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The preparation of ceria colloids dispersed by polyvinyl alcohol

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Abstract

Nanocrystalline CeO_2 colloids were synthesized from cerium nitrate under the catalysis of ammonia at near the room temperature. The polyvinyl alcohol (PVA) dispersant was used in mixed raw solutions to prevent the aggregation of CeO_2 colloids. By means of the measurements of transmission electron microscope (TEM) and Zeta potential, the ceria colloids were proved to be dispersed effectively via PVA. The average diameter of CeO_2 colloids was about 220 nm by dynamic light scattering (DLS) analysis. Otherwise, the effects of Zeta potential and ammonia catalyst were researched to verify the possible stabilization mechanism of the CeO_2 hydrosol. The main application of nanocrystalline CeO_2 colloids was considered as abrasive material in the field of chemical mechanical planarization (CMP).

Keywords: A. Sol–gel processes; D. CeO_2 colloids; PVA dispersant

1. Introduction

Ceria is a kind of typical rare-earth oxide with the crystal structure of face-centred cubic fluorite. Owing to the unique properties of electronic and crystal structure, CeO_2 has been intensively researched and applied in the fields of solid oxide fuel cells (SOFC) [1–4], industrial catalytic [5–7], gas sensor [8], UV absorber [9–12], and polishing abrasive [13–15] etc. However, as used in polishing abrasive, the commercial CeO_2 powder prepared by calcination, gas combustion or high energy ball milling method easily leads to the scratches and defects of polished surface due to irregular shape, severe agglomeration and uneven distribution of the particles. The disadvantage is the limited application of CeO_2 abrasive for chemical mechanical polishing (CMP) in the very large scale integration circuits.

In our previous work [16], we adopted polyvinylpyrrolidone (PVP) as dispersant and synthetized ceria hydrosol at 65 °C to solve above mentioned problems. The sizes of CeO_2 colloids are in the range of several nanometers to several of 10 nm. Especially, the ceria hydrosol is very stable and can be stored for several months, it means that the hydrosol is used as original solution of CMP possibly or precursors for any other fields. In this paper, ceria colloids were synthesized using polyvinyl alcohol (PVA) dispersant. The effects of reaction factors on grain size, dispersion and stability of CeO_2 colloids were studied. Otherwise, the stabilization mechanism of the hydrosol was also discussed by measurement of zeta potential and colloidal size.

2. Experimental

The synthesis process was described as follows: at first, PVA was dissolved into deionized water at 95 °C for several hours to form homogeneous solution, and then the transparent solution was divided into two parts when the temperature of the solution reduced to room temperature. Secondly, a certain amount of ammonia was dropped into one group of PVA solution, the solid raw materials of cerium nitrate $Ce(NO_3)_3 \cdot 6\,H_2O$ and urea $CO(NH_2)_2$ were added into another part. The raw solutions were stirred for few minutes to be homogeneous. Lastly, the two kinds of solutions were mixed according to preset temperature and time till the reaction process completed. The pale yellow CeO_2 sol was obtained finally without further treatment. Fig. 1 shows the flow chart of cerium dioxide hydrosol.

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X-Ray diffraction (XRD), transmission electronic microscope (TEM), Zeta potential (ZP) and dynamic light scattering (DLS) measurements were adopted to get the concerned information from the samples with different synthesis conditions.

3. Results and discussions

A series of experiments were carried out to research the effects of reaction factors on the particle size, crystal structure, size distribution and stability of CeO_2 colloids, such as content of raw materials, solution temperature, reaction time and pH value. The properties of CeO_2 hydrosol obtained at optimizing conditions were showed as follows.

