Fabrication and Characterization of Sesame Ball-like CeO₂:Y³⁺/P (St-AA)

Composite Microspheres Based on Electrostatic Interaction

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Abstract

CeO₂-based hybrid materials represent a unique class of functional composites with various applications in catalysis, sensors, solid oxide fuel cells, solar cells, and mechanical polishing. In this work, based on electrostatic interaction between carboxylic groups and rare earth cations, a facile and feasible approach to fabricate sesame ball-like CeO₂:Y³⁺/P (St-AA) composite microspheres with excellent stability was established. Carboxylic functionalized monodisperse P(St-AA) microspheres were prepared by soap-free emulsion polymerization and then by compositing with positively charged CeO₂:Y³⁺ nanoparticles (NPs) at ambient temperature. The morphology of as-prepared samples was observed by SEM, TEM, HAADF-STEM characterization, and XRD, FT-IR, zeta-potential, EDS, DLS and conductometric titration were also used to investigate the structure and formation mechanism of the composite microspheres. With advantages of tunable functional groups and loaded ions on the surface of P(St-AA) microspheres and CeO₂:Y³⁺ NPs, respectively, this method could be further expanded to the preparation of various oxide/ polymer hybrid composite microspheres.

Keywords: CeO₂ nanoparticle; Polystyrene microsphere; Surface modification; Composite materials; Electrostatic Interaction

1. Introduction

CeO₂ (ceria) has attracted great attention due to its unique optical [1,2], electrical [3,4], magnetic [5] properties and oxygen storage capacity (OSC) [6,7], and it has been utilized in many practical applications including solid oxide fuel cells (SOFCs) [8-11], catalysts for conversion of automobile exhaust [12], and abrasives for chemical mechanical polishing (CMP) [13]. Much interest has recently been shown by chemical and material researchers in the preparation and morphology control of nano-sized CeO₂. CeO₂ nanoparticles (NPs) can be synthesized by many methods, including chemical precipitation [14,15], ultrasonic synthesis [16], hydrothermal treatment [17,18], thermal

hydrolysis [19] and the sol-gel method [20]. Recently, some novel approaches come forth, for instance, electrospinning is a conventional approach used to produce polymer nanofibers [21], now it has been extended to fabricate CeO_2 nanofibers by H.Over et.al [22]. Moreover, new applications of CeO_2 NPs are possible by compositing with a polymer [23,24]. Among the numerous polymers, polystyrene (PSt) latex spheres are attractive because of the easy preparation of uniform-sized PSt microspheres as well as the flexibility in control of chemical compositions and functional groups [25]. For instance, Caruso et.al developed a layer-by-layer (LbL) self-assembly method to fabricate organic/inorganic core-shell materials including TiO_2/PS [26], SiO_2/PS [27] and $\text{Fe}_3\text{O}_4/\text{PS}$ [28]. They utilized PSt as a template and deposited anion and cation surfactants alternately on the PSt surface. However, such layer-by-layer technology is a multistep process, involving many pre-treatment and post-treatment steps as well as the high cost of manufacturing on a large scale, so the complicated approach restricts its further applications.

Herein, we report a facile and feasible approach to prepare $\text{CeO}_2\cdot\text{Y}^{3+}/\text{P}$ (St-AA) composite microspheres just by tuning the surface potential of CeO_2 NPs and PSt microspheres. In this study, we first obtained Y^{3+} ions loaded CeO_2 NPs with uniform diameters by solvothermal treatment. Then carboxylic functionalized monodisperse PSt microspheres were synthesized in the presence of acrylic acid as a comonomer by soap-free polymerization. Eventually, based on electrostatic interaction between carboxylic groups and rare earth cations, sesame ball-like $\text{CeO}_2\cdot\text{Y}^{3+}/\text{P}$ (St-AA) composite microspheres were fabricated for the first time.

