PVP-Assisted Synthesis of Fe/Ceo_2 Nano-Alloys Prepared by Solgel Method

Majid Farahmandjou*, Mahkameh Dastpak

Department of Chemistry, Faculty of Pharmaceutical Sciences, Tehran Medical Sciences, Islamic Azad University ,Tehran, Iran

majidfarahmandjou@gmail.com

Abstract

Fe/CeO_2 nanoparticles (NPs) were synthesized by simple co-precipitation method Iron chloride hexahydrate ($FeCl_3.6H_2O$) and cerium chloride ($CeCl_2{\cdot}5H_2O$) as precursor in the presence of polyvinylpyrrolidone (PVP) surfactant and ethylene glycol agent. The samples were characterized by high resolution transmission electron microscopy (HRTEM), field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD) and electron dispersive spectroscopy (EDS) in different temperature. The XRD results showed that Fe-doped CeO_2 was single-phased with a cubic structure. The particle size of as-prepared sample was in the range size of 15-45 nm and annealed sample was around 22 nm in diameter at 800°C for 3 hours. The TEM studies showed the 17 nm squared-like shaped nanosized particles. EDS shows peaks of iron and cerium with less impurity in prepared samples and Fe/Ce ratio was also decreased with increasing annealing temperature.

Keywords: Fe-doped, CeO_2 semiconductor, Nanocomposites, PVP, Solgel Synthesis

Introduction

Metal oxide NPs are of great interest for researchers from a broad range of disciplines, including magnetic fluids, data storage, catalysis, and bioapplications [1–28]. Nanostructured materials have reached significant impact in practical applications due to general improvement of catalytic, electrical, optical and electrooptical properties [29-36]. Technology of solid oxide fuel cells is currently the most relevant field where CeO_2 found applications [37]. It was found that ferromagnetic and photocatalytic properties as well as grain growth stabilization at higher temperatures can be significantly improved by doping CeO_2 nanocrystals with transition metal elements such as Fe [38]. CeO_2 nanocrystals and their solid solutions that are substituted with Fe^{3+} ions have been prepared by various methods such as sol–gel [39], hydrothermal synthesis [40], conventional mixed-oxide method [41] and ball-milling process [42]. Among them, the sol-gel method has been widely used due to synthesis at low temperatures, the fabrication of homogeneous compounds with high purity, and the easy control of the reaction conditions [17]. In this paper, FeCe magnetic nanocomposites were synthesized using iron chloride and cerium chloride precursors in presence of PVP surfactant. Structural and surface morphological properties are discussed by XRD, HRTEM, FESEM and EDS analyses.

Experimental detail

Iron-cerium NPs were synthesized by a simple synthesis according to the following manner. Firstly, 3.1 g $CeCl_2{\cdot}5H_2O$ and 3g PVP surfactant was dissolved in 50 mL pure water and then 3 g $FeCl_3.6H_2O$ was added to the solution with stirring at room temperature. After 10 min, 20 mL ethylene glycol was slowly added to the orange-colored solution and synthesis temperature was increased to 90°C. The color of solution changed from milky color to red color by adding iron precursor. The pH=3 was maintained during the synthesis. The product were evaporated for 2 hours, cooled to room temperature and finally calcined at 800 °C for 3 hours. All analyses were done for samples without any washing and purification.

The specification of the size, structure and optical properties of the as-synthesis and annealed NPs were carried out. X-ray diffractometer (XRD) was used to identify the crystalline phase and to estimate the crystalline size. The XRD pattern were recorded with 2θ in the range of 4-85° with type X-Pert Pro MPD, Cu-K_α: λ = 1.54 Å. The morphology was characterized by field emission scanning electron microscopy (SEM) with type

KYKY-EM3200, 25 kV and transmission electron microscopy (TEM) with type Zeiss EM-900, 80 kV. The Fe and Ce elemental analysis of the samples was performed by energy dispersive spectroscopy (EDS) type VEGA, 15 kV. All the measurements were carried out at room temperature.

Result and discussion

XRD analysis was used to identify crystalline phases and to estimate the crystalline sizes. Figure 1 shows the X-ray diffraction patterns of the powder after heat treatment at 800 °C for 3 hours. The exhibited peaks correspond the cubic structure. The mean size of the ordered FeCe NPs has been estimated from full width at half maximum (FWHM) and Debye-Sherrer formula as follows [43]:

$$D = \frac{0.89\lambda}{B\cos\theta} \qquad (1)$$

where, 0.89 is the shape factor, λ is the x-ray wavelength, B is the line broadening at half the maximum intensity (FWHM) in radians, and θ is the Bragg angle. The mean size of as-prepared samples was around 17 nm from this Debye-Sherrer equation.