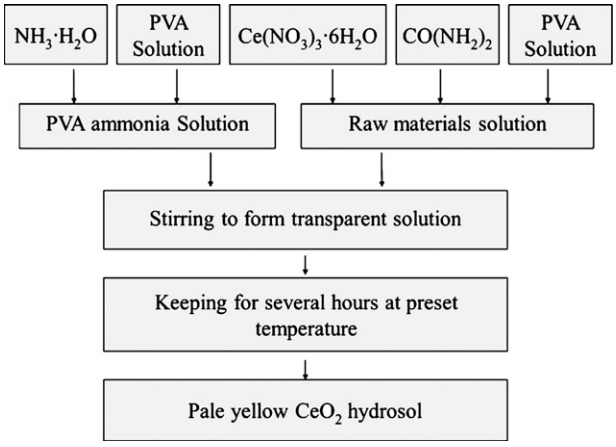

Fig. 1. Flow chart of cerium dioxide hydrosol.

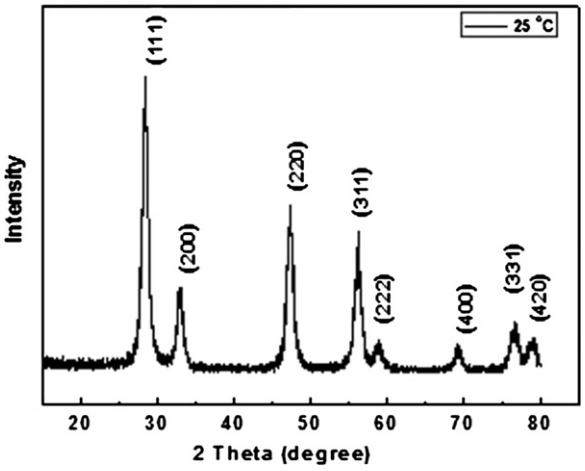

Fig. 2. X-ray diffraction pattern of the dried ceria colloids.

As we know, Ceria is a kind of typical calcium fluoride (CaF_2) structure with space group Fm3m. From Fig. 2, the XRD pattern of the dried ceria colloids showed a good matchwith literature data (JCPDS no. 34-0394). The main Bragg peaks with Miller indices (1 1 1), (2 0 0), (2 2 0), (3 1 1), (2 2 2), (4 0 0), (3 3 1) and (4 2 0) could be identified clearly, which is indicative of a face-centered cubic structure. It means that the pure crystallized ceria particles were synthesized by PVA at near room temperature.

As shown in Fig. 3(a), the TEM image of ceria sol showed a pearl necklace-like pattern and the primary particle size is about 10 nm. It is considered that the pearl necklace-like pattern resulted from PVA chains probably. In Fig. 3(b), the electron diffraction pattern proved the face-centred cubic structure of the CeO_2 colloids again.

DLS measurement showed that size distribution of colloid is 120 nm to 460 nm, the average particle size is 221 nm (see Fig. 4). The nanocrystalline CeO_2 colloids have relatively uniform size. The CeO_2 hydrosol is also very stable and can be stored for over three months without precipitate.

It is well known that the phenomenon of colloids coagulation is caused by micelle aggregation because of Brownian motion. In colloidal electrostatic stabilization mechanism, zeta potential value is a very significant parameter related to the stability of colloids. As shown in Fig. 5, the values of zeta potential changed from positive to negative with the pH value increase from 3 to 11. It was confirmed the existence of electrical double layer in the hydrosol, however, low zeta potential revealed that the thickness of the layer is too small to keep the balance of colloids.

In Fig. 6, it can be seen that the values of zeta potential and average colloid size changed with changed amount of ammonia. As a result, the zeta absolute value is below 0.8 mv and the range of particle size is from 150 to 400 nm basically. Ammonia concentration of 0.459 mol/L is the critical point. When the amount of ammonia is below the point, the average size is in the range of 150 to 200 nm. In contrast, the colloid size increased rapidly up to about 400 nm with increased ammonia concentration. If the amount of ammonia is increased continuously, the ceria particles grow to micron