2. Experimental section

2.1. Materials

Cerium nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$, 99.9% purity), yttrium nitrate hexahydrate ($\text{Y}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$) and polyvinylpyrrolidone (PVP-K30) were used as original materials for synthesizing the precursor. Styrene (St, chemically pure), as the main monomer, was purified by treatment with aqueous NaOH (5 wt %), then distilled at reduced pressure to remove the inhibitor, and acrylic acid (AA) was used as a comonomer for soap-free emulsion polymerization, initiating by potassium persulfate (KPS). All of the above chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. Distilled water and anhydrous ethanol were used during sample preparation.

2.2. Preparation of CeO_2/PSt composite microspheres

The preparation procedures of PSt, P(St-AA) microspheres and CeO_2 , $\text{CeO}_2\cdot\text{Y}^{3+}$ NPs are described in Supplementary Information. First, 0.5 g as-synthesized PSt or P(St-AA) microspheres were dispersed in 5 mL ethanol under sonication, and then 0.1 g as-synthesized CeO_2 or $\text{CeO}_2\cdot\text{Y}^{3+}$ NPs were added into a flask with 20 mL ethanol/water (1:1) mixed solution. After dispersing under sonication for 30 min, 5 mL PSt or P(St-AA) solution was added dropwise to CeO_2 or $\text{CeO}_2\cdot\text{Y}^{3+}$ solution with a constant pressure dropping funnel for 30 min under vigorous stirring at room temperature. After keeping stirring for 1 h additional, the products were washed and dried for characterization.

2.3. Characterization

Morphology of the as-prepared samples were observed by using FE-SEM (Hitachi, S-4800, 15 kV), TEM (Philips, Tecnai 12, 120 kV), and HAADF-STEM (FEI, Tecnai G2 F30 S-TWIN, 300 kV). The structural information on the as-prepared samples was obtained by using XRD (Rigaku, MiniFlex II, Cu K α ($\lambda=1.5406$ Å)), FT-IR (Bruker, Tensor 27), EDS (USA, EDXA) and a Zeta-potential & Particle size Analyzer (Photal, ELSZ-1000ZSO). More information on diameter calculation and measurement of actual carboxylic concentration on the PSt surface is provided in Supplementary Information.

3. Results and discussion

3.1 Morphology Characterization of Composite Microspheres

The morphology of the composite microspheres was investigated by TEM and SEM. Fig. 1 (a) and (b) show SEM images of PSt and P(St-AA) microspheres, indicating the formation of a rough surface with acrylic acid as a comonomer. It is obvious that P(St-AA) microspheres have a larger diameter as well as better monodispersity by comparison with PSt microspheres in the absence of acrylic acid, which is further confirmed by comparison the statistical results of average diameter (d) and polydispersity index (PDI), as shown in Fig.S1a-b. From the viewpoint of the polymerization mechanism, lower reactivity ratio of acrylic acid means greater co-polymerization tendency with styrene [29,30]. In addition, the good water-solubility of acrylic acid results in uniform distribution of the carboxylic group on the oligomer surface, and then the oligomer with carboxyl group modification has better stabilization in the mixed ethanol/water solution. In other words, the addition of acrylic acid comonomer promotes synthesis of polymer microspheres with larger diameter and rougher surface due to the formation of a longer oligomer critical chain length as well as the density difference between the surface and bulk of the latex particles. Fig. 1 (c) and (d) show TEM images of CeO₂ NPs with and without Y³⁺ ions loaded. The images show that the morphology of CeO₂ NPs changed from polyhedra to spheres after the introduction of Y³⁺ ions. The formation of spherical CeO₂ is temporarily ascribed to the adsorption of positively charged Y³⁺ ions on CeO₂ nuclei, so the CeO₂ crystal nuclei can be stabilized and gained identical surrounding environment as well as enough time to grow as relatively bigger and more spherical CeO₂ NPs than that of in the absence of Y³⁺ ions. Besides, polyhedral CeO₂ NPs with predominantly exposed {111} facets are energetically favorable shapes in typical aqueous solution condition, which has been validated experimentally and theoretically according to previous literatures [31,32].

