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Facile Deposition of Nanodimensional Ceria Particles and Their Assembly into Conformal Films at Liquid−Liquid Interface with a Phase Transfer Catalyst

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The regions surrounding the interface of two immiscible liquids possess properties distinct from the bulk phases, due to the dominance of viscosity and surface tension effects as well as formation of interfacial emulsions.[1] This interface has been used to prepare a number of materials,[2−5] such as pyramidal PbS nanocrystals with (331) facets,[2a] CdSe nanocrystal assemblies,[3] ultrathin single-crystalline sheets of CuS,[4] and ordered arrays of Cu_2S nanocrystals.[5] Attractive features of this method include simplicity, low cost, and scalability. Integrated synthesis and assembly at the liquid−liquid interface could lead to the easier construction of functional architectures.

Deposition by this method involves a metal precursor dissolved in a solvent such as toluene in contact with an aqueous layer containing a reducing, oxidizing, or precipitating reagent. The reaction proceeds at the interface of the two liquids, and the deposits are mainly suspended in the interfacial region. The interface has a dual role in controlling charge transport and directing the structure of the deposit. A key challenge in this area is to control the delivery of ions to the interface. Relatively, little is known about the suitability of compounds for this purpose. The need for specific metal precursors can be perceived as one limiting factor hindering the widespread application of this technique. Herein, we present a particularly straightforward route for interfacial synthesis and assembly of crystalline nanoceria by the use of phase-transfer reagents.

Cerium oxide is an interesting material due to its catalytic properties, which are attributed to the high mobility of oxygen vacancies at the surface.[6] Nanodimensional ceria can have enhanced catalytic ability and redox properties due to reduced dimensions and an increased relative surface area.[7,8] It has previously been difficult to obtain crystalline nanoceria, and postsynthetic calcination has often been necessary to enhance crystallinity, making its use in functional architecture difficult.[9] In this work, particulate assemblies of nanoceria are obtained in crystalline form in a single step.

In a typical preparation, ceric ions (as a solution of the chloride) are transferred to toluene using tri-*n*-octylmine as a phase transfer catalyst, and the resulting solution is layered with aqueous NaOH (pH 12.7) in a beaker. The reaction vessel is introduced into an oven at 70 °C for periods between 3 and 18 h. At the end of the reaction, an elastic pale yellow film suspended at the interface aqueous−organic interface was obtained.

The films lifted from the water−toluene interface onto a glass substrate exhibit diffraction patterns characteristic of cubic CeO_2 with the fluorite structure (JCPDS no: 75-0151) (see Figure 1). The films synthesized over 3 h consist of granules with an average size of 5 nm, as estimated from the XRD pattern using the Scherrer equation. A similar estimate of particle size (5 nm) was obtained from films synthesized over 6 or 18 h (Figure S1, Supporting Information). This observation is surprising since the films visibly increase in thickness with the passage of time. The X-ray patterns suggest that the growth of the films takes place in continuous cycles of nucleation and growth that is self-limiting rather than from an initial burst of nucleation followed by extended periods of growth. Such a growth mechanism has previously been by others for films grown at fluid interfaces.[2c,d]

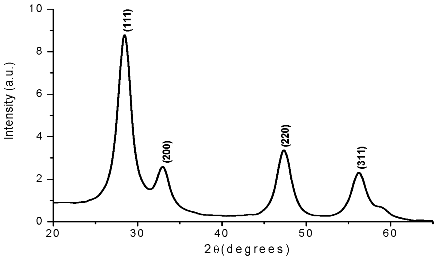

Figure 1. XRD pattern of CeO_2 films obtained after 3 h of deposition at a pH of 12.4.

Scanning electron microscopic images show that the CeO_2 films undergo marked changes in morphology as a function of time, even though the grain sizes remain constant (see Figure 2). Films obtained after a period of 3 h consist of large spherical aggregates with diameters ranging from hundreds of nanometers to a few microns. A similar observation has been made in the case of Pd nanoparticles which assemble into submicroscopic spherical aggregates at the interface.[10]

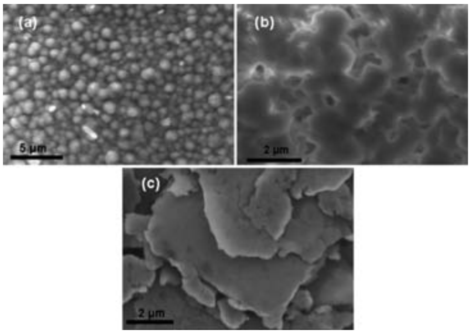

Figure 2. SEM images of CeO_2 films synthesized over 3, 6, or 18 h maintaining the pH at 12.4.

When the reaction time is lengthened to 6 h, the spherical aggregates disappear and are replaced by a flaky structure with rounded edges. Longer reaction times result in smoother and larger flakes with well-defined jagged edges.

