



Surface-sensitive magnetism of mesoscopic hollow CeO₂ spheres

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ABSTRACT

This study demonstrates magnetism of mesoscopic hollow ceria spheres (H-CeO₂) with different defect distribution characteristics. The content and distribution of defect of micro-scale hollow spheres are controlled by varying the reaction with HNO₃ and the annealing process. The obtained spheres are divided into three groups according to the surface structure, defect content and defect distribution of the shell. Group I is characterized by rough sphere surface and with large ceria clusters. Group II has relatively continuous surface defective layers and reduced surface roughness of the sphere. Group III has a continuous and smooth surface defective layer, and a decreasing gradient of Ce³⁺ concentration inside this layer. All spheres were ferromagnetic at room temperature. Saturation magnetization from high to low is in the sequence: group III, group II, and group I. The strongest magnetism is obtained for the samples subjected to the reaction with 1 M HNO₃ for 60 min and then annealed, in which defects are distributed homogeneously within the surface thin layer and the sphere surface is smooth. We thus conclude that the surface plays the major role in the magnetic behavior of micro-scale hollow sphere.

1. Introduction

Several oxides with wide band gaps and high Curie temperatures, notably if their structures and processes are close to those of semiconductors, act as candidate materials in the field of spintronics. Researchers have examined ferromagnetism in such oxides, e.g., TiO₂, [1,2] ZnO, [3,4] CeO₂, [5,6] in the past decade. The occurrence of magnetism in these materials have been experimentally clarified. Scholars attribute magnetism of oxide to the existence of defects in addition to magnetic dopants. [7,8,9] To further improve the ferromagnetism of oxide, different experimental procedures have been presented to adjust the content as well as defect structure. [10,11,12]

However, the origin of this magnetism is still unclear. Several models have been developed, including the bound magnetic polaron model [13] and F-center exchange. [14] Coey *et al.* recently proposed that magnetic saturation in agglomerations formed with oxide nanoparticles is not derived from collective spin ferromagnetism, but is related to giant magnetic orbitals. [15] The preferred structure for such orbital magnetism is believed to be a quasi-two-dimensional mesostructure, such as surface layers occurring on aggregates of oxide nanoparticles or granular oxide. [16] This magnetic model is expected to be particularly

applicable for materials with low electron density, high dielectric constant and surface layers with modified properties relative to the bulk with nearly atomic dimensions. Consequently, a micro-scale hollow sphere with tunable defect distribution such as surface oxygen vacancies is an ideal model structure to reveal the effect of mesoscopic structure on magnetism.

Among oxides with room-temperature ferromagnetism, CeO₂ has attracted extensive interests. Many groups devoted to unravel the relation between defects and magnetism. In undoped CeO₂ nanoparticles, strong magnetic signals correspond with a determinate range of Ce³⁺ content at the surface. [17,18] Other similar quasi-two-dimensional mesostructures have been developed, including sub-micro core-shell structures and micro-scale hollow spheres. Both these structures are ferromagnetic, with the enhanced magnetism attributed to the presence of a defective thin surface layer. [10,19] However, the character of this defective surface layer and its relation with magnetic behavior have not been clarified.

Accordingly, this study systematically tunes the defective layer structures of micro-scale CeO₂ hollow spheres. Hollow sphere is a model structure for the demonstration of surface effect on the modulation of ferromagnetism, but is not yet widely studied, notably due to the