On the basis of the as-prepared P(St-AA) microspheres and CeO₂:Y³⁺ NPs, we fabricated sesame ball-like CeO₂:Y³⁺/P (St-AA) composite microspheres (as shown in Fig. 1 (e)-(f)). The composite microspheres exhibit a sesame ball pattern with CeO₂:Y³⁺ NPs dispersed uniformly on the surface of P(St-AA) microspheres, sesame ball is a popular Chinese traditional food called “matuan”. Fig. S1 (E) and (F) show control experimental results for CeO₂:Y³⁺/PSt and CeO₂/P (St-AA) composite microspheres. The smooth surface of PSt microspheres exhibits weak interaction with CeO₂:Y³⁺ NPs as well as CeO₂ NPs without Y³⁺ doped are prone to agglomerate, which results in undesirable composite results. As a consequence, we can conclude that AA and Y³⁺ ions distributed on the surface of PSt and CeO₂ play a decisive role in constructing the sesame ball-like composite microspheres. More morphological information on composite microspheres is shown in Fig. S1.

3.2 Structure Analysis of Composite Microspheres

Fig. 2 (a) shows XRD patterns of as-prepared samples. The red broadened peak at 19.5° is a characteristic peak of amorphous P(St-AA) microspheres [33, 34]. The diffraction intensity of this peak was weakened dramatically after compositing, so we can deduced that the surface of P(St-AA) microspheres was well covered by $\text{CeO}_2\text{:Y}^{3+}$ NPs, it is also in good accordance with TEM and SEM results. From the XRD patterns shown in Fig. S2, the sharp diffraction peaks are assigned to faced-centred cubic (fcc) fluorite CeO_2 (JCPDS, 34-0394), and no impurity peaks appeared, indicating that the CeO_2 NPs are of high purity and that loaded Y^{3+} ions have no effect on the crystalline phase of CeO_2 .

FT-IR spectra were also measured to identify structure components of the as-prepared samples. Fig. S3 shows that the absorption bands are almost the same except for the doublet peaks at 1700 and 1740 cm^{-1} in the P(St-AA) sample, confirming the existence of carboxylate on the microsphere surface. The peaks at $2850\text{--}3080$, 1600 , 1500 , 760 , 700 and 540 cm^{-1} are characteristic peaks of polystyrene [35, 36]. In Fig. 2 (b), the FT-IR spectrum of $\text{CeO}_2\text{:Y}^{3+}/\text{P}(\text{St-AA})$ composite microspheres shows the characteristic peaks of ceria ($\nu_{\text{Ce-O}}$ at 480 cm^{-1}) and polystyrene. Together with the results of TEM and XRD analyses, it can be concluded that $\text{CeO}_2\text{:Y}^{3+}/\text{P}(\text{St-AA})$ composite microspheres were successfully fabricated.