It is possible to resolve the individual nanoparticles forming the spherical aggregates by high resolution transmission electron microscopy (HRTEM) (Figure 3). The images reveal particulates with spherical, cubic, and hexagonal shapes with dimensions of 5−10 nm. HRTEM reveals that the jagged edges of the platelets obtained at long growth times are facets of single-crystalline particulates. Lattice planes corresponding to the separation distance between (111) planes of the fluorite structure were seen in all resolved particulates.

The nature of the film obtained at the interface can be related to the properties of the interface and forces associated with colloidal

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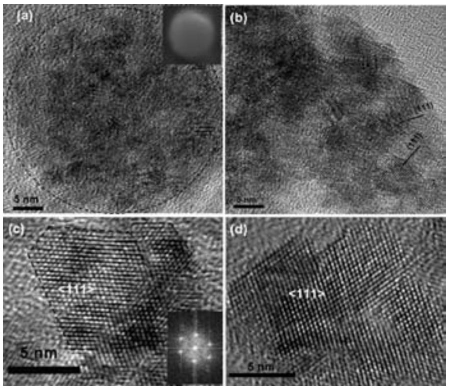

Figure 3. HRTEM images of CeO_2 films: (a) from deposits obtained after 3 h, showing particulates (*ca.* 5 nm) making up large spherical aggregates (SEM of the spherical grain is inset); (b) nanoparticulate grains forming ill-defined aggregates at times under 3 h; (c and d) hexagonal and cubic nanoparticles showing the (111) planes from samples obtained over 3 and 6 h, respectively. A Fourier transform of the image is inset to image c.

adsorption. When liquids such as water and toluene are layered atop each other, they mix to a limited extent at the interface. This mixing changes the mechanism of heat and ion transport in the vicinal region.[1] Ceria grains nucleate and grow in this region and are adsorbed by the interface to form a Pickering emulsion.[1] The emulsion formation lowers the interfacial tension, promotes ionic diffusion, and results in autocatalytic growth and aggregation. We believe the particles aggregate to lower the interfacial tension; the fall in interfacial tension is directly proportional to the dimensions of the crystallites. In this environment, further seeding takes place and particulates created fill the voids between the aggregates. Over longer growth times, the aggregate becomes flatter to better fill the remaining voids in the interfacial region. The different steps in the interfacial deposition process are illustrated in Figure 4. A similar stepwise growth resulting in hierarchical $Cd(OH)_2$ nanostructures at fluid interfaces has been observed by us.[2b] The large spherical aggregates are probably held together by weak van der Waals forces, while the platelet structures are more likely due to stronger chemical bonds between the particulates.[11]

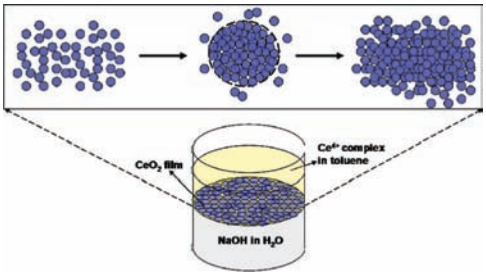

Figure 4. A cartoon illustrating the growth and agglomeration mechanism for CeO_2 nanoparticles. The particles grow in three stages, first forming primary agglomerates followed by the formation of secondary agglomerates with circular outlines whose further agglomeration forms dense sheets (tertiary agglomerates).

Exploiting the stability of the phase-transferred ceria ions, we have carried out depositions at different values of pH and temperature. We find that the grain size is critically dependent on these parameters. X-ray diffraction patterns show that the average grain size reduces from 5 to 1 nm as the pH value is decreased from 12.7 to 11.5 (Figure S2, Supporting Information). A similar decrease in grain size from 5 to 1 nm was seen when the deposition temperature was lowered from 70 to 50 °C (Figure S3, Supporting Information).

The crystallinity of the nanoparticulate CeO_2 films can be improved by annealing. X-ray diffraction patterns of thin films of CeO_2 annealed at 450 °C for 18 h show the presence of microscopic grains (Figure 5a). SEM images show that the annealed samples consist of flat microscopic disks (Figure 5b).

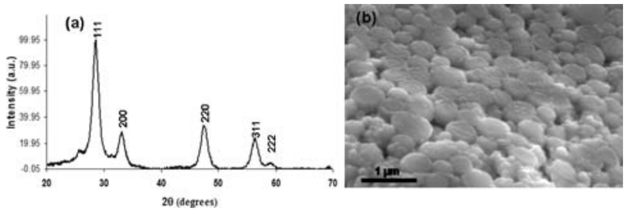

Figure 5. (a)XRD pattern and (b)SEM image of annealed CeO_2 films.

In this report, we demonstrate, for the first time, that interfacial deposition can be accomplished by using a phase transfer catalyst to produce a dispersion of metal ions in organic solvent. We envisage that this approach can significantly facilitate interfacial deposition for thin film fabrication.

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Supporting Information Available: XRD patterns of ceria deposits at different conditions. This material is available free of charge via the Internet at http://pubs.acs.org.

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