XANES Investigation of the Valance States of Ce in the CeO_2 Nanoparticles with Different Concentration of Oxygen Vacancies

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To reveal the relation between defects and ferromagnetism in undoped transition metal (TM) oxides, the magnetism and electronic structure of TM oxides nanoparticles undergo various oxygenation processes were analyzed. TEM and XRD results indicate that CeO_2 nanoparticles prepared by thermal decomposition method are well dispersed and with uniform size. The average diameter of particles was about 2 nm. The size of particles varies only with annealing temperature. The magnetic measurement results show that at room temperature, as-prepared sample is paramagnetic, which was different to those in literature synthesized by other methods. After redox treatment, all samples became ferromagnetic. Notably, with increasing the oxygen partial pressure, the saturation magnetic moments (M_s) was not decrease monotonously. The samples annealed in air at 500°C for 2 hrs possessed the highest M_s value in this study (0.23 emu/g), as shown in Fig. 1. This value is much larger than those in literature (of one order).

XANES were then investigated to study the electronic states and the structural symmetry of the sites of Ce atoms. The X-ray absorption measurements of Ce *M* and *L* edge were carried out with synchrotron radiation at the 20A and 17C beam line, respectivity. Our investigations show that CeO_2 particles prepared by using thermal decomposition method contain high concentration of oxygen vacancies. It is worth to notice that the change of electronic structure strongly depends on the annealing conditions, i.e. oxygen partial pressure and temperature. It is expected that with annealed under higher annealing temperature or lower oxygen partial pressure, the concentration of oxygen vacancies of particles will be higher. Ce *M* edge spectra show this results in the more delocalization of 4*f* electrons (as shown in Fig. 2). Also, according to the change of values of the intensity ratio, (I_B/I_A) from Ce *L* edge, it is indicated that the increase of oxygen vanancies will cause an increase of covalence between Ce(4*f*) and O(2*p*), as shown in Fig. 3.

The above XANES analysis implied that the increase of annealing temperature or the decrease of oxygen partial pressure both result in the stronger interation between Ce and O atoms. It indicates that the concentration and distribution of oxygen vacancy play an important role in the magnetism of TM oxides. The particular finding of M_s-P_{O2} dependence in this study could be attributed to the high concentration of oxygen vacancies of the samples in as-prepared state. After redox treatment, the size of particles as well as the concentration of oxygen vacancies changed, thus gave rise to the variation in ferromagnetism.

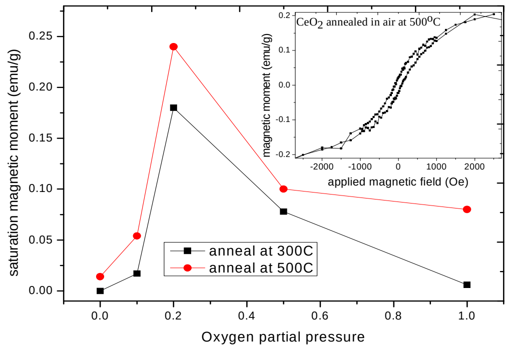

Fig. 1: The oxygen partial pressure dependence of saturation magnetic moment (*Ms*) of CeO_2 nanoparticles synthesized by thermal decomposition method. Inset shows the M-H results at room temperature of samples annealed in air at 500°C.

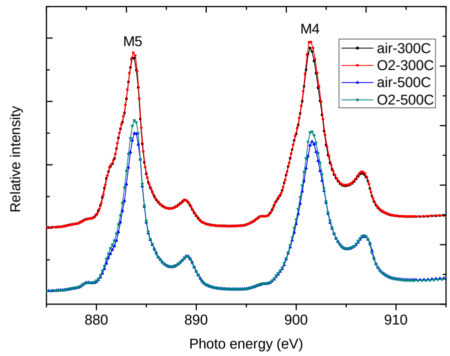

Fig. 2: Ce *M* edge spectra of CeO_2 nanoparticles annealed in different oxygen partial pressure (air and O_2) and temperature (300 and 500°C). The only obvious difference between samples annealed in different oxygen partial pressure is the relative intensity of main peak and the satellite, which indicates the delocalization of 4*f* electrons changed.

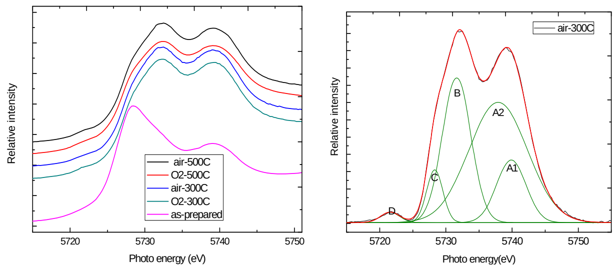

Fig. 3: (Left) Ce L_3-edge spectra of CeO_2 nanoparticles anneled at different condictions; (right) theoretical fitting of L_3 edge. Peak A is assigned to a core excited Ce^{4+} final state, peak B corresponds to a $2p4f^1 5d^* L$ state, where *L* stands for a hole in the anion ligand orbital.