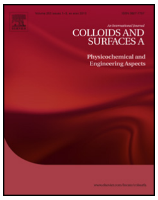
Colloids and Surfaces A: Physicochem. Eng. Aspects 441 (2014) 638–642

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa



Ceria nanoparticle vesicles formed in sodium oleate aqueous solution with mesoporous silica coating

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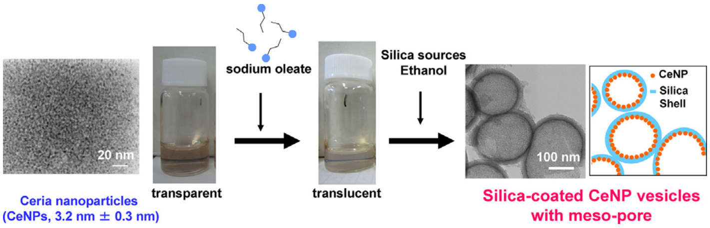
HIGHLIGHTS

- An environment-friendly method preparing nanoparticle vesicle was presented.
- The vesicle consists of hollow assembly of ceria nanoparticle with outer silica shell.
- A self-assembly structure formed in the suspensions of ceria nanoparticle and sodium oleate.
- The novel method can be applied to the preparations of various kinds of nanoparticle vesicles.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 1 April 2013
Received in revised form 8 September 2013
Accepted 2 October 2013
Available online 17 October 2013

Keywords:
Nanoparticle vesicle
Sodium oleate
Ceria nanoparticle
Silica coating

ABSTRACT

Fabrications of nanoparticle-assembled hollow structures have intensively been studied because of their unique properties applicable to catalysts, plasmonic materials and drug delivery systems. The present work proposes a novel method for the synthesis of nanoparticle vesicles in the presence of sodium oleate (NaOA). Our method is composed of two processes, one of which is self-assembly formation in the suspension of ceria nanoparticles (CeNPs) and NaOA, and the other is the fixation of the self-assembled structures with silica coating. The method is a facile one-pot synthesis conducted in weak basic conditions with and without ammonia. *N*-trimethoxysilyl-propyl-*N*,*N*,*N*-trimethylammonium chloride (TMAPS) and tetramethoxysilane were successively added for the silica coating. The structure of the product was submicron-meter sized hollow assembly of the ceria nanoparticles with outer silica shell, silica-coated CeNP vesicle. The calcined sample had meso-pore structures in the silica shells. The present method may open the door for application to various kinds of metal oxides and inorganic nanoparticles for obtaining nanoparticle vesicles.

1. Introduction

Nanoparticle (NP)-assembled spheres with hollow structures have attracted increasing attention because of their novel properties different from NP itself in potential applications to drug delivery systems [1,2], catalysts [3,4], and plasmonic materials [5,6]. Various template routes have been explored for fabrication of the hollow NP assemblies, which use liquid-liquid interfaces in emulsions [1,7–9] and multilayer of polyelectrolytes accumulated on particle surface [10,11]. Although these template methods can precisely control physical properties of hollow NP assemblies such as permeability and mechanical strength, preparation in the methods requires multiple and tardy processes. Spontaneous formations of hollow NP assemblies, (called NP vesicles), have been reported as facile methods. One route is surface modification of NPs with ligands or polymer chains [5,6,12,13]. The surface-modified NPs assemble to a vesicular structure in appropriate liquid media via association between the modifiers on the NP surface. Other inducers for the spontaneous formation are surfactant, lipid, and block copolymers. After hydrophobic NPs are mixed with the additives in organic solvent, vesicles composed of the NPs and additives were

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http://dx.doi.org/10.1016/j.colsurfa.2013.10.018

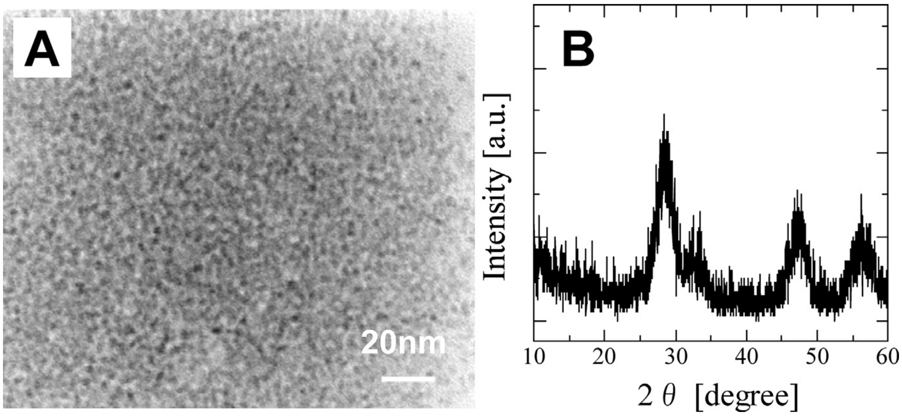

Fig. 1. (A) TEM image of ceria nanoparticles prepared in the presence of trisodium citrate and ammonia. (B) XRD pattern of the ceria nanoparticles.

obtained with hydration of dried film of the mixture [14] or addition of other solvent to the mixture [15,16]. Their methods, however, have drawbacks that are low yield of vesicle formation and use of hazardous solvent. Stucky and co-workers have recently fabricated hollow NP assemblies in aqueous solution of polyelectrolytes [17–19]. The vesicles composed of water-dispersible NPs and polyelectrolytes are generated by interactions such as coordination effect, electrostatic force, and hydrogen bond. The spontaneous formation of NP vesicles in aqueous media is an environment-friendly method without hazardous solvent.