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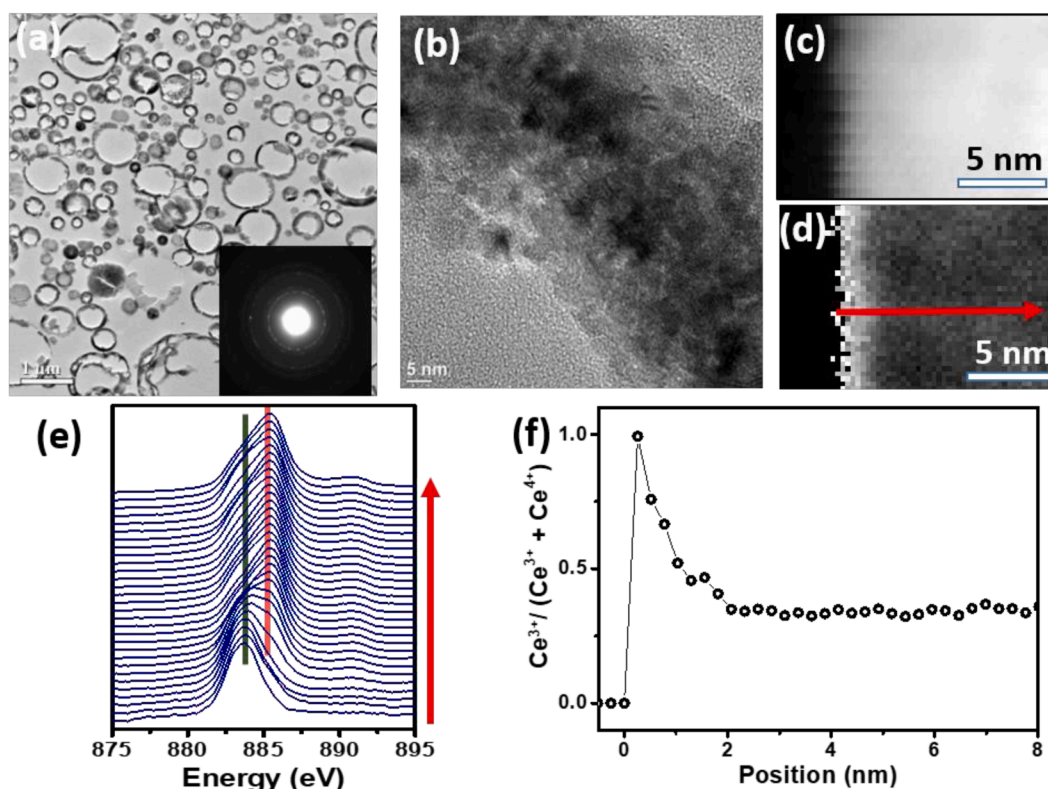


Fig. 1. (a) TEM image of cross-section of CeO₂ sphere. (b) High-resolution TEM image of CeO₂ shell. (c) STEM/HAADF image and (d) EELS mapping of Ce³⁺ of H-CeO₂. (e) Variation of ELNES of Ce M₅ edge from surface to bulk region, as represented by the red line. (f) The intensity profile of Ce³⁺ obtained from surface to bulk region. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

difficulty in preparing hollow spheres with different defect gradients. This work uses the spray pyrolysis synthesis method, owing to its large yield possibility for such hollow structures. The spheres are immersed in acidic solutions for different times. Researchers have noted that dissolution of ceria in acid solution promotes reduction of Ce ions. The quantitative dissolution of ceria has been studied by Nikitenko *et al.* [20] A recently study showed that formic acid adsorbed on the CeO₂ surface leads to the partial reduction of Ce⁴⁺ to Ce³⁺. [21] The reductive dissolution of CeO₂ in HNO₃–H₂O₂ and HNO₃–HCOOH mixtures can also be accelerated under the effect of 20 kHz ultrasound. [22] Since the dissolution of actinides dioxides is affected by microstructure, temperature and acidity, [23] this work also presents a post-annealing process to control the densification of spheres. The concentration as well as the distribution of defects in hollow spheres is investigated by using EELS and X-ray absorption spectroscopies, and is then related to the magnetic behavior.

2. Experimental procedure

2.1. Sample preparation

Hollow CeO₂ spheres were first prepared by spray pyrolysis. Ceric ammonium nitrate (CeAN, (NH₄)₂Ce(NO₃)₆, 99.5%, Alfa Aesar) and Glycine (GN, C₂H₅NO₂, 98%, Acros Organics) were used as precursors. CeO₂ particle was prepared first from a 1 wt% solution CeAN and GN in de-ionized water with molar ratio of 4:6. The precursor solution was initially atomized into small droplets (nebulizer, King Ultrasonics Co., Ltd, Taipei, Taiwan), and then underwent solvent evaporation, solute precipitation and precursor decomposition in the heated tubular reactor at 700 °C in atmosphere. The hollow CeO₂ spheres were collected by a cylindrical electrostatic collector with high voltage potential. The obtained spheres are named sample A. The as-prepared spheres were then

heated up to 300 °C at 10 °C/min and isothermally held for 2 h in air followed by furnace cooling. The annealed sample was labelled C. The as-prepared and the annealed hollow CeO₂ spheres were then immersed in 1 M HNO₃ solution for different times set as 15, 30, 45, 60, 90 and 120 min.

