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Spontaneous Self-Assembly of Cerium Oxide Nanoparticles to Nanorods through Supraaggregate Formation

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Self-assembly of cerium oxide nanoparticles to nanorods is reported. Such nanorods have an aspect ratio of 6 with a diameter of approximately 40 nm. The formation of cylindrical supraaggregates and their subsequent growth by preferential assembling of ceria nanocrystallites along the longitudinal direction was proposed to be the probable mechanism of spontaneous self-assembly of nanorods. The supraaggregate formation was facilitated by influencing the local curvature of the micelle surface in the presence of nitrate ions as a precursor solution. The nanorods were characterized using high-resolution transmission electron microscopy with energy dispersive spectroscopy and selected area electron diffraction for their morphology, chemistry, and crystal structure.

Introduction

A great deal of research efforts have been directed toward controlling the shape and size of the nanoparticles for potential optical, electronics, catalysis, gas-sensing, and gas-storage applications. Numerous theoretical and experimental studies on the synthesis of rod-shaped nanoparticles have been attempted by previous researchers.[1−14] Bruggen and co-workers[1] studied the isotropic−nematic phase transition in dispersions of sterically stabilized rodlike boehmite colloids in toluene. Such individual nematic droplets grow and sediment, forming the nematic phase after 1 week of aging time at ambient condition. Lindgren et al.[2] synthesized a nanostructured rodlike morphology of hematite (α-Fe_2O_3) with the objective of the direct splitting of water at the hematite/electrolyte interface. The synthesis, structure, and properties of nanowires of various inorganic materials, which include elements, oxides, nitrides, carbides, and chalcogenides, have recently been reviewed.[3] It was observed[4] that aqueous suspensions of goethite (α-FeOOH) nanorods form a mineral lyotropic nematic phase that changes the orientations from parallel to the perpendicular from a very low magnetic field to a field beyond 350 mT. Filankembo et al.[5] have reported that the presence of chloride ions enhanced the chances of the formation of copper nanorods over nanoparticles in the bis(2-ethylhexyl sulfosuccinate)/isooctane/water microemulsion system. Sterligov and co-workers[6] had studied the optical properties of tin nanorods. The growth of metallic gold nanorods with the help of a seed-mediated approach using a surfactant template was studied by others.[7] Milliron et al.[8] demonstrated the fabrication of heterostructures consisting of inorganically coupled and epitaxially grown branched nanorods. Lisiecki et al.[9,10] prepared copper nanorods by reducing copper(II) bis(2-ethylhexyl sulfosuccinate) compounds using hydrazine in an isooctane medium. Results of high-resolution transmission electron microscopy (HRTEM) investigations suggested that such Cu nanorods have a truncated decahedra lattice structure with a 5-fold symmetry. Pinna and co-workers[11,12] synthesized divanadium pentoxide nanorods by a reverse micelle system of bis(2-ethylhexyl sulfosuccinate)/isooctane/water. Zhou et al[13] attempted to synthesize nanorods and nanoparticles of cerium oxide using a hydrothermal method to prepare a more efficient catalysis. Wu and co-workers[14] have attempted to utilize a sol−gel process inside a porous anodic alumina template to prepare ceria nanorods.

All of the above experimental studies involved the formation of nanorods by the process of nucleation and growth. Synthesis of ceria nanorods by self-assembly of nanoparticles using the microemulsion technique has not been reported. In view of various potential technological applications of cerium oxide nanostructures[15,16] and in continuation to the development of tubular[17] and rod-shaped[18] nanostructured materials, the present research was focused on the formation of nanorods by self-assembling the crystalline cerium oxide nanoparticles into nanorods using the microemulsion synthesis technique. These nanorods and the nanoparticles have been characterized using HRTEM with selected area electron diffraction (SAED) and scanning transmission electron microscopy (STEM) with energy dispersion spectroscopic studies.

Experimental Section

Materials. Toluene of HPLC grade (99.8% pure) with water content less than 0.03%, sodium bis(2-ethylhexyl) sulfosuccinate (AOT) with 98% purity, cerium(III) nitrate hexahydrate with 99% purity, and 30 wt % hydrogen peroxide solution in water were obtained from Sigma-Aldrich and used as-received for the synthesis of cerium oxide nanorods.