NP vesicles can be applied as currently developed tools to the preparation of hollow NP assemblies which show high catalytic activity [3,4] and thermal stability [4,20]. However, NP vesicles are easily destabilized when dispersed in different media, which requires stabilization techniques. Mesoporous silica coating is an approach for suppressing NP aggregation and keeping substrate access to the active site on NP surface [21]. In addition, stabilization of NPs with surfactants has recently been reported for the silica coatings [22,23]. This study presents a novel synthesis of NP vesicles in the presence of an anionic surfactant, sodium oleate (NaOA). Self-assembled structure is obtained by the NaOA addition to CeNP aqueous suspensions. Silica coating of the assembly is then performed to fix the structure. The silica products obtained are observed with scanning transmission electron microscope (STEM) and characterized with X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDX) analysis, and N_2 adsorption/desorption isotherms.

2. Materials and methods

2.1. Materials

$(NH_4)_2Ce(NO_3)_6$ (95%), sodium oleate (NaOA, 95%), trisodium citrate (95%), and ethanol (99.5%) were purchased from Wako Pure Chemical Industries (Osaka, Japan). Silica sources, tetramethoxysilane (TMOS, 99%) and *N*-trimethoxysilyl-propyl-*N*,*N*,*N*-trimethylammonium chloride (TMAPS, 50% in methanol) were purchased from Shin-Etsu Chemical Co., Ltd. (Tokyo, Japan). The other chemicals of analytical grade were purchased from the Wako Pure Chemical Industries.

2.2. Preparation of ceria nanoparticles (CeNPs)

Well-dispersed CeNPs were synthesized with citrate as a protecting agent [24]. Briefly, ammonia solution (25 wt%, 10 ml) was added to an orange aqueous suspension (56.9 ml) of $(NH_4)_2Ce(NO_3)_6$ and trisodium citrate. The concentrations of the ceria source, trisodium citrate, and ammonia were 0.1 M, 0.1 M, and 2.0 M, respectively. After the ammonia addition, the color of the mixture changed to dark brown, which indicated the precipitation of CeNPs. The dark brown suspension was stirred at 25 °C for 30 min and then aged at 80 °C for 5 h. To collect CeNPs, an excess of ethanol (80 vol%) was added to the suspension and CeNPs were separated by centrifugation in a relative centrifugal field of 22,540 *g* for 15 min. CeNPs were washed again with ethanol–water mixture (80/20, v/v) and re-dispersed in water.

2.3. Preparation of CeNP vesicles with silica coating

The preparation was performed typically in the following procedure. The aqueous suspension of CeNPs was mixed with NaOA solution. The concentrations of Ce and NaOA were both 13.3 mM and ammonia solution was added to the mixture for pH adjustment. After the mixture (22.5 ml) was stirred for 30 min, TMAPS solution (0.17 ml) was added to the suspension which was stirred for 30 min. For the silica coating, TMOS/ethanol solution (7.33 ml) was added to the suspension which was stirred for another 30 min. Suspension temperature was maintained at 35 °C throughout the procedure. The final concentrations of TMOS, TMAPS, Ce and NaOA were 100, 10, 10 and 10 mM, respectively, in water-ethanol solutions (75/25, v/v) with and without ammonia (10 mM). The suspension was heated to 80 °C that was kept for more than 5 h under stirring. The products finally obtained were washed with water and dried under vacuum at 60 °C, followed by calcination at 550 °C for 4 h to remove the anionic surfactant and other organic compounds.

2.4. Characterization

Dispersion sizes of suspensions were measured with dynamic light scattering (DLS, ELS-8000, Otsuka Electronics, Japan). Each size distribution of the suspensions was calculated from the result with non-negative least squares (NNLS) method. Images of the products were taken with scanning transmittance electron microscope (STEM, Hitachi, HD-2700B) at an accelerating voltage of 200 kV. Energy dispersive X-ray spectroscopy (EDX) analyses were performed for elementary analysis of products after silica coating on a 200 mesh copper grid with the STEM equipped with an EMAX Energy (Horiba). X-ray diffraction (XRD) analyses was performed with RIGAKU Ultima IV diffractometer (Rigaku Japan). N_2 adsorption–desorption isotherms were measured at −196 °C with BELSORP-mini II (Bel Japan Inc., Japan). Surface area and pore size distributions were calculated from the isotherms with