2.2. Characterization

All the spheres were characterized by X-ray Diffractometer (XRD) with Cu K radiation (Bruker D8 Advance). The morphology was investigated using a transmission electron microscope (TEM) operated at 200 keV (FEI Tecnai G2 and Thermo Fisher Scientific Talos F200X). The shell thickness of hollow sphere was estimated from 100 measurements. Electron energy loss spectroscopy (EELS) was performed by using a C_s-corrected STEM NION. X-ray absorption measurements were carried out at National Synchrotron Radiation Research Center (NSRRC) in Taiwan. The X-ray absorption near edge structure (XANES) spectroscopy measurements at the Ce L₃-edge were conducted at Wigger beamline 17C at room temperature through the monochromator silicon (111) crystal, and its energy resolution at Ce L₃-edge (5723 eV) was approximately 0.4 eV. The magnetization was measured at room temperature using the vibrating sample magnetometer (VSM) in the Institute of Physics, Academia Sinica, Taiwan.

3. Results and discussion

3.1. Mesoscopic H–CeO₂

Fig. 1 (a) shows a cross-sectional TEM image of as-prepared spheres synthesized by using the spray pyrolysis method, revealing that the spheres are hollow. The insert pattern confirms that the crystal structure of the spheres is CeO₂. As seen in Fig. 1 (b), the shell had thickness of

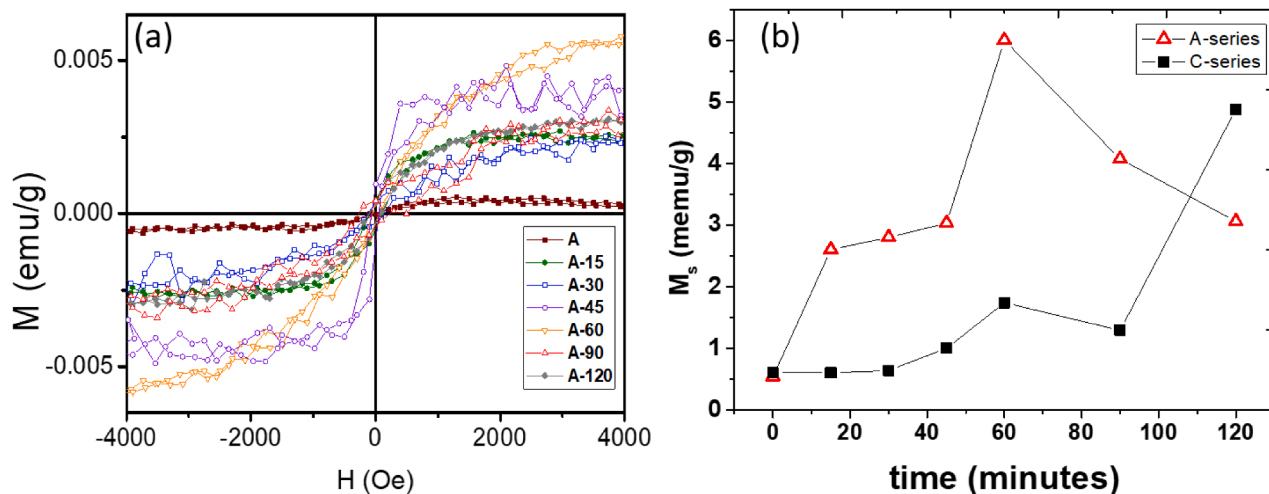


Fig. 2. M–H curves of the (a) as-prepared and (b) annealed hollow spheres after reacting with 1 M HNO_3 for different times.

about 60 nm, and (comprised well crystallized CeO_2 particles with size 4–6 nm. The spatial distribution of defects, i.e. Ce^{3+} , was investigated by using STEM combined with EELS. Fig. 1 (c) illustrates the STEM/HAADF image of as-prepared hollow spheres. Hundreds of Ce M edge energy loss near edge structure (ELNES) measurements were taken in this region. As comparing to the standard sample, the content of Ce^{3+} can be estimated. The process has been described detailed in elsewhere. [19] The image in Fig. 1 (d) shows that Ce^{3+} tends to concentrate at the surface region in these spheres. Fig. 1 (e) displays the variation of ELNES of Ce M_5 edge with position along the red arrow. The green and orange lines denote the peak positions of the M_5 edges contributed by Ce^{3+} and Ce^{4+} , respectively. Clearly, the peak position of M_5 edge shifts to high energy side as it moves to the bulk region, implying a decrease in Ce^{3+} content. Fig. 1

(f) presents the variation of Ce^{3+} content from surface layer to bulk region, demonstrating that the Ce^{3+} concentration decreases from ca. 100 % to 30 % as the distance from the surface increases from 0 nm to 2 nm.