3.3 Fabrication Mechanism of Composite Microspheres

In order to achieve a uniform composite material, surface modification was performed for both CeO_2 NPs and PSt microspheres prior to fabrication. Through systematical experiments, we found that the surface potentials play a vital role in the composite effect and that the system stability is directly proportional to the absolute surface potential value of the particles. Consequently, in this study, we focused on improving the surface properties of CeO_2 NPs and PSt microspheres. The zeta potentials and mean diameters (obtained by DLS and TEM) of the samples are summarized in Table 1. First, we prepared positively charged $\text{CeO}_2\text{:Y}^{3+}$ NPs in order to improve the dispersity of the nanoparticles. Fig. 1 (e) and Table 1 indicate severe agglomeration of CeO_2 NPs without Y^{3+} loading. Fig. 3 shows HAADF-STEM and EDS mapping images of $\text{CeO}_2\text{:Y}^{3+}$ NPs, indicating that Y^{3+} ions were dispersed evenly on the CeO_2 surface, and the actual Y^{3+} ions loaded content was $1.77\text{ wt}\%$ (shown in Fig. S4). Next, negatively charged monodisperse P(St-AA) microspheres were synthesized by acrylic acid co-polymerization. P(St-AA) microspheres had numerous carboxylic groups, distributing uniformly on its surface. In comparison with PSt microspheres without AA copolymerization, the zeta potentials of P(St-AA) microspheres changed from -12.80 to -66.23 mV , indicating the stability was thus improved greatly. On the other hand, the rough surface provided many more physicochemical combinative “activated” sites than did PSt microspheres, therefore, $\text{CeO}_2\text{:Y}^{3+}$ NPs are more easily anchored on the surface of P(St-AA) microspheres under carboxylic groups guidance. In this study, conductometric titration method was also used to quantify the carboxylic group concentration on the surface of P(St-AA) microspheres. The concentration of surface carboxylic groups was 1.238 mmol/g (as shown in Fig. S5). About 74% of the carboxylic groups were distributed on the surface of P(St-AA) microspheres, thus guaranteeing the desirable composite effect with $\text{CeO}_2\text{:Y}^{3+}$ NPs. Therefore, based on electrostatic interaction, negatively charged P(St-AA) microspheres and positively charged $\text{CeO}_2\text{:Y}^{3+}$ NPs were efficiently recombined to obtain sesame ball-like $\text{CeO}_2\text{:Y}^{3+}/\text{P}(\text{St-AA})$ composite microspheres.

4. Conclusions

In conclusion, carboxylic functionalized monodisperse P(St-AA) microspheres were prepared by soap-free emulsion polymerization, and then by compositing with positively charged $\text{CeO}_2\text{:Y}^{3+}$ NPs at ambient temperature, sesame ball-like $\text{CeO}_2\text{:Y}^{3+}/\text{P}(\text{St-AA})$ hybrid composite microspheres with excellent dispersity were successfully fabricated based on electrostatic interaction. The approach was shown to be feasible and effective, and it can also be further expanded to the preparation of many other oxide/ polymer hybrid composite microspheres. The as-prepared sesame ball-like $\text{CeO}_2\text{:Y}^{3+}/\text{P}(\text{St-AA})$ hybrid composite microspheres are promising materials for practical applications in abrasive materials, UV shielding plastics and electrorheological fluids as well as for chemical-mechanical planarization of advanced integrated circuits.

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Figure captions

Fig. 1: SEM and TEM images of as-prepared samples (a) PSt, (b) P(St-AA), (c) CeO₂, (d) CeO₂:Y³⁺, and (e)-(f) CeO₂:Y³⁺/P(St-AA).

Fig. 2: XRD patterns (a) and FT-IR spectra (b) of as-prepared samples

Table 1: Summary of zeta potentials and mean diameters (Remark: 1---data obtained from DLS value; 2---data calculated from TEM or SEM image).

Fig. 3: HAADF-STEM and EDS mapping images of CeO₂:Y³⁺ NPs

Fig. S1: Low magnification SEM and TEM images and diameter distribution histograms of (A)-(a) PSt, (B)-(b) P(St-AA), (C)-(c) CeO₂, (D)-(d) CeO₂:Y³⁺, (E) CeO₂:Y³⁺/PSt, and (F) CeO₂:Y³⁺/P(St-AA).

Fig. S2: XRD patterns of CeO₂ and CeO₂:Y³⁺ NPs.

Fig. S3: FT-IR spectra of PSt and P(St-AA) microspheres.

Fig. S4: EDX spectra of CeO₂:Y³⁺ NPs.

Fig. S5: Conductometric titration curve of P(St-AA) microspheres.

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Sample	Zeta potential ¹ ξ / mV	Mean diameter ¹ D / nm	Mean diameter ² d / nm	Polydispersity index ² PDI / %
PSt	-12.80	1005	833 ± 27	3.2
P(St-AA)	-66.23	970	914 ± 24	2.6
CeO ₂	+5.55	198	55 ± 4	7.2
CeO ₂ :Y ³⁺	+20.50	103	78 ± 3	3.8

Graphical abstract