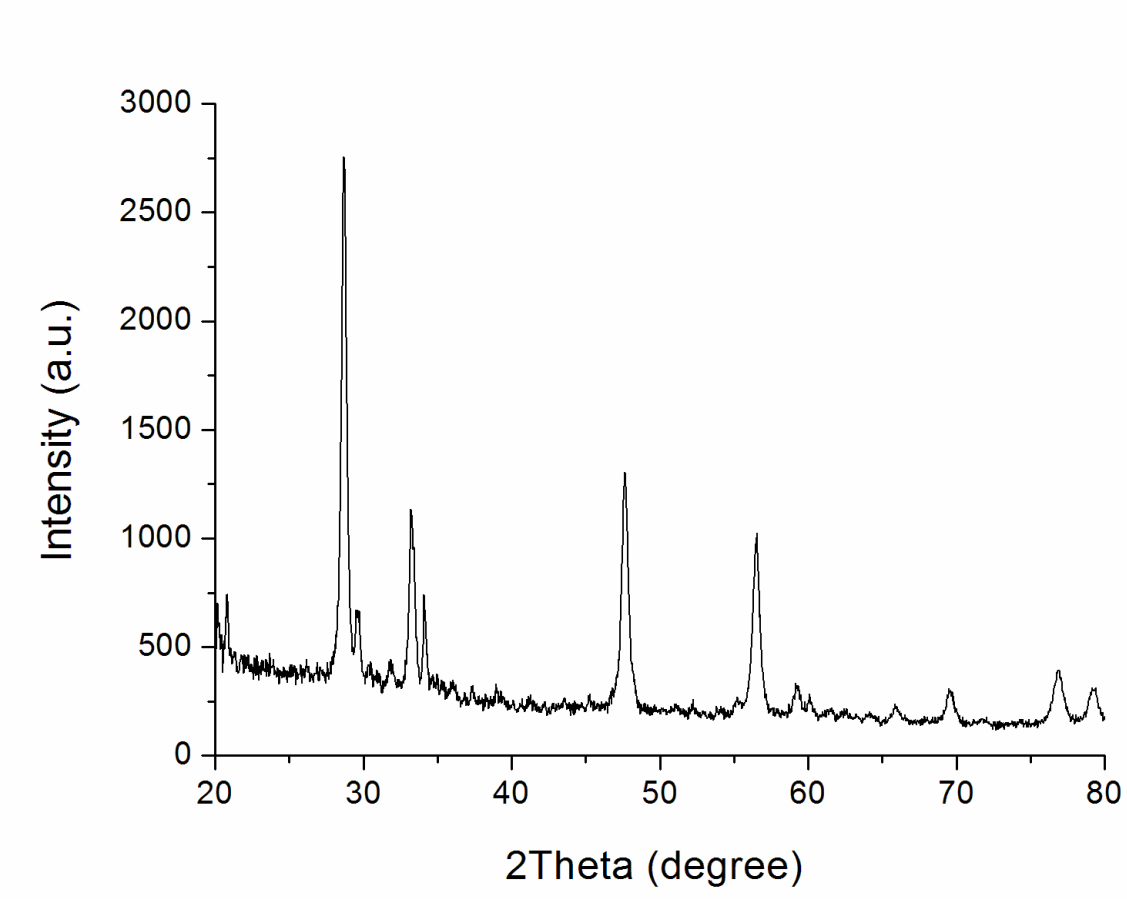


Figure 1. XRD patterns of annealed FeCe samples

SEM analysis was used for the morphological study of NPs of samples. With increasing temperature size of the particles decreased from 30 nm to 22 nm. Figure 2(a) shows the SEM image of the as-prepared FeCe NPs

prepared by this method. In this figure, the particles prepared with formation of clusters. Figure 2(b) shows the SEM image of the annealed FeCe NPs at 800 °C for 3 hours. The particle size of as-prepared samples was measured in the range size of 15-45 nm and crystallite size of annealed nanocrystals about 22 nm in diameter.