Fig. S1 (a) shows the microstructure investigations of the spheres annealed in air at 300 °C for 2 h, demonstrating that the annealing process produced a dense shell, with growth and the inter-grain sintering. As for the defect distribution, Ce^{3+} was still concentrated at the surface region of the shell, but the width of the Ce^{3+} rich layer decreased to only 1.5 nm (Fig. S1 (b)). Moreover, the annealed spheres had a lower Ce^{3+} concentration than the unannealed spheres], at only 33% and 17% of the surface layer and bulk region, respectively.

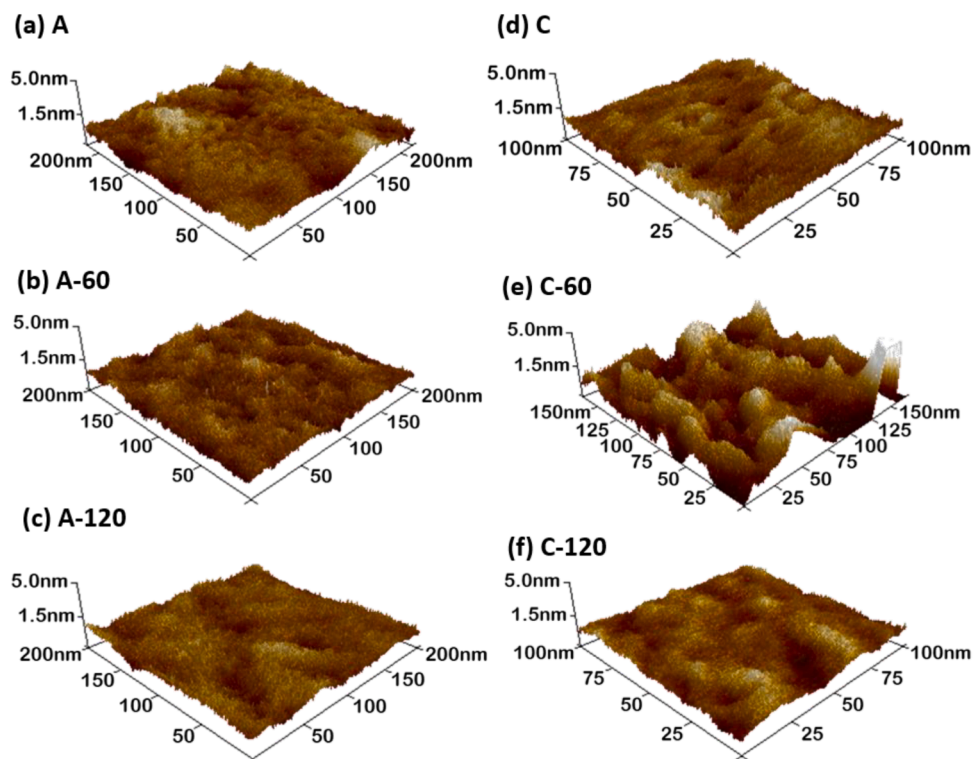


Fig. 3. Surface roughness of hollow CeO_2 spheres after immersing in 1 M HNO_3 for different times measured by AFM for samples (a) A, (b) A-60, (c) A-120, (d) C, (e) C-60 and (f) C-120.

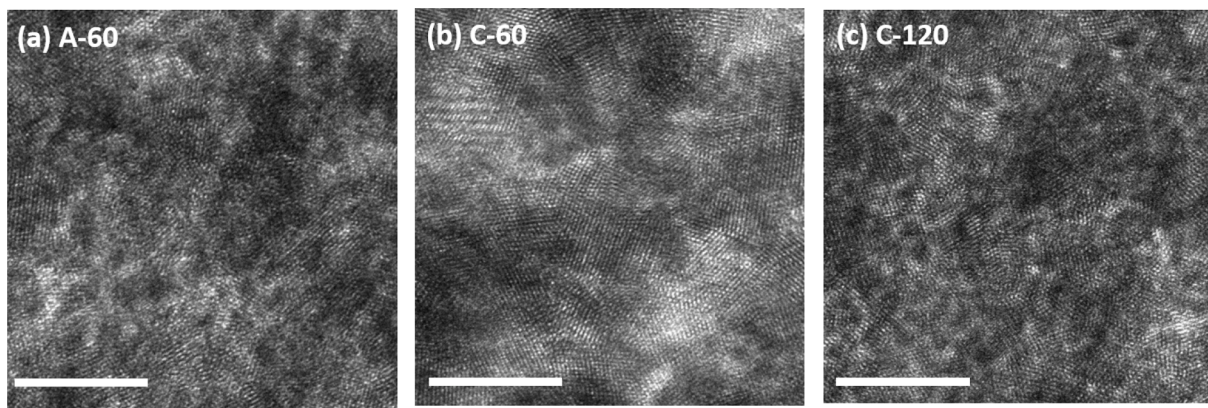


Fig. 4. Top-view TEM images of samples (a) A-60, (b) C-60 and (c) C-120. The scale bar represents 10 nm.

