

# Preparation of a novel fluorescent nanocomposite: CeO<sub>2</sub> / ANS by a simple method

X. LIU\*, X. LIAN, Y. LI, N. ZHANG

Civil Aviation University of China, College of Science, Tianjin 300300, China

For the first time, a novel fluorescent material, composed of CeO<sub>2</sub>/ANS nanocomposites was successfully synthesized by a simple ultrasonic method, using CeO<sub>2</sub> nanoparticles and 8-anilino-1-naphthalenesulfonic acid (ANS) as the raw materials. The samples were characterized by scanning electron microscope (SEM), photoluminescence spectroscopy and Fourier transformation infrared spectroscopy (FTIR). The results showed that the PL intensity of the CeO<sub>2</sub>/ANS nanocomposites was higher than that of both CeO<sub>2</sub> nanoparticles and ANS powders, and the peak wavelength was also different from the peak wavelength typical of each of the used materials, which suggests that the chemical reaction occurs between CeO<sub>2</sub> nanoparticles and ANS molecules. In addition, the effect of the ANS concentrations on the photoluminescence of the nanocomposites was also investigated.

Keywords: *CeO<sub>2</sub> nanoparticles, ANS, nanocomposites, photoluminescence*

© Wroclaw University of Technology.

## 1. Introduction

Cerium oxide, as a rare earth oxide, has attracted intense interest due to its high potential applications such as light-emitting material, polishing agent, ultraviolet absorbent, automobile exhaust catalyst and solid oxide fuel cells (SOFC), etc [1–7]. Moreover, ultra-fine CeO<sub>2</sub> not only can reduce the sintering temperature, but can also increase the density of ceramics [1, 8, 9]. In addition, after deoxidizing at high temperatures, CeO<sub>2</sub> can be converted into nonstoichiometric CeO<sub>2-x</sub> (0<x<0.5), which could be transformed into CeO<sub>2</sub> when it is exposed to the oxidizing environment. For this reason, CeO<sub>2</sub> has a very good ability to store and release oxygen [10]. So both the preparation and properties of CeO<sub>2</sub> have been widely investigated. There are also many reports on CeO<sub>2</sub> composites for their interesting properties [11–14]. ANS is an amphipathic dye, with hydrophobic naphthalene and phenyl groups and a charged sulfonate group and it has been used to investigate the structural and physicochemical characteristics of the aggregates of transthyretin,

which provides insights into the mechanism of protein misfolding and misassembly [15, 16]. At the same time, it is generally claimed that the binding of ANS with protein does not affect the protein conformation and activity, and that ANS usually functions as a hydrophobic probe [17–19]. In addition, ANS is nearly non-fluorescent in water, but shows extremely strong fluorescence in non-polar solvents [20, 21]. Dramatic enhancement in the fluorescence of ANS has been observed when encapsulated in cyclodextrins [22] and cucurbiturils [23]. To our knowledge, there have been no reports on CeO<sub>2</sub>/ANS fluorescent nanocomposites till now. In this paper, we report the results of the preparation and characterization of CeO<sub>2</sub>/ANS fluorescent nanocomposites by a simple ultrasonic method.

## 2. Experimental

### 2.1. Preparation of CeO<sub>2</sub>/ANS nanocomposites

The starting materials in our experiments are CeO<sub>2</sub> nanoparticles (with average particle size of 20 nm), 8-anilino-1-naphthalenesulfonic acid

\*E-mail: xl.liu@cauc.edu.cn

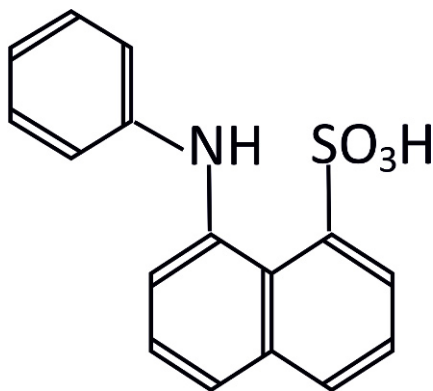


Fig. 1. Schematic structure of ANS molecule

(98%). Fig. 1 shows the schematic structure of the ANS molecule and anhydrous alcohol (A.R.).

Five aliquots of 0.5 g CeO<sub>2</sub> nanoparticles were firstly added into five conical flasks, and then mixed with 50 ml ANS alcohol solutions of 10<sup>-7</sup>, 10<sup>-6</sup>, 10<sup>-5</sup>, 10<sup>-4</sup> and 10<sup>-3</sup> mol/L, respectively. Then all of them were treated ultrasonically at 60 °C, 70 Hz for 2 h. The obtained liquid CeO<sub>2</sub>/ANS nanocomposite was rinsed for several times with alcohol to remove the excessive ANS molecules. Eventually, the nanocomposites were dried in an oven at 60 °C for 6 h. The obtained samples were marked as CA-1, CA-2, CA -3, CA -4 and CA -5, respectively.