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Synthesis. The ceria nanorods were synthesized utilizing a double microemulsion procedure. The molar ratio of the aqueous phase to the surfactant was kept at 25. The composition of AOT, toluene, and water in weight percent was 1.78, 96.44, and 1.78, respectively. Such composition results in a water-in-oil microemulsion and forms a reverse micelle that contains the aqueous phase in the core. The aqueous core of such a reverse micelle consists of spherical space with a diameter less than 10 nm that acts as a nanoreactor. Since particle growth is restricted within such a spherical space, it maintains the size of the nanoparticles. AOT-in-toluene solution was prepared by dissolving AOT in toluene with the help of magnetic stirring for 15 min. Microemulsion I was prepared by adding 1.6 mL of 0.6 M cerium nitrate solution to 100 mL of an AOT-in-toluene solution, followed by magnetic stirring for 45 min. Microemulsion II was prepared by adding 1.6 mL of hydrogen peroxide under constant stirring to an AOT-in-toluene solution and stirring further for 45 min. Subsequently, microemulsion II was added to microemulsion I and stirred for an hour. The microemulsion was kept for a few weeks for aging during which time the self-assembly of ceria nanoparticles into nanorods took place.

Characterization. A transmission electron microscopy (TEM) specimen was prepared from the aged sol to study the shape and crystal structure of the resulting materials. HRTEM and STEM coupled with energy dispersion spectroscopy (EDS) studies were carried out, using a Philips 300 TECNAI at 300 kV, to investigate the elemental composition, size, and structure of the ceria nanorods. The SAED pattern of ceria nanorods was also collected from the TEM studies.

Results and Discussion

Figure 1, parts a and b, show TEM images of the cerium oxide nanorods at low and at high magnifications, respectively, which were obtained in the present microemulsion-mediated synthesis process after 6 weeks of aging. The diameter and length of the nanorods were found to be approximately 40 and 250 nm, respectively. Although some of these nanorods were found to be aligned parallel to their longitudinal axis, the orientation of most of them was random on the TEM grid. Perhaps for complete ordering, a larger aspect ratio than that of the present value of 6 is needed. Figure 2, part a, shows a HRTEM image near the tip of one cerium oxide nanorod (shown in the inset), which reveals that such a rod is not made of single crystals but rather nanocrystallites of approximately 3 nm in size, as demonstrated by the presence of the lattice fringes of such randomly oriented crystallites. A cluster of five such ceria nanoparticles are indicated by dotted circles in Figure 2, part a. It should be mentioned that the formation of cerium oxide nanocrystallites of a similar dimension using the microemulsion process was also reported for various applications from this laboratory.[15,16] However, the formation of nanorods can only be achieved in the microemulsion process with the present set of process parameters that were developed in this laboratory. Changing the shape of the micelles using various compositions of the surfactant, oil, and water phases is well-known.[19] To confirm the composition and lattice structure of the nanorods, EDS and SAED studies were carried out with the transmission electron microscope. The selected area electron diffraction pattern taken of the ceria particles is presented in Figure 2, part b, which shows the presence of three distinct diffraction rings corresponding to (111), (220), and (311) lattice planes. Figure 3, part a, shows a STEM image featuring two nanorods with a superimposed rectangular area marker over which EDS was carried out. The corresponding EDS spectrum is depicted in Figure 3, part b, which revealed the presence of elemental Ce and oxygen signals along with a copper signal from the TEM grid used.