3.2. $H\text{-CeO}_2$ after acid treatment

Both the as-prepared and annealed hollow spheres were then immersed in 1 M HNO_3 for different times. The acid treated hollow spheres were named samples A-15, A-30, A-45, A-60, A-90 and A-120 for the as-prepared series, and C-15, C-30, C-45, C-60, C-90 and C-120 for the annealed series. The crystal structure of the spheres after acid treatment was identified with XRD, and the results are plotted in Figs. S2 (a) and (b). These plots demonstrate that the acid treatment did not change the crystalline phase of any of the hollow spheres. All the characteristic peaks of CeO_2 were still clearly visible even after a reaction time of 120 min. Cross-sectional TEM observations in Fig. S2 (c) and (d), indicate that both systems maintained the hollow structures even at a reaction time of 120 min.

The magnetic behavior of all hollow CeO_2 spheres was measured using VSM at room temperature. The diamagnetic behavior of sample holder was subtracted from the magnetization curves. Fig. 2 (a) plots the M/H curves of the A-series, demonstrating clear hysteresis loops. Fig. 2 (b) shows the variation of saturation magnetization M_s with reacting times of both A and C series. The value of M_s of both as-prepared and annealed CeO_2 hollow spheres before reacting with HNO_3 was about 0.5 memu/g. The magnetism M_s of both hollow spheres rose after reacting with acid solution, but evolved differently with reaction time in

the two systems. The A-series had a two-step transition, where M_s rose from 0.5 memu/g to 6 memu/g as the reaction time increased to 60 min, then declined rapidly with further immersion. Conversely, in the C-series, the value of M_s rose gradually from 0.5 memu/g to 5 memu/g as the reaction time reached 120 min.

The surface structures of hollow CeO_2 spheres after immersing in HNO_3 solution were investigated by AFM, with experimental results displayed in Fig. 3. Six samples with distinct magnetic behavior were investigated. The as-prepared spheres (sample A) had a small cluster-like structure, which became more obvious after immersing in HNO_3 for 60 (sample A-60) to 120 min (sample A-120), the cluster size rising from several nanometers to tens of nanometers. However, the surface roughness among these samples did not change significantly. The average surface roughness of samples A, A-60 and A-120 was 0.287 nm, 0.256 nm and 0.252 nm, respectively. Conversely, acid treatment had a stronger effect on the surface structure of the annealed series. Sample C had a flat surface before acid treatment. The cluster structure became significant after immersion in acid solution for 60 min (sample C-60). The average roughness of samples C, C-60 and C-120 was 0.308 nm, 0.818 nm and 0.322 nm, respectively.

The cluster-like surface structure was then examined using TEM. Fig. 4 (a–c) present the top-view TEM images of samples A-60, C-60 and C-120. Clear fringes were initially seen in these three samples,

