

ESI FOR:

Facile and Predictable Synthesis of Dual Mesoporous-Mesosize Structures through Thermally-Driven Self-Assembly of Nanodroplets

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Experimental Section

Chemicals: All chemicals reactants (purity >99.9%) were purchased from Sigma Aldrich and used without additional purification. $ZrOCl_2 \cdot 6H_2O$, $TiOSO_4$ (1.25 M solution in H_2SO_4), $Fe(NO_3)_3 \cdot 9H_2O$ and $Y(NO_3)_3 \cdot 6H_2O$ were used as precursors. Igepal CO-520 and cyclohexane dehydrated with zeolites were used as the surfactants and the continuous oil phase, respectively. Deionized water was used in all experiments.

Samples Preparation: Water-in-oil microemulsions were prepared at room temperature by mixing and strong stirring a mixture of surfactant with cyclohexane and adding the adequate volume of an aqueous solution containing the inorganic salt. A summary of the experimental conditions used to prepare the samples is shown in Table S1. In a typical experiment 35 mL of NH_4OH aqueous solutions was placed below a porous ceramic plaque (0.5 μm). A surfactant volume of 0.1 mL was deposited above the plaque and then 4.9 mL of cyclohexane/surfactant were added (0.4 M total surfactant concentration referred to a volume of 5 mL of cyclohexane plus surfactant). Finally, 40 mL of a microemulsion (cyclohexane, 0.4 M surfactant concentration) containing the inorganic salt precursor dissolved in the aqueous nanophase were added (Height/Surface ratio = 3). For TiO_2 the surfactant concentration was restricted to 0.3 M. For the production of almost monodisperse zircona nanostructures the volume above the plaque was scaled 1:4 (Height/Surface ratio = $3/4 = 0.75$). A few words deserve the reproducibility of the method. Following the conditions given in ESI the method leads to similar results. It is, however, important to remark an atypical factor that must be controlled for reproducibility (the height/surface ratio of the top layer, i.e. the contact area of the gas with the microemulsion). The lack of control of this parameter leads to an increase in size polydispersity though spherical aggregates are still formed.

Characterization techniques: Morphology, particle size and EDX analyses of the obtained samples were studied with a TEM JEOL microscope working at 200 KeV. The mean size (X), the standard deviation (SD) and the polydispersity index (defined as X/SD) were evaluated from the electron micrographs by counting 100 particles. Phase identification was performed by X-ray analysis. X-ray diffraction (XRD) patterns were collected from 5 to 70° (2θ) by using a Bruker D8 Advance instrument with $\text{CuK}\alpha$ radiation ($\lambda=0.15406$ nm) and a SOLX detector operating at 40 kV and 30 mA. The crystal domain size (DXRD) was determined from the X-ray profiles following the Scherrer equation by using the DIFRACPLUS EVA software (BRUKER AXS). Nitrogen adsorption and desorption isotherms were performed at -196°C in a Micromeritics ASAP 2010 volumetric adsorption system. The BET surface area was deduced from the analysis of the isotherm in the relative pressure range from 0.04 to 0.20. Pore size distributions were estimated using the BJH model. Dynamic light experiments (DLS) were carried out in a Nanosizer ZS (Malvern Instrument) to determine the variation in scattering intensity and hydrodynamic size with time or temperature in reverse micelles.

Table S1. Summary of the experimental conditions used to prepare colloidal nanostructures. Igepal Co-520 was used in all cases except for CeO₂ in which Igepal CA-520 was used. The surfactant concentration was in all cases 0.4 M except for TiO₂ that was 0.3 M.

Sample	T (°C)	Aqueous Precursor	Aqueous Content Organic Layer (Vol. %)	[NH ₃] in aqueous layer	TEM Size (nm) and SD*
ZrO ₂	35	2.5 M ZrOCl ₂	4%	28%	Nanoparticles
ZrO ₂	60	2.5 M ZrOCl ₂	4%	17%	118 (41)
ZrO ₂	60	1.25 M ZrOCl ₂	2%	17%	60 (14)
ZrO ₂	60	2.5 M ZrOCl ₂ + 2.5 M KNO ₃	2% (Zr) + 2% (K)	2%	95 (9)
TiO ₂	60	1.25 M TiOSO ₄	8%	28%	71 (18)
Fe ₂ O ₃	60	2.5 M Fe(NO ₃) ₃	4%	2%	36 (7.9)
Y ₂ O ₃ -ZrO ₂ (Y= 20 mol%)	60	2.5 M (ZrOCl ₂ + Y(NO ₃) ₃)	4%	4%	100 (13)
Fe ₂ O ₃ -ZrO ₂ (Fe= 20 mol%)	60	2.5 M (ZrOCl ₂ + Fe(NO ₃) ₃)	4%	4%	68 (18)

* Standard deviation between parenthesis

Figure S1: SEM pictures clearly show the aggregates are spherical. Close-up views with TEM show that the mesosize colloids are indeed nanostructures (aggregates of nanoparticles).

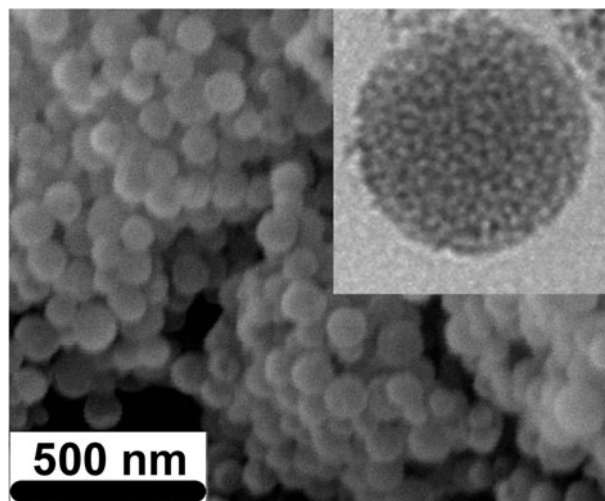


Figure S2: (A) N_2 adsorption-desorption isotherms and (B) pore size distributions calculated based on the BJH model for (a) ZrO_2 , (b) TiO_2 , (c) Fe_2O_3 , (d) $Y_2O_3-ZrO_2$ and (e) $Fe_2O_3-ZrO_2$ nanostructures heated at 350/24 h in Air except sample (c) which was heated at 250/24 h. N_2 isotherms are similar for all the samples and show a relatively low irreversibility (large fraction of accessible pores). The BET specific surface areas for ZrO_2 , TiO_2 , Fe_2O_3 , $Y_2O_3-ZrO_2$ and $Fe_2O_3-ZrO_2$ are 179, 185, 143, 152 and 131 $m^2 g^{-1}$, respectively. Pore size distributions (BJH model) indicate a broad mesopore population centered about the value of the particle size (interparticle porosity) and a narrow mesopore population corresponding to the intraparticle pores (3.9 nm for ZrO_2 , 4.7 nm for TiO_2 , 3.6 nm for Fe_2O_3 , 3.9 nm for $Y_2O_3-ZrO_2$, 3.7 nm for $Fe_2O_3-ZrO_2$).