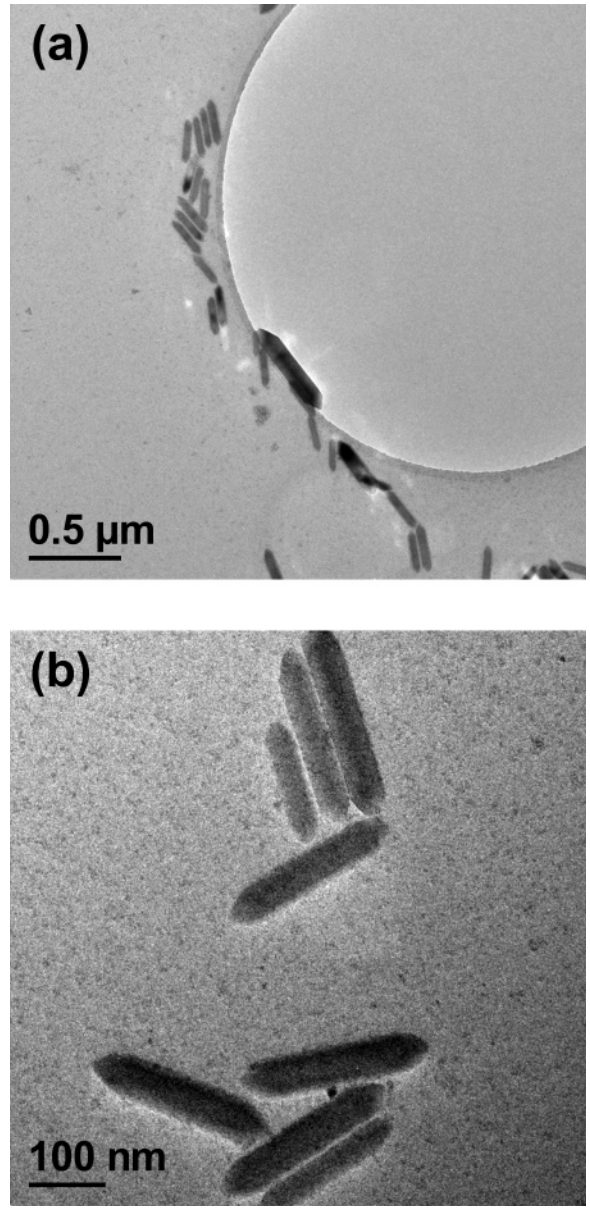

Figure 1. TEM images of nanorods of cerium oxide at (a) low and (b) high magnifications.

A ceria nanoparticle was formed in the inner core of each reverse micelle that consists of a spherical space with a diameter of a few nanometers that acted as a nanoreactor. Initially, the presence of coordinated surfactant molecules around the spherical nanoreactor restricted the aggregation of the nanoparticles, thereby helping to maintain the size in the nanometer range. In the present case, micelles in microemulsion I contain the precursor solution bearing Ce ions. After addition of microemulsion II, which contains the hydrogen peroxide solution to microemulsion I, the mutual interaction among two such types of micelles took place by random collisions as described earlier.[20] During such interactions, transfer of reactants took place, and subsequently the nanoparticles form by the process of nucleation and growth inside the cores of the micelles. The ceria nanoparticle forms as per the following scheme of reactions

