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# Synthesis and photoluminescence properties of $Nd_2O_3$ nanoparticles modified by sodium bis(2-ethylhexyl) sulfosuccinate*

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This paper reports that $Nd_2O_3$ nanoparticles modified by AOT(sodium bis(2-ethylhexyl) sulfosuccinate) were prepared using microemulsion method in the system of water and propanol/AOT/toluene. Transmission electron microscopy shows that the $Nd_2O_3$ nanoparticles take the shape of sphere with 18 nm and 31 nm with different preparation. The organic sol of $Nd_2O_3$ nanoparticles is very stable at room temperature. X-ray diffraction results show that the product has hexagonal phase structure. Two ultraviolet emission band at 344 nm and 361 nm corresponding to the transition of $^4D_{3/2} \rightarrow 4I_{9/2}$ and $2P_{3/2} \rightarrow {}^4I_{11/2}$ or $^4D_{3/2} \rightarrow {}^4I_{13/2}$ were observed.

**Keywords:** $Nd_2O_3$ nanocrystals, photoluminescence spectrum, surface modification
**PACC:** 8115H, 6170T, 6146

## 1. Introduction

Nanoparticles have chemical and physical properties which are different from those of the corresponding bulk materials due to their small size and large surface to volume ratio, and attract much attention because of their potential applications in many fields including optics, electrics, magnetism, ceramics, catalysis.[1−3] Rare earth compound has unique properties and wide uses owing to their special electronic configuration.[4] To develop their application as novel materials, it is important to control the spontaneous formation of organized structures at nanoscales.

Among rare-earth ions, neodymium is a unique element for use as a luminescent centre[5−9] in laser systems because the four-level energy structure of neodymium is considered to be more ideal for laser transition. $Nd_2O_3$ has a large variety of applications such as ultraviolet absorbent, glass-polishing materials, catalysts for the automotive industry, hence preparation of $Nd_2O_3$ nanoparticles is a subject of deep practical interest nowadays. Recently, Que *et al*[10] reported the strong room temperature emission at 1064 nm of needlelike $Nd_2O_3$. Several approaches have been developed to synthesize $Nd_2O_3$ nanoparticles. So far, few works have investigated the preparation and microstructure of $Nd_2O_3$ nanoparticles.[11−13] Based on the dehydrating peculiarity of propanol,[14,15] here we report a simple and convenient method to prepare $Nd_2O_3$ nanoparticles organic sol in the system of AOT/toluene and propanol. To the lest of our knowledge, there has been virtually no report on the synthesis of $Nd_2O_3$ by using microemulsion in the system of AOT/toluene and 2-propanol. In this paper, we have successfully developed a new synthetic route, and employed directly surfactant as both protective agents and phase-transfer reagent to prepare $Nd_2O_3$ nanoparticles, which avoid the introduction of impurities.

## 2. Experimental procedure

A complex system was used to prepare $Nd_2O_3$ organic sol. A typical preparation describes as follows. 1.565 g and 2.125 g of sodium bis(2-ethylhexyl) sulfosuccinate (AOT) was dissolved, respectively, in 100 ml of toluene under vigorous stirring at room temperature, two transparent solutions were obtained. 10 ml

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of 0.1 mol·dm$^{-3}$ neodymium nitrate 10% water -2-propanol solution was added to above two solutions, the mixed solution was stirred rapidly for 0.5 h, while continuing to stir, 10 ml of 1.5 mol·dm$^{-3}$ ammonium hydroxide 2-propanol solution was slowly added dropwise to above two mixed systems, the solution gradually turned bright purple indicating the formation of colloidal particles. After addition, the reacted mixture was further stirred for 1 h and the colour of the solution gradually turned deep, then was left until the mixture was separated thoroughly into two layers, the upper layer was purple colour toluene sol containing nanoparticles, and the lower layer was aqueous phase with the relict such as $NH_4^+$and $NO_3^-$. The organic phase was refluxed for 1 h, then, the organic sol including $Nd_2O_3$ nanoparticles was obtained, named sample A and B. The resulting purple organic sol were stored at room temperature under an ambient atmosphere, and showed no sign of precipitation for over three months. The nanometre $Nd_2O_3$ powder was obtained by removing the solvent from the organic sol and heating at 600°C for 1 h. The product was kept in vacuum box for x-ray diffraction (XRD) characterization.