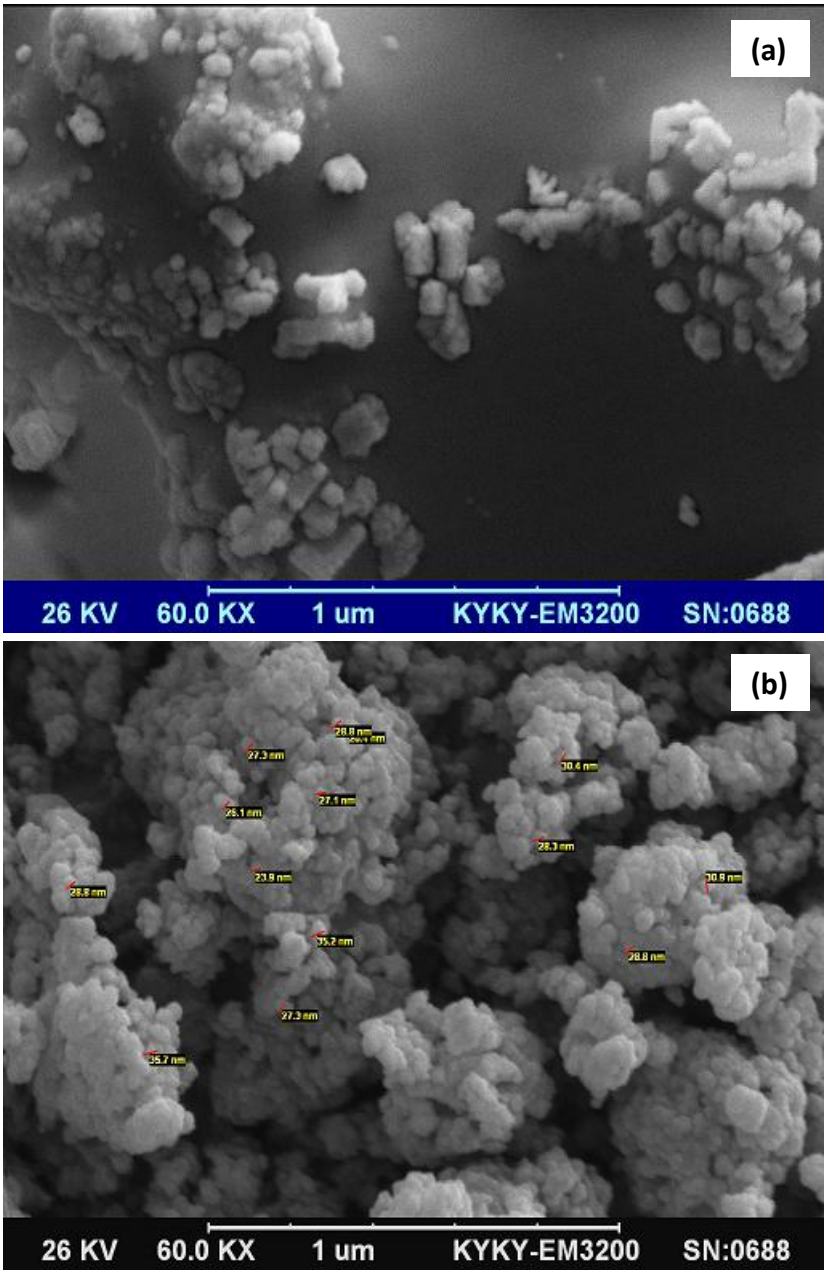


Figure 2. SEM images of the (a) as-prepared (b) annealed FeCe NPs at 800 °C

The transmission electron microscopic (TEM) analysis was carried out to confirm the actual size of the particles, their growth pattern and the distribution of the crystallites. Figure 3 shows the as-synthesized TEM image of FeCe NPs with average diameter of 17 nm prepared by chemical reduction route.