$$Ce^{3+} + OH^- + \frac{1}{2}H_2O_2 \rightarrow Ce(OH)_2{}^{2+} \qquad (1)$$

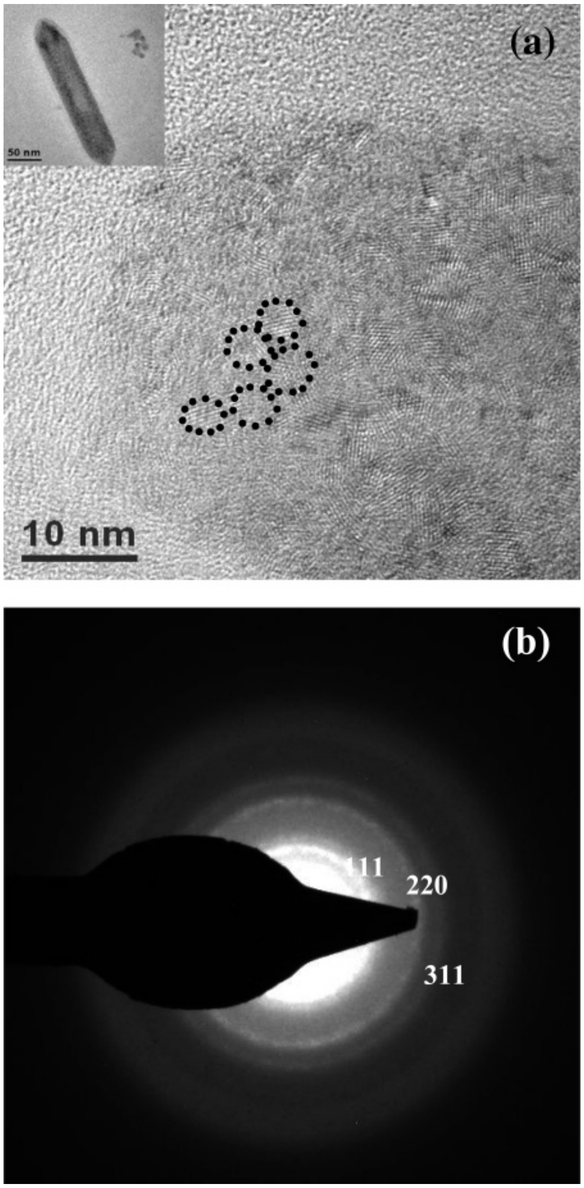

Figure 2. (a) HRTEM image of the tip of a nanorod of cerium oxide (inset) revealing the presence of ceria nanocrystallites and (b) the SAED pattern of nanorods of cerium oxide.

$$Ce(OH)_2^{2+} + 2OH^- \rightarrow CeO_2 + 2H_2O \qquad (2)$$

Hydroxyl ions are formed locally inside each micelle core as an intermittent product of the dissociation of hydrogen peroxide[21] during the interaction. A similar reaction mechanism for the formation of a cerium oxide film on copper during electrodeposition was also suggested by others.[22] It is interesting to note that the nanorods formed during such a microemulsion synthesis are made of a number of ceria nanocrystals, as demonstrated by the presence of diffraction rings, which are presented in Figure 2, part b. The lattice fringes of such ceria nanoparticles are also visible in the HRTEM image in Figure 2, part a.

The self-assembly process was observed during aging of the sol, a few days after the formation of such cerium oxide nanoparticles, leading to the gradual evolution of ceria nanorods. The aspect ratio of the nanorods was observed to be approximately 6. The formation of the rod type of structure in the microemulsion system under the influence of various cations and anions, which affects the rigidity of the interface between the hydrophilic polar headgroups and the aqueous core of the micelle, is reported.[1,4,5,7] In the present investigation, however, no such ions were used to form the nanorod morphology. The nanorods of AlOOH,[1] α-FeOOH,[4] and gold[7] synthesized by previous researchers were not characterized using HRTEM, and hence it is not clear whether such rods were single crystals or consisted of directionally aggregated nanocrystals. However, HRTEM results, as shown in Figure 2, part a and b, confirmed that the ceria nanorods synthesized in the present study were made of a large numbers of nanocrystallites of approximately 3 nm in size. It should be mentioned that Lisiecki et al.[9,10] have observed the presence of a 5-fold symmetry in the lattice of Cu nanorod single crystals, after extensive HRTEM studies. According to them, the preferential growth leading to the formation of Cu nanorod single crystals was attributed to the presence of the surfactant molecules in excess.