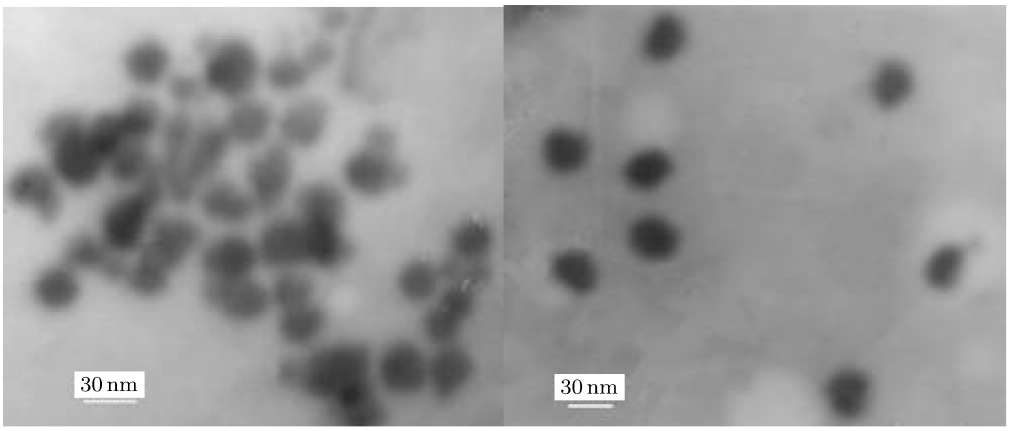
The size and morphology of the nanoparticles were investigated by transmission electron microscopy (TEM). The TEM experiments were performed at 150kV accelerating voltage using an H-800 TEM.

The XRD diagrams of sample 1 were recorded on a Rigaku RINT/Dmax-2000 diffractometer using Cu-K$\alpha$ radiation, the diffraction patterns were scanned over the range of 20° to 80° (2$\theta$).

Room temperature photoluminescence (PL) spectra were recorded on RF–5301 Spectrofluorophotometer as the excitation source at 300 nm. In order to thoroughly explore the luminescence affected by AOT and solvents, the spectra of $Nd_2O_3$ organic sol and AOT/solvent free of $Nd_2O_3$ was recorded at the comparative experimental condition.

## 3. Results and discussion

Samples were prepared by placing a drop of the colloidal suspension on holey carbon-coated copper grids, then, produced sample was kept in vacuum condition to get rid of the excess solvent under 60°C. Figure 1 shows the TEM image of the sample A and sample B. From Fig.1, it is found that the product nanoparticles take the shape of ellipse with the narrow distribution. The mean diameter for the sample A and sample B is 18 nm and 31 nm, respectively. This near monodispersity favours spontaneous organization of nanosized $Nd_2O_3$ particles.




(a) (b)

**Fig.1.** Transmission electron micrograph of $Nd_2O_3$ nanoparticles modified by AOT. (a) average diameter of 18 nm; (b) average diameter of 31 nm.

The XRD diagrams of $Nd_2O_3$ powder sample were recorded on a Rigaku RINT/Dmax-2000 diffractometer using Cu-K$\alpha$ radiation, the diffraction patterns were scanned over the range 20° to 80° (2$\theta$). Figure 2 shows a comparison of the XRD patterns from $Nd_2O_3$ standard specimens and the synthesized nanoparticles. The dried sample shows diffraction peaks that can be indexed as $Nd_2O_3$. It was suggested that the

sample consisted of the hexagonal $Nd_2O_3$ as indicated by diffraction peaks (111), (002), (101), (102), (110), (103), (112), (004), (202), (104), (203), (201), (211). The average size of $Nd_2O_3$ nanoparticles as estimated by the Scherrer's formula is about 42 nm, a little bit larger than the TEM results, which arise from the increase of temperature under the heating treatment. The broadening in diffraction peaks also shows that the product is composed of small $Nd_2O_3$ particles.