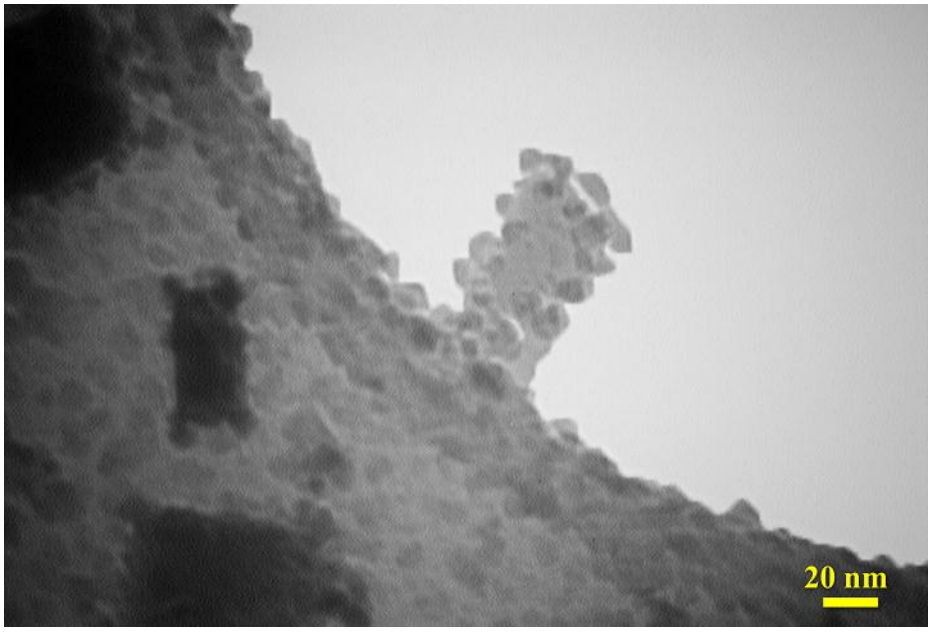
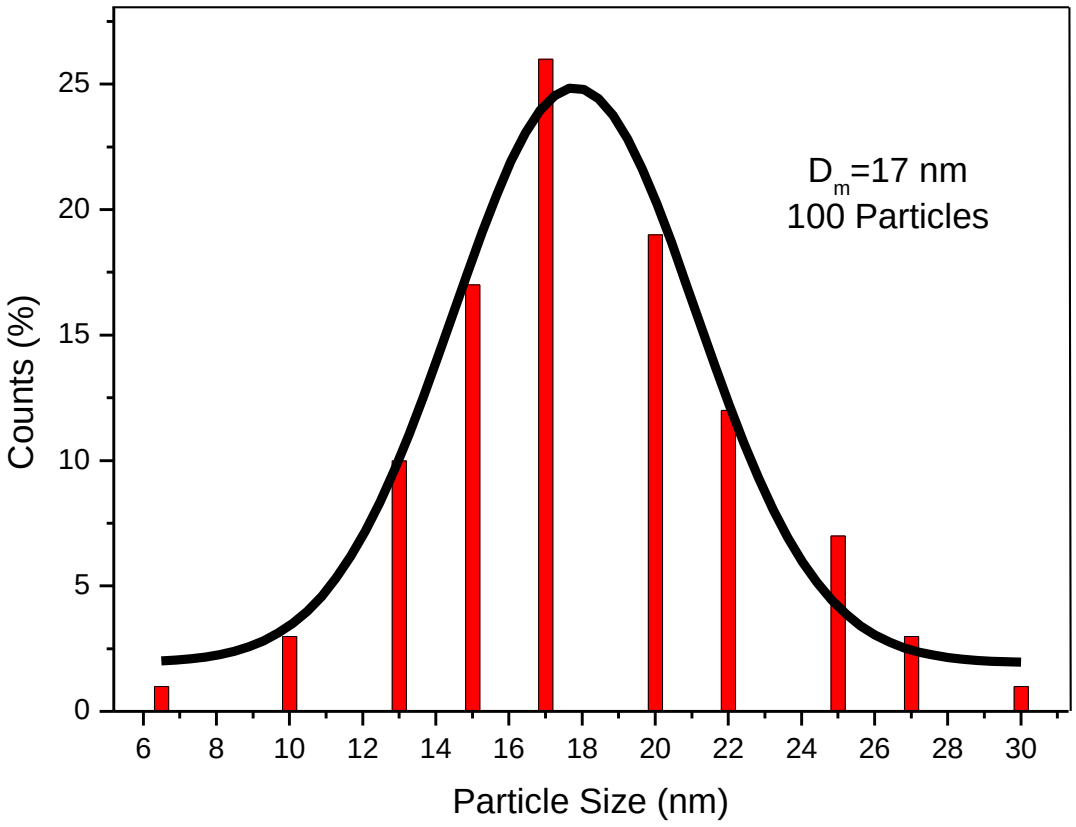


