Aerosol Route as a Versatile Method for the Processing of Hierarchically Organized Hybrid Nano Particles

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Introduction: Hierarchical structures, which refers to the materials that have more than one length scale, organized as the assemblage of primary units with high surface-to-volume ratio, play an important role in advanced materials design. Especially, the building of complex hierarchical structures exhibiting the hybrid organic-inorganic interfaces might be of special importance for the creation of advanced nanostructured materials having either improved or novel characteristics that bridges various scientific areas for the future diverse technological applications in catalysis, optics, energy, life science etc. Applying the bottom-up building blocks approaches, it is possible to create the hierarchical structures in a controlled manner having different morphologies, starting from aqueous, organic or colloidal precursor solutions. Among the diversity of the “bottom-up” chemical approaches, synthesis through dispersion phase (aerosol) enables generation of ultrafine, either single or complex structures with controlled stoichiometry, chemical and phase content. The opportunities of the hot wall aerosol processing, provided by high heating and cooling rates, short residence time and high surface reaction, refers to the synthesis of spherical three-dimensional (3D), hierarchically organized nanostructured particles with uniformly distributed components and phases. The particles composite inner structure, representing an assembly of nanosized primary particles, opens the possibility for particle surface modification and functionalization emphasizing their application in photovoltaics, energy transfer and bioimaging. This versatile technique has been used for the successful synthesis of hierarchically organized submicronic titanium (IV) oxide or Y_2O_3 up-conversion phosphor particles having the diverse levels of structural, morphological and functional complexity explored by means of appropriate selection of different precursor solutions, either true or colloid, surface modification and proper selection of rare-earth based dopants.

Experimental procedure: The fine and uniformly distributed aerosol droplets are continuously generated from precursor solution using the ultrasonic atomizer operated at 1.7 MHz. As a precursor, either TiO_2 colloidal solution (colloid particle size 4.5nm, c=0.05 mol/dm^3) or 0.1mol/dm^3 nitrate common water solution of $Y(NO_3)x6H_2O$, $Yb(NO_3)x5H_2O$ and $Er(NO_3)x5H_2O$ are prepared and decomposed in the gas stream in a high-temperature tubular flow reactor at the temperatures ranging from 150 to 800^{o}C. Additional particles drying at the reactor exit is performed in Diffusion Dryer unit 3062 (TSI Inc., USA) prior their collecting in electrostatic precipitator. Physical properties as density, viscosity and surface tension of the solution are measured at 25^{o}C. All the chemicals are of the highest purity available (Aldrich, 99 %); distilled deionized water is used with a resistivity of 18.2 MΩcm^{-1} (Milipore, UK). Hybrid TiO_2-organic ligand structures are made by aerosol derived-TiO_2 particle suspension in cathechol, $C_6H_4(OH)_2$.

Characterization: The morphology and chemical purity are investigated by means of Field Emission Scanning Electron Microscopy, FESEM (HITACHI SU-70) with energy dispersive X-ray Analysis. The particle substructure is analyzed on a 200kV JEOL-JEM-2100F Transmission Electron Microscopy (TEM) coupled with energy dispersive X-ray Analysis and STEM mode. The powders phase composition are determined using a PW 1050 (Philips) diffractometer with CuKα radiation in the 2θ range from 15-95^o with a step scan of 0.02^o and scanning rate of 10 s per step. Structural refinement is done based on Rietveld analysis in Topas Academic 4.1 program. For the determination of microstructural parameters the Fundamental Parameter Approach is used; FWHM based LVol (volume weighted mean column height) calculation to determine the intermediate crystallite size broadening modelled by a Voigt function and FWHM based strain calculation for the strain broadening is used.

Results and Discussion: Typical particle morphology is presented at Fig.1a,d, showing the spherical secondary particles represent an assembly of nanosized (<50nm) primary particles. The prevailing blueberry-like structure and the gradual change of