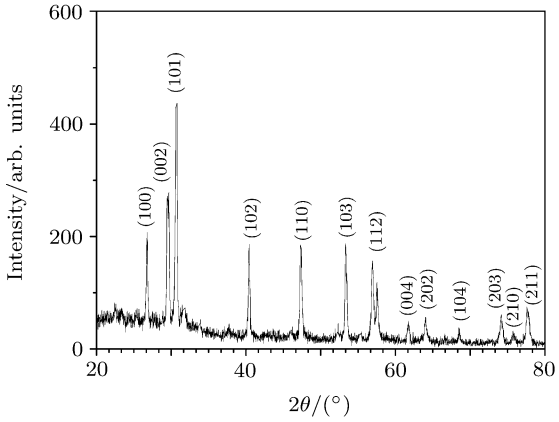



**Fig.2.** The two angle XRD data for the heat treatment at 600°C.

Room temperature photoemission spectra of samples A and B were shown in Fig.3.

In order to thoroughly explore the luminescence affected by AOT and solvents, the spectra of AOT/solvent free of $Nd_2O_3$ was recorded at the comparative experimental condition, as is shown in the insert of Fig.3. The curve in the insert shows clearly that the emission band appears at 302 nm for AOT/solvent. For the organic sol including $Nd_2O_3$ nanoparticles, we can find that for both of samples A and B, there exist two broad emission bands around 342 nm and 365 nm. No emission band was observed at 302 nm, it is said that the emission was quenched due to the existence of $Nd_2O_3$nanoparticles. From Fig.3, it is obvious that the PL intensity increases with the decrease of particle size of the $Nd_2O_3$ nanoparticles. The ultraviolet (UV) emission transitions at 344 nm and 365 nm arise from the transition of $^4D_{3/2} \rightarrow 4I_{9/2}$ and $2P_{3/2} \rightarrow {}^4I_{11/2}$ or $^4D_{3/2} \rightarrow {}^4I_{13/2}$, respectively. Our present experimental results are very similar to the report by G. Roshan Deen.[16,17] The results of $^4D_{3/2} \rightarrow 4I_{9/2}$ and $2P_{3/2} \rightarrow {}^4I_{11/2}$ match better with their results. There is only a little bit of blue shift for the transition peak position of $^4D_{3/2} \rightarrow {}^4I_{13/2}$. We suggest that it is due to the different particles size and surface modification environment between our and their samples.

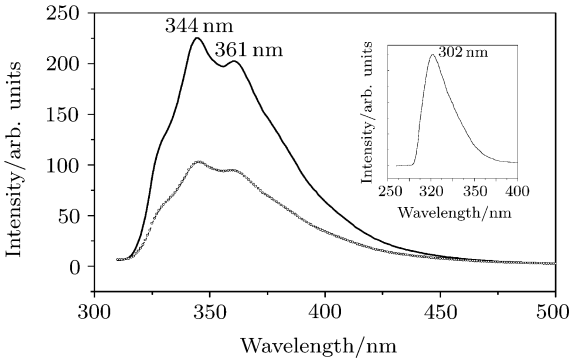



**Fig.3.** Photoemission spectra of $Nd_2O_3$, solid 18 nm and dot 31 nm. The insert is PL spectrum of AOT/solvent free $Nd_2O_3$ nanoparticles.

# 4. Conclusion

$Nd_2O_3$ nanoparticles had been prepared successfully by using microemulsion method in the AOT/toluene and propanol. By adjusting the ratio between the $Nd^{3+}$ and surfactant AOT, different particles sizes of $Nd_2O_3$ nanoparticle were obtained. XRD results show that the product is hexagonal phase. The product $Nd_2O_3$ nanoparticles organic sol shows very stable due to surface modification of AOT. The PL experiment reveals that there exist two UV emission bands (at 344 nm and 361 nm corresponding to the $^4D_{3/2} \rightarrow 4I_{9/2}$ and $2P_{3/2} \rightarrow {}^4I_{11/2}$ or $^4D_{3/2} \rightarrow {}^4I_{13/2}$ transition) and the PL intensity increases with the decrease of $Nd_2O_3$ particle size. This work is interesting not only for the possible technical application about the synthesis of other rare earth oxide nanoparticles, but also from a scientific point of view, it opens a way to manufacture novel rare earth composite materials of inorganic and organic.

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