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Synthesis of $CeO_2@SiO_2$ core–shell nanoparticles by water-in-oil microemulsion. Preparation of functional thin film

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Abstract

Synthesis of nanoparticles under restricted environment offered by water-in-oil (W/O) microemulsions provides excellent control over particle size and shape, and inter-particle spacing. Such an environment has been involved to synthesize silica nanoparticles with a CeO_2 core, so-called $CeO_2@SiO_2$. Aqueous fluids made up of ceria nanoparticles with a size close to 5 nm have been used as the water phase component. The starting CeO_2 sols and obtained $CeO_2@SiO_2$ nanoparticles have been characterized by dynamic light scattering (DLS), X-ray diffraction, scanning and transmission electron microscopy, and specific surface area measurements. The microemulsion process has been characterized by DLS. Preliminary results on $CeO_2@SiO_2$ thin films are presented.

Keywords: Nanocolloids; Microemulsion; DLS; CeO_2; Silica; Core–shell; Nanoparticles

1. Introduction

CeO_2-based materials have attracted considerable attention from both scientific and technological point of view (examples of commercial products: Anti-UV: RHODIGARD^{TM}; catalysis: EOLYS®, etc.). Particularly, CeO_2 nanoparticles have generated a large research effort in the past twenty years [1–21]. If a large number of reports can be found on the synthesis of CeO_2 nanoparticles, there are only a few dealing with surface modification. Recently, the nanostructured SiO_2–CeO_2 system has become very popular for chemoselective catalysis thanks to the fact that the mineral binder SiO_2 is able to generate high specific surface area and thermal stability in nanoparticles arrays [22–27]. In the case of coating oxide particles with silica, various routes have been investigated: aggregation of small colloids [28], condensation of silica oligomers produced by solubilization of silica particles in highly basic medium [29], hydrolysis of functionalized or not silicon alkoxides [22–27,30–33], microemulsion route [34–37].

In this study, the water-in-oil (W/O) microemulsion route was chosen because it provides a unique environment to synthesize novel inorganic materials with interesting designs and/or specific properties [34], resulting in non-aggregated nanoparticles with a controlled surface and/or coating properties. Nevertheless, at present, a major problem with the microemulsion process remains the effect of the reactants and products on the microemulsion stability domain, particularly the metal concentration in the aqueous pseudo-phase used for precipitation reactions [27,34]. That is why, avoiding the classical precipitation process, we describe in this paper an original method to synthesize designed nanoparticles using a colloidal suspension as the starting water pseudo-phase [35,36]. This colloidal suspension allows the metal concentration to be increased without destabilizing the microemulsion, and to avoid the classical calcination process [27]. The present work aimed at obtaining well designed and characterized core–shell $CeO_2@SiO_2$ nanoparticles, as well as more information about the W/O microemulsion process.

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Table 1
Experimental preparation conditions of the microemulsions 1 and 2

	Heptane (wt%)	Surfactants (wt%)	Aqueous phase (wt%) (H_2O/TEOS/NH_3)
Microemulsion 1	63.5	27.5	3.2/3.7/2.1
Microemulsion 2	63.1	27.6	3.2/3.8/2.3

2. Experimental

2.1. Products

Two CeO_2 sols (A and B) were provided by Rhodia laboratory. The surface chemistry informations are described in Refs. [20,21]. The pH values ranged from 1.1 to 2, the CeO_2 concentration from 10 to 100 g/L and the viscosity from 1.12 to 1.45 mPa s. All the reagents were of 99% min. purity, they were used without further purification: Acetone, ethanol, *n*-heptane, aqueous ammonia solution (28%), tetraethoxysilane (TEOS). Sulfosuccinic acid bis [2-ethylhexyl] ester sodium salt (AOT) and polyoxyethylene(4) lauryl ether (Brij30) were provided from Aldrich Chemical Co. Those AOT and Brij30 surfactants were selected for this study because at room temperature they are readily soluble in saturated hydrocarbons like *n*-heptane.