## 2.2. Characterization

The morphology of the samples was examined with a S-4800 scanning electron microscope with the accelerating voltage of 150 kV. The photoluminescence spectra of the samples were measured on a WGY-10 fluorescent spectrometer. The FTIR spectra were collected on an Avatar 330 spectrometer (Nicolet). The samples were mixed with KBr in accordance with the mass ratio of the sample to KBr of 1:100 and pressed into slices for characterization. All measurements were carried out at room temperature.

## 3. Results and discussion

Fig. 2 shows the FTIR spectra of CeO<sub>2</sub> nanoparticles, nanocomposites and ANS particles.

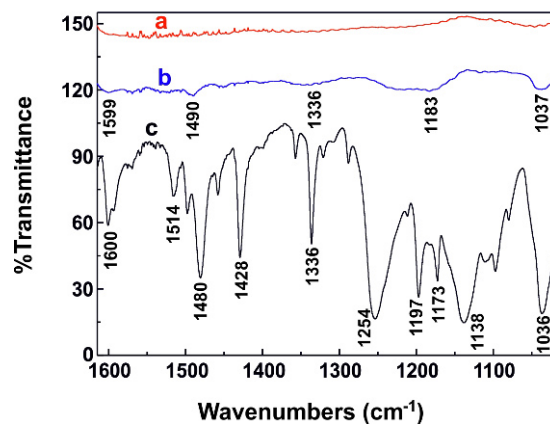


Fig. 2. The FTIR spectra of CeO<sub>2</sub> nanoparticles (a), nanocomposites (b) and ANS particles(c).

The absorption peaks at 1600, 1514, 1480 and 1428 cm<sup>-1</sup> in Fig. 2 (c) can be attributed to the vibration mode of benzene rings, whereas the peak at 1254 cm<sup>-1</sup> is attributed to the stretch vibration of C-N. The other peaks at 1197, 1173 and 1138 cm<sup>-1</sup> are the symmetry stretch vibration of O=S=O, and the peak at 1336 cm<sup>-1</sup> represents the asymmetry stretch vibration. The peak at 1036 cm<sup>-1</sup> can be attributed to the stretch vibration mode of S=O [24].

It can be also seen from Fig. 2 that the characteristic absorption peaks of ANS (such as 1599, 1336, 1037 cm<sup>-1</sup>) can be found in the nanocomposite (see spectrum b). Compared with the spectrum (c), the position of the peak at 1336 cm<sup>-1</sup> (asymmetry stretch vibration of O=S=O) almost remains unchanged, but there is a significant widening in the spectrum (b). The peak at 1173 cm<sup>-1</sup> (attributed to symmetry stretch vibration of O=S=O) shifts to 1183 cm<sup>-1</sup>. In addition, the peak at 1254 cm<sup>-1</sup> (the stretch vibration of C-N) is not observed in the spectrum of the nanocomposite (as it is shown in Fig. 2b). The results reveal that a complex structure may have formed between CeO<sub>2</sub> nanoparticles and ANS particles [25].

In Fig. 3, we present the photoluminescence (PL) spectra of ANS, CeO<sub>2</sub> nanoparticles and nanocomposites, which provide the evidence that chemical bonds have formed between the surface

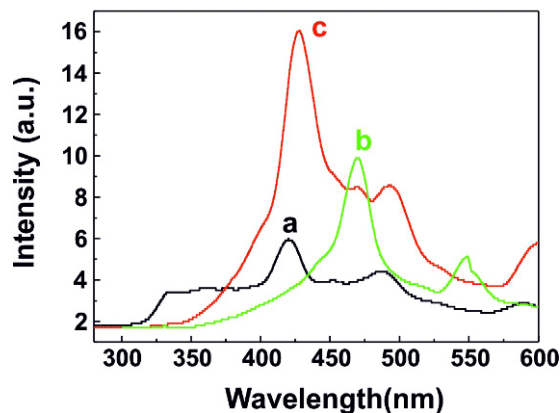


Fig. 3. The PL spectra of ANS particles (a), CeO<sub>2</sub> nanoparticles (b) and nanocomposites (c).