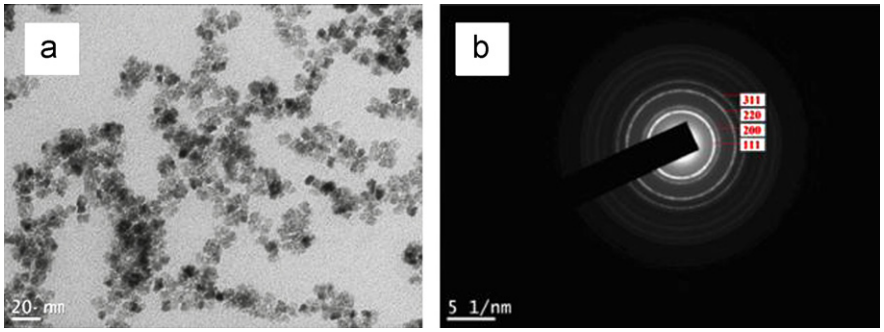

Fig. 3. TEM image (a) and electron diffraction pattern (b) of CeO_2 hydrosol.

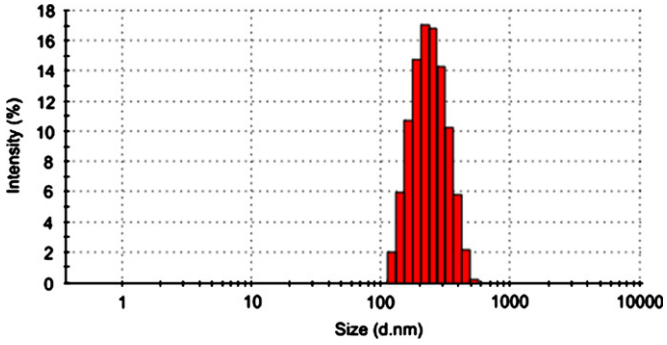

Fig. 4. The size distribution of CeO_2 colloids.

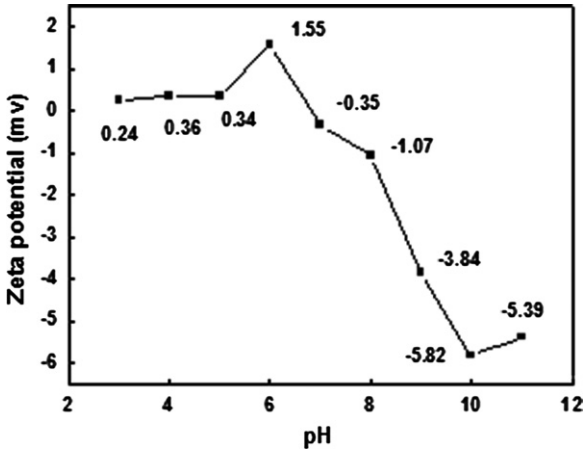

Fig. 5. pH dependency of zeta potential of CeO_2 colloids

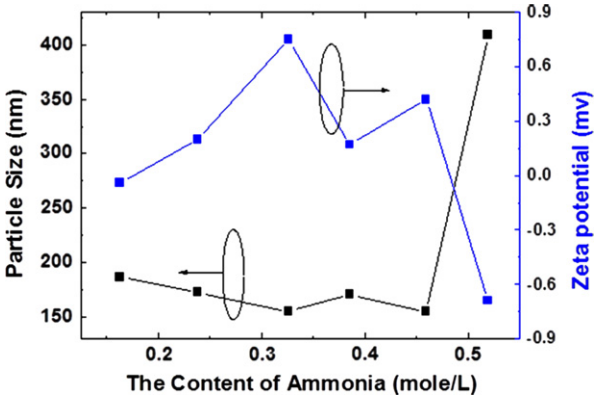

Fig. 6. The effects of ammonia content on particle size and zeta potential.

level directly. Smaller values of zeta potential and larger particle size are major factors leading to colloid precipitation. According to the experimental result, the ammonia concentration should be controlled under 0.459 mol/L in order to avoid larger particles. Generally speaking, stable colloids should possess a larger value (30 mv) of zeta potential. Here, we believed that the stability of CeO_2 colloids benefit by steric effect of PVA.

4. Conclusions

Stable nanocrystalline CeO_2 hydrosol was prepared at near room temperature by PVA and simple process, the size distribution is relatively narrow. The mechanism of dispersing and stabilizing the CeO_2 colloids was considered as stereohindrance effect of PVA. The possible application and preparation of CeO_2 hydrosol should be developed further.

Acknowledgments

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