles. This endurance result indicates that Pr doped CeO$_2$ is a potential candidate material for RRAM application.

As it is acknowledged that the oxygen migration model could be one of the frequently reported for the origin of the bipolar resistance switching effect. The previous study reported that the resistive switching behaviour in the CeO$_2$ films mainly attributes to switching in oxygen concentration which results in different resistance switching[9]. Without any external stimuli, the oxygen vacancies would gather on the surface of nanomaterials. Under the trigger of the electric field, the positively charged oxygen vacancies would align with the electric force forming a conductive filament towards the anode. These localized filaments give rise a current flow through the oxide layer from the metal electrode (Au) to the conductive substrate (FTO) which leads to LRS and turn ON the memory cell. While a reverse voltage was applied, the oxygen vacancies would reorder results in breaking the oxygen vacancies’ interactions hence rupturing the conductive filaments, which switch the memory cell from ON state to OFF. The doping of Pr element into the cerium oxide lattice as an effective way to induce the oxygen vacancies defects greatly, therefore, a prominent resistive switching property can be exhibited.

4. Conclusion

In summary, a unique Pr doped CeO$_2$ monodispersed nanocubes were successfully synthesized. The characterization suggested that the oxygen defects level can be tuned easily by adjusting the dopant concentration during a facile solvothermal method. Doping Pr with Ce atom introduces the oxygen vacancies which give rise to resistive switching behaviours. The thin film was prepared by drop-coating the nanoparticle suspension solution and further fabricated to sandwich structure devices (Au/Pr doped CeO$_2$/FTO) which exhibit resistance switching characteristics after 1000 cycles. The distinct monodispersed nanocubes and self-assembly film make the materials a promising candidate to fabric 3D memory device as nano building blocks which has potential in fielded such as AI system and machine learning.

5. References

[1] Wang Y, Liu Q, Long S, Wang W, Wang Q, Zhang M, Zhang S, Li Y, Zuo Q, Yang J and Liu M 2010 Investigation of resistive switching in Cu-doped HfO$_2$ thin film for multilevel non-volatile memory applications Nanotechnology 21 045202
[2] Kim D C, Seo S, Ahn S E, Suh D-S, Lee M J, Park B-H, Yoo I K, Baek I G, Kim H-J, Yim E K, Lee J E, Park S O, Kim H S, Chung U-I, Moon J T and Ryu B I 2006 Electrical observations of filamentary conductions for the resistive memory switching in NiO films Appl. Phys. Lett. 88 202102
[3] Nili H, Wallia S, Kandjani A E, Ramanathan R, Gutruf P, Ahmed T, Balendhran S, Bansal V, Strukov D B, Kavehei O, Bhaskaran M and Sriram S 2015 Donor-Induced Performance Tuning of Amorphous SrTiO$_3$ Memristive Nanodevices: Multistate Resistive Switching and Mechanical Tunability Adv. Funct. Mater. 25 3172–82
[4] Li Y, Sun X-Y, Xu C-Y, Cao J, Sun Z-Y and Zhen L 2018 Ferroelectric resistive switching behavior in two-dimensional materials/BiFeO$_3$ hetero-junctions Nanoscale 10 23080–6
[5] Waser R, Dittmann R, Staikov G and Szot K 2009 Redox-Based Resistive Switching Memories - Nanionic Mechanisms, Prospects, and Challenges Adv. Mater. 21 2632–63
[6] Cho S, Yun C, Tappertzhofen S, Kursumovic A, Lee S, Lu P, Jia Q, Fan M, Jian J, Wang H, Hofmann S and MacManus-Driscoll J L 2016 Self-assembled oxide films with tailored nanoscale ionic and electronic channels for controlled resistive switching Nat. Commun. 7 12373
[7] Younis A, Chu D, Lin X, Yi J, Dang F and Li S 2013 High-Performance Nanocomposite Based Memristor with Controlled Quantum Dots as Charge Traps ACS Appl. Mater. Interfaces 5 2249–54
[8] Imagawa H, Suda A, Yamamura K and Sun S 2011 Monodisperse CeO$_2$ Nanoparticles and Their Oxygen Storage and Release Properties J. Phys. Chem. C 115 1740–5
[9] Younis A, Chu D and Li S 2012 Oxygen level: the dominant of resistive switching characteristics in cerium oxide thin films J. Phys. D. Appl. Phys. 45 355101
[10] Tok A I Y, Boey F Y C, Dong Z and Sun X L 2007 Hydrothermal synthesis of CeO$_2$ nano-particles J. Mater. Process. Technol. 190 217–22
[11] Sun C, Li H, Zhang H, Wang Z and Chen L 2005 Controlled synthesis of CeO$_2$ nanorods by a solvothermal method Nanotechnology 16 1454–63
[12] Huang M, Yan Y, Feng W, Weng S, Zheng Z, Fu X and Liu P Controllable Tuning Various Ratios of ZnO Polar Facets by Crystal Seed-Assisted Growth and Their Photocatalytic Activity and S Y and Gao* L 2006 Controlled Synthesis and Self-Assembly of CeO2 Nanocubes
[13] Qian L, Zhu J, Du W and Qian X 2009 Solvothermal synthesis, electrochemical and photocatalytic properties of monodispersed CeO2 nanocubes Mater. Chem. Phys. 115 835–40
[14] Yang Y, Mao Z, Huang W, Liu L, Li J, Li J and Wu Q 2016 Redox enzyme-mimicking activities of CeO2 nanostructures: Intrinsic influence of exposed facets Sci. Rep. 6 35344
[15] Chen N, Younis A, Chu D and Li S 2018 Controlled Fabrication of Pr(OH)3 Nanowires for Enhanced Photocatalytic Activities J. Rare Earths