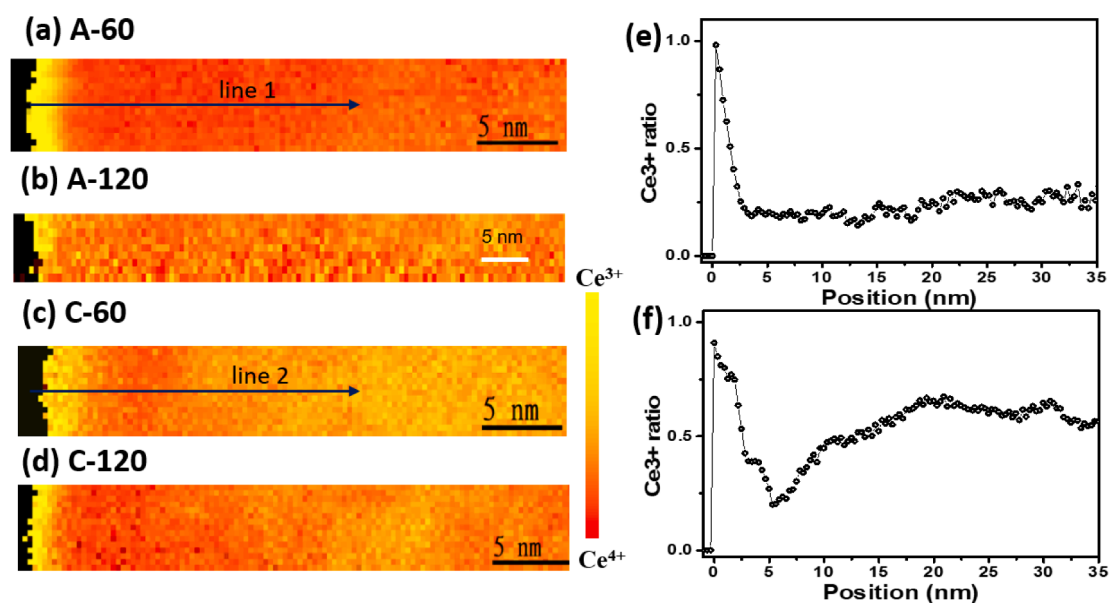


Fig. 5. Variation of the $\text{Ce}^{3+}/\text{Ce}^{4+}$ ratio throughout the shell in samples (a) A-60, (b) A-120, (c) C-60 and (d) C-120; Ce^{3+} concentration distribution curves of samples (e) A-60 and (f) C-60.

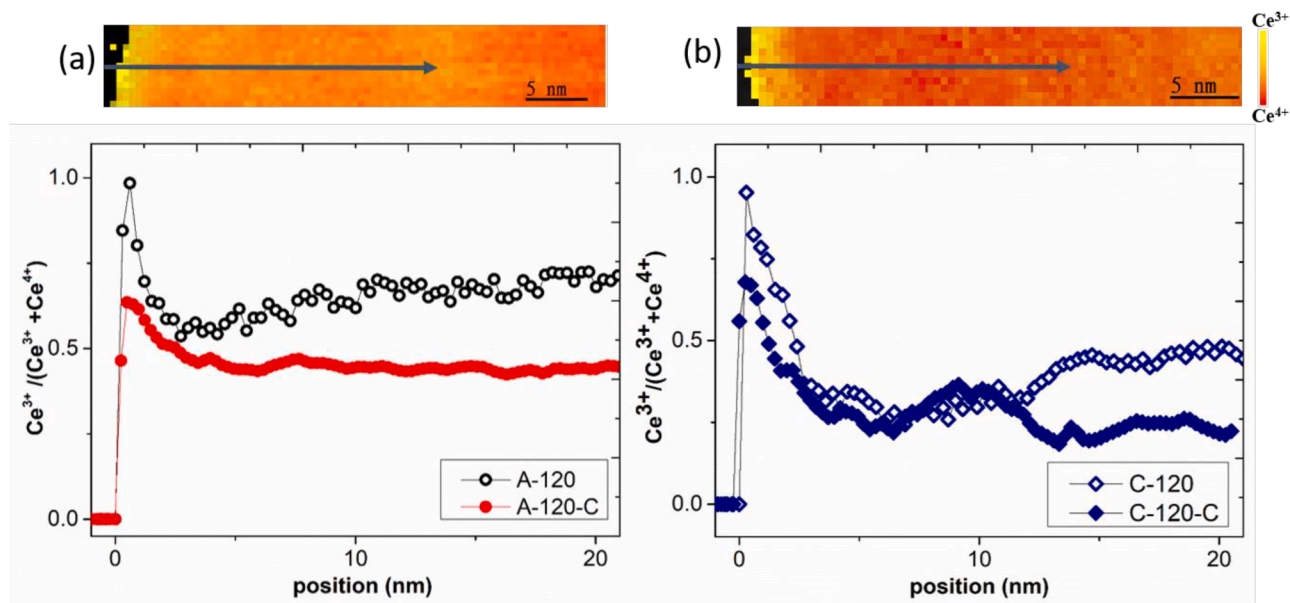


Fig. 6. Effect of post-annealing process on the acid treated spheres. (a) Ce^{3+} mapping and Ce^{3+} distribution profile throughout the shell of the sample A-120-C. (b) Ce^{3+} mapping and Ce^{3+} distribution profile throughout the shell of the sample C-120-C. The distribution profiles of sample without post-annealing (sample A-120 and sample C-120) are plotted together in both figures.

particularly the latter two samples, confirming the high degree of crystallization. Sample A-60 and C-120 had similar substructures, while sample C-60 had large cluster-like structures of about tens of nanometers, being separated with contrast areas due to lower density. These TEM observations were consistent with the AFM results. The formation of cluster-like structure can be explained from the TEM and AFM observations. In the as-prepared spheres (sample A), the shell was formed by CeO_2 particles with no preferred orientation. During the annealing process, CeO_2 particles started to assemble to form a larger cluster, resulting in dense clusters and loose space regions between clusters. These substructures were exposed after immersing in acid solution.