Figure 3. TEM image of the as-prepared FeCe NPs

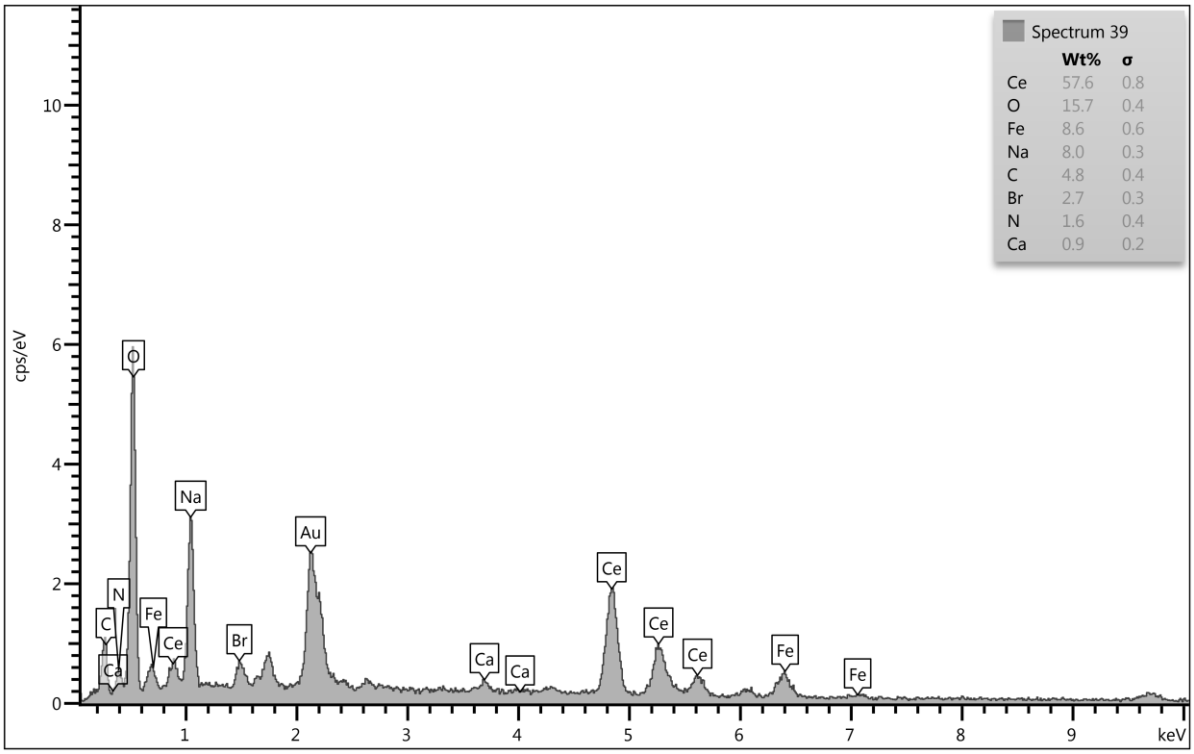
Figure 4 shows the size measurement of 100 randomly selected particles. By fitting it with a log normal curve leads to a measured mean diameter of 17 nm with standard deviation of about



8%.

Figure 4. Particle diameter histogram of as-prepared Fe-Ce NPs

Energy dispersive spectroscopy (EDS) of FeCe samples prepared by wet synthesis is shown in Figure 5 which confirms the existence of Fe and Ce with weight percent. EDS was used to analyze the chemical composition of a material under SEM. EDS shows peaks of iron and cerium with fewer Bromide and sodium element for as-prepared samples, according to our previous study [15]. The weight percent of C and N elements was decreased by increasing temperature from room temperature to 800 °C. The samples were not washed and purified to prevent oxidation. It can be seen that the Fe/Ce ratio is 0.68 and 0.15 for as-prepared and annealed one respectively. It is realized that the Fe diffused into the CeO_2 matrix are decreased by increasing annealing temperature because of atomic interaction.



Conclusion

Fe-doped ceria NPs have been successfully synthesized using iron chloride and cerium chloride in the presence of CTAB surfactant. XRD spectrum shows cubic structure of the samples. From SEM images, it is clear that with increasing temperature the size of the NPs decreased with less agglomeration. TEM image exhibits that the as-synthesized FeCe NPs with an average diameter about 17 nm with good uniformity. The EDS spectrum showed peaks of iron and cerium with less impurity and Fe/Ce ratio was also decreased with increasing annealing temperature.

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