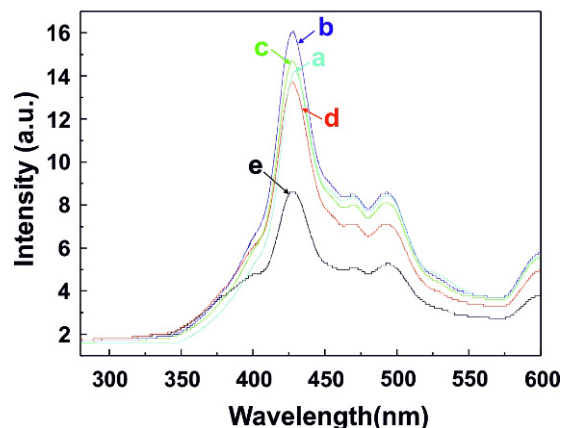


Fig. 5. The PL spectra of nanocomposites CA-1 (a), CA-2 (b), CA-3 (c), CA-4 (d) and CA-5 (e).

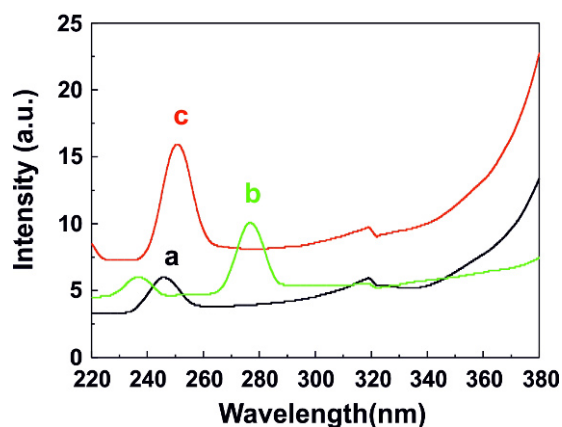


Fig. 4. The excitation spectra of ANS particles (a), CeO<sub>2</sub> nanoparticles (b) and nanocomposites (c).

atoms of CeO<sub>2</sub> nanoparticles and ANS molecules. These bonds prevent the aggregation of ANS molecules, thereby enhancing the fluorescence efficiency of the nanocomposites. Obviously, the PL intensity of the nanocomposite is higher than that of CeO<sub>2</sub> nanoparticles and ANS powders. The peak wavelength (428 nm) of the nanocomposite shows a red shift of 8 nm compared to that (420 nm) of ANS powders, and a blue shift of 42 nm compared to that (470 nm) of CeO<sub>2</sub> nanoparticles.

In addition, from the excitation spectra of the samples (shown in Fig. 4), it can be seen that the absorption intensities of ANS and CeO<sub>2</sub> nanoparticles are weak, whereas

the nanocomposite shows a strong and broad absorption band. Clearly, the high PL efficiency is based on the intense absorption of the excitation light, so it can be claimed that the nanocomposite exhibits more intense photoluminescence than that of CeO<sub>2</sub> nanoparticles and ANS. In order to better explain the mechanism of the above phenomenon, we have conducted a series of experiments.

It is well known that the luminescence of a dye depends to a great extent on its state of aggregation in a solution. The PL intensity will greatly reduce when the molecules become too concentrated. This means that the more the dye molecules disperse, the more efficient the luminescence is. It follows from the above results that the ANS molecules are adsorbed on the surface of CeO<sub>2</sub> nanoparticles, and so the interaction between the ANS molecules decreases [26], which directly causes the PL enhancement of the ANS molecules.

In order to study the effect of the ANS concentrations on the PL of the nanocomposites, let us follow the PL spectra of nanocomposites CA-1, CA-2, CA-3, CA-4 and CA-5 shown in Fig. 5. With the increase of ANS concentration from  $10^{-7}$  mol/l to  $10^{-6}$  mol/l, the PL intensities of the nanocomposites become higher. By further increasing the concentration to  $10^{-3}$  mol/l, the PL intensities of the nanocomposites decrease significantly. However, the peak positions remain unchanged. These results reveal that the PL

intensity of the nanocomposite has reached its optimum value in CA-2. At low concentrations, ANS molecules are dispersed on the surface of CeO<sub>2</sub> nanoparticles, but their number is sufficient to prevent the interaction of the dye molecules. So with the increase of ANS concentration, more and more ANS molecules contribute to the PL intensity. However, if a growing number of ANS molecules are adsorbed on the surface of CeO<sub>2</sub> nanoparticles, they interact with each other, and dimers or polymers are formed. This would result in a decrease of the energy band gap of the molecules and an increase in the interactions between electrons and phonons [26]. This explains why the decrease in the PL efficiency is observed.