2.2. Synthesis of CeO_2@SiO_2 core–shell nanoparticles and thin films

n-Heptane was used as the oil phase component of the microemulsion, with different amounts of AOT/Brij30 mixture and aqueous phase (Table 1). The weight ratio between AOT and Brij30 was 1. The aqueous phase contained the CeO_2 sol, TEOS and aqueous ammonia solution. In more detail, the microemulsion (noted 1 or 2 using the sol A or B, respectively) was prepared by adding acidic CeO_2 sol into a surfactant/heptane mixture. Then, TEOS as the precursor of silica nanoparticles was added to the microemulsion. Finally, ammonia solution was carefully added for the condensation of TEOS. In the case of Brij30, in order to avoid any complications due to the presence of a possible thermally induced phase inversion, the reaction temperature was kept below 25 °C. After 48 h, all the samples were washed with *n*-heptane, ethanol and acetone to remove surfactant and oil, and a separation followed in a centrifuge at 5000 rpm for 15 min. The resulting powders were dried at 60 °C under vacuum. Concerning wet films prepared from the microemulsion solutions via dip coating of glass slides, they were pre-sintered at 400 °C in air to remove organic residues.

2.3. UV–vis spectra

UV–vis spectra of the colloids were recorded with a Varian CARY 5 spectrometer.

2.4. Dynamic light scattering (DLS)

To determine the mean hydrodynamic diameter ($d(\mathrm{H})$) of the nanocrystals or nanodroplets, DLS investigations on microemulsions or sols were performed with a Zetasizer Nano ZS from Malvern Instruments with the new non-invasive back scatter (NIBS) technology. The DLS technique measures the particle or droplet diffusion due to Brownian motion and relates it to the particle size. The particle size is classically calculated by using the Stokes–Einstein equation

$$d(\mathrm{H}) = \frac{kT}{3\pi\eta D},$$

where D is the translational diffusion coefficient, k the Boltzmann's constant, T the absolute temperature and η the viscosity. As can be seen from the Stokes–Einstein equation, there is a direct relationship between viscosity and particle size. The viscosity required for this technique is the dynamic viscosity of the sample at zero shear rate and the accuracy of the determined particle size is directly related to that of the viscosity. The viscosity of the sols A and B was measured with the viscosimeter SV10 from Malvern.

2.5. X-ray intensity measurements

X-ray diffraction data were recorded at room temperature on a Philips PW 3020 using the Bragg–Brentano geometry with Cu$K\alpha$ radiation (40 kV, 30 mA, integration time range from 0.5 to 10 s) and a secondary monochromator. The average apparent crystallite size (ε_β) was evaluated from a whole diffraction pattern profile analysis, using last developments implemented in the Fullprof program (version 2.0 Nov 2001, LLB, J. Rodriguez-Carvajal). By description of instrumental and intrinsic profiles by normalized Voigt function (convolution of Gaussian and Lorentzian functions), size and strain effects can be separated from the whole profile analysis based on the different angular dependence of the Gaussian and Lorentzian full-width-at-half-maximum (H_G and H_L, respectively), according to the following equations

$$H_\mathrm{G}^2 = \left(U_\mathrm{strain\_iso} + (1-\xi)D^2_\mathrm{strain\_aniso}\right)\mathrm{tg}^2\,\theta + \frac{G_\mathrm{size\_iso}}{\cos\theta},$$

$$H_\mathrm{L} = (X_\mathrm{strain\_iso} + \xi D_\mathrm{strain\_aniso})\,\mathrm{tg}\,\theta + \frac{Y_\mathrm{size\_iso} + F_\mathrm{size\_aniso}}{\cos\theta},$$

where U, X, ξ, G and Y are refinable parameters, and D and F are analytical functions (which depend on a set of additionable refinable parameters) to model the *hkl*-dependent broadening due to strain and size effects, respectively. "Perfect" Y_2O_3 powder was used as a standard to determine the instrumental resolution function (IRF) of the diffractometer. The observed line broadening was modeled by isotropic size effects, leading to $1/\cos\theta$ dependent terms of H_G and H_L (Y and G parameters in Fullprof, respectively) contribution to the size effects. Refinement of $\mathrm{tg}\,\theta$ dependent isotropic strain parameters (U and X parameter in Fullprof) did not improve significantly the profile fitting. For each diffraction pattern, a counter zero point and the unit-cell parameters were refined in addition to the Y and G parameters. The background level was defined by a polynomial function. After refinement of the coefficients, the program calculates the apparent size along each reciprocal lattice vector. The average apparent crystallite size (ε_β) can be related