The variation of Ce valence among the spheres was then investigated by XAS. Fig. S3 (a) displays the XANES spectra of the Ce *L*-edge of the A-series. The change in valence of Ce can be expressed in terms of the concentration of Ce^{3+} , which was estimated by fitting the spectra. As demonstrated in the figure, an arctangent function was subtracted from all spectra to eliminate the electronic transition to continuum states, and the spectra were then fit by five Gaussian functions. Interpretations of these peaks have been given elsewhere. [24] The concentration of Ce^{3+} impurities in the CeO_2 matrix can be expressed as the ratio I_C/I_{total} , where I_C denotes the intensity of peak C, and I_{total} refers to the sum of deconvoluted peaks of A, B, and C. The calculated results of both A and C-series are shown together in Fig. S3 (b). The A-series initially had higher Ce^{3+} concentration than the C-series, which can be attributed to the oxidation caused by the annealing process. The difference of the Ce^{3+} concentration among samples in each series was small. The largest difference was only 0.5%, indicating that the overall Ce^{3+} content was only changed slightly by immersion in 1 M HNO_3 even for 120 min.

The spatial distribution of defects, i.e. Ce^{3+} was investigated by using STEM combined with EELS. Fig. 5 (a), (b), (c) and (d) show the obtained Ce^{3+} distribution throughout the shells of samples A-60, A-120, C-60, and C-120, respectively. In these samples, all the shells were divided into two parts. The first was the Ce^{3+} rich surface layer, and the thickness of the layer ranged from 1 nm to 5 nm. Interestingly, the distribution character of Ce^{3+} within the layer varied with samples. In sample A-60 particularly as well as sample C-120, Ce^{3+} was distributed homogeneously within the layer. In contrast, the distribution of Ce^{3+} within the layer was less homogeneous in samples A-120 and C-60, resulting in discontinuous defective layer in the direction along the sphere surface.

The second part was the defect-deficient bulk region. The Ce^{3+} content was lower in the bulk region of all samples. The distribution of Ce^{3+} inside the bulk region also varied by sample, as seen in Fig. 5 (e) and (f), and was estimated according to the ELNES of Ce *M* edge obtained along line 1 and 2, respectively. The Ce^{3+} -rich region inside the shell could be attributed to the surface of the cluster-like structure caused by the sintering process, as revealed by the AFM and TEM observations.

3.3. H-CeO₂ after post annealing

The above analysis results indicate that acid treatment of the hollow spheres causes the formation of cluster-like structures in shells, particularly sintered shells. A sample with such a structure has a weak magnetization. To suppress the formation of cluster structure and improve the homogeneity of defect distribution, a post-annealing process was conducted on the acid-treated spheres. The annealing condition was in air at 300 °C for 2 h. The resulting samples were named as A-30-C, A-60-C, A-120-C, C-30-C, C-60-C, and C-120-C, respectively. The spatial variation of Ce^{3+} concentration of these samples was verified using EELS analysis. Fig. 6 (a) and (b) show the obtained Ce^{3+} mapping and the distribution curve of Ce^{3+} content through the shells of samples A-120-C and C-120-C, respectively, confirming that the post-annealing process improved the homogeneity of Ce^{3+} content compared to samples A-120 and C-120. Conversely, the Ce^{3+} concentration near the surface dropped to ca. 70 % and 65 % in samples A-120 and C-120, respectively.

Fig. S4 (a) illustrates M–H curves of the spheres with post-annealing process, measured with VSM at room temperature. Clear hysteresis loops were observed, indicating that all samples were ferromagnetic with the coercivity, H_c , ranging from 80 Oe to 120 Oe. Notably, the spheres with post-annealing process had higher magnetization than the spheres without post annealing process during acid treatment, in particular based on the as-prepared spheres as start material. As shown in Fig. S4 (b), the rise in magnetization M_s was larger than 5 memu/g, at 7 memu/g, 16 memu/g and 10 memu/g, in samples A-30-C, A-60-C and A-120-C, respectively. Conversely, annealing had a weak effect on C-30, C-60 and C-120 was weak, even decreasing value of M_s in the latter two samples.