## 4. Conclusions

CeO<sub>2</sub>/ANS nanocomposites have been successfully synthesized by the simple ultrasonic method, using ANS and CeO<sub>2</sub> nanoparticles as the raw materials. The FTIR spectra reveal that complex interactions had occurred between the surface atoms of CeO<sub>2</sub> nanoparticles and ANS molecules. Furthermore, the PL spectra proved that chemical bonds were formed between CeO<sub>2</sub> and ANS, and thus the luminescence properties of the nanocomposites were significantly different from that of the starting materials. In addition, the PL intensity of the nanocomposites was also affected by ANS concentrations.

## Acknowledgement

This project is supported by Natural Science Foundation of Tianjin (NO.09JCYBJC04200) and Basic Science Study Foundation of National Universities (NO.2010D008).

## References

- [1] KIORK R. E., OTHMER D. F., Encyclopedia of Chemistry and Technology, Wiley, New York, 1979.
- [2] MORI TOSHIYUKI, DRENNAN JOHN, WANG YARONG, LI JI-GUANG, IKEGAMI TAKAYASU, *J. Therm. Anal. Calorim.*, 70 (2002), 309.
- [3] KASPAR J., FORNAIERO M., GRAZLAM M., *Catal Today*, 50(2000), 285.
- [4] SHINOBU F., MASASHI O., *Appl. Phys.*, 95(2004), 8002.
- [5] NORIYA I., WOOSUCK S., *Sensors and Actuators B*, 87(2002), 95.
- [6] ZHANG T. S., MA J., CHAN S. H., KILNER J. A., *Solid State Ionics*, 176(2005), 377.
- [7] MONTE R. D., KASAPAR J. J., *J. Mater. Chem.*, 15 (2005), 633.
- [8] YUAN S., JU W., ZHANG Y., XUE Q., CHEN N., XIAO Y., *J. Chin. Soci. Rare Earths*, 21 (2003), 84 (in Chinese).
- [9] DONG X., HONG G., YU D., *J. Chin. Ceram. Soci.*, 25(1997), 56.
- [10] STEELE B. C. H., *Solide state Ion.* 129(2000), 95.
- [11] JIANG B., ZHANG S., GUO X., JIN B., TIAN Y., *Appl. Surf. Sci.*, 255(2009), 5975.
- [12] ELENA KONYSHEVA, JOHN T. S. IREINE, ASTRID BESMEHN, *Solid State Ion.*, 180 (11-13) (2009), 778.
- [13] ZHU YI, LI GAI, ZHANG SHENYI, SONG JIMING, MAO CHANGJIE, NIU HELIN, JIN BAKANG, TIAN YUPENG, *Electrochimica Acta.*, 56(2011), 7550.
- [14] SEIICHIRO IMAMURA, HIROYUKI YAMADA, KAZUNORI UTANI, *Applied Catal. A: General*, 192(2000), 221.
- [15] LINDGREN M., SORGIFERD K., HAMMARSTROM P., *J. Biophys.*, 88 (2005), 4200.
- [16] MONTSERRAT ANDUJAR-SANCHEZ, ANA CAMARA-ARTIGAS, VICENTE JARA-PEREZ, *J. Chem. Thermodynamics*, 42(2010), 337.
- [17] MENDOZA J. A., ROGERS E., LORIMER G. H., HOROWITZ P. M., *Biol. J. Chem.*, 266(1991), 13044.
- [18] CHOI J. K., KIM I. S., KWON T. I., PARKER W., SONG P. S., *Biochemistry*, 29(1991), 6883.
- [19] YU XUAN-CHUAN, STROBEL HENRY W., *Molecular and Cellular Biochemistry*, 162(1996), 89.
- [20] KOSOWER E. M., DODIUK H., KANETY H., *J. Amer. Chem. Soc.*, 100(1978), 4179.
- [21] EBBESEN T. W., GHIRON C. A., *J. Phys. Chem.*, 93(1989), 7139.
- [22] WAGNER B. D., MACDONALD P. J., *J. Photochem. Photobiol. A: Chem.*, 114(1998), 151.
- [23] WAGNER B. D., FITZPATRICK S. J., GILL M. A., MACRAE A. I., STOJANOVIC N., *Can. J. Chem.*, 79(2001), 1101.
- [24] XIE J. X., Applications of Infrared Spectroscopy in Organic Chemistry and Drug Chemistry. Science Publishing Company, Beijing, 1987, 41 (in Chinese).
- [25] LIU XIULIN, LI YAN, WANG XUEYAN, *Mater. Lett.*, 60(2006), 1943.
- [26] HASHIMATO K., HIRAMOTO M., SAKATA T., *Chem. Phys. Lett.*, 148(1988), 215.

Received 2011-08-05

Accepted 2012-05-11