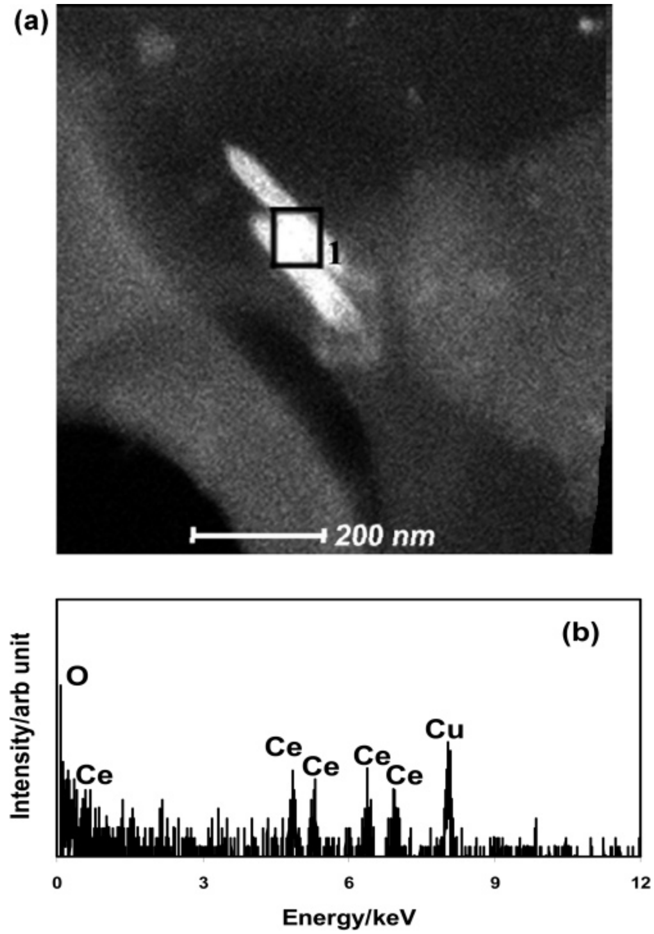

Figure 3. (a) STEM image of two nanorods of cerium oxide. The rectangle indicates the area on which EDS was carried out. (b) Corresponding EDS spectrum.

In the present investigation, the nanocrystals of cerium oxide were initially formed in the microemulsion-mediated synthesis process, followed by self-assembling of such particles into nanorods during the aging process. The self-assembling resembles a controlled agglomeration process with the help of random collisions among the micelles that contain the nanocrystals. The formation of such "supraaggregates" was observed by others[5] during synthesis of Cu nanoparticles in the AOT/isooctane microemulsion system. In the present case, the alkyl chains of the surfactant were highly solvated and probably adjusted by rotation to form the cylindrical shape. The presence of NO_3^- ions in the present situation from the precursor solution may also have influenced the interfacial properties of the

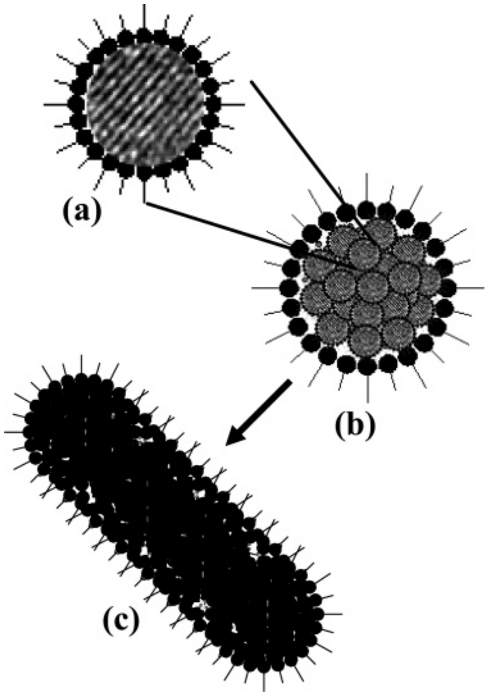

Figure 4. Schematic picture showing the self-assembly of (a) ceria nanoparticles to form (b) a supraaggregate and finally to form (c) nanorods.

micelles in such a way that the distance of separation between the two anionic polar heads of the AOT was increased. Such an increase in the distance of separation facilitated the formation of the cylindrical shape by decreasing the local curvature of the micelle surface as suggested by others.[23] The probable mechanism by which the ceria nanorods were self-assembled is shown in Figure 4 with a schematic diagram. A ceria nanoparticle inside the micelle, a supraaggregate, and the nanorod formed from the supraaggregate are shown in Figure 4, parts a−c, respectively. The cone-shaped portions at both the ends of the nanorods were possibly formed to accommodate the abrupt change in surface free energy that would otherwise exists due to the presence of a sharp curvature. The growth of the nanorods took place by self-assembling of ceria nanoparticles at both the ends.

Conclusions

Cerium oxide nanocrystallites synthesized using a microemulsion process self-assemble into nanorods during aging. The aspect ratio of such nanorods is 6 with a diameter of approximately 40 nm. The self-assembly of cerium oxide nanocrystallites to form nanorods consisted of the formation of cylindrical supraaggregates and their subsequent growth by preferential assembling of nanocrystallites along the longitudinal direction. The process of the formation of supraaggregates was facilitated by influencing the local curvature of the micelle surface with the help of nitrate ions that were present in the microemulsion system.

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