The above structural analysis demonstrates that acid treatment and annealing on the hollow spheres mainly affected the surface region. Therefore, zeta potential measurement was conducted to reflect the

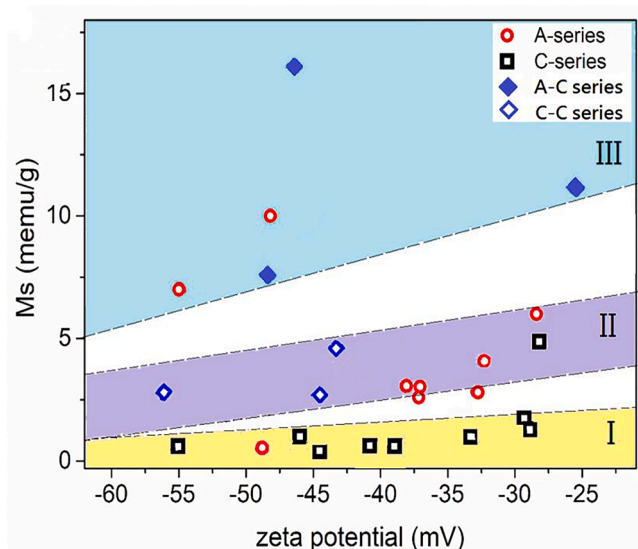


Fig. 7. The relation between M_s and zeta potential of H-CeO₂ with different post-treatments. A-series and C-series represent acid-treated as-prepared spheres and acid-treated annealed spheres, respectively. A-C series and C-C series represent A-series and C-series with post-annealing process.

difference of surface state of hollow spheres. The relationship between M_s and zeta potential of hollow CeO₂ spheres including A-series, C-series, A-C-series, and C-C series were investigated. As demonstrated in Fig. 7, it can be divided into three groups, which are labeled as group I (yellow), group II (purple), and group III (blue). Several phenomenon should be noted. At first, it is found that the relation is independent on either the synthesis or the treatment. Second, the magnetization of the three groups of samples was proportional to the zeta potential, which is expected because the zeta potential is related to the number of surface defects. However, the magnetization of the three groups of samples rose at different rates with increasing zeta potential. The highest rate of increase occurred in group III, followed by group II, and finally group I. Furthermore, the difference in magnetization of these three groups of samples with the same zeta potential could reach more than one order of magnitude, indicating that the regulation of magnetism may be different in the three groups of samples.

Accordingly, the structural characteristics of the three groups of samples should be considered. The microstructure analysis reveals most of the samples in group I were from the C-series, characterized by rough sphere surface and with large clusters. Sample C-60 is representative of this type of sample. Most samples in group II were from the A-series and part of the third series, having relatively continuous surface defective layers and reduced surface roughness of the sphere compared to group I, thus having similar characteristics to sample A-60. The sample in group III had a continuous and smooth surface defective layer, and a decreasing gradient of Ce³⁺ concentration inside this layer is. Sample A-120-C is representative of this type of sample.

Several interesting features can be summarized from the above results. First, introducing separated clusters with Ce³⁺-rich surfaces into the shell did not enhance the overall magnetic properties of the hollow spheres. Second, the magnetism of the mesoscopic hollow spheres depended not only on the defect concentration of the defective layer, but also on its substructure, including the surface roughness and homogeneity. As the defective layer was uniform with a continuous defect distribution, the magnetic saturation of the hollow sphere was high. For example, the M_s of sample A-30-C reached 16 memu/g, which is comparable to the thin CeO₂ layer deposited on Ag [19], and higher than that of undoped CeO₂ nanoparticles. [17,26] Present results support the feasibility of the collective orbital paramagnetism developed recently by Coey et al. [15,25] Additionally, the hollow sphere could be further

improved by reducing the shell thickness and suppressing the agglomeration phenomenon between the grains in the shell layer caused by sintering.

4. Conclusion

This work successfully obtains micro-scale CeO₂ hollow spheres with different defect distribution character by varying the immersion in acid solution and the annealing process. Magnetic behavior is found to depend closely on the nature of defective layer at surface, but not the total defective volume of the sphere. A stronger magnetism is observed in hollow spheres with a thin defective layer and continuous surface structure. The experimental results provide guidance for handling the magnetic properties of micro-scale oxides.

Declaration of Competing Interest

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.mseb.2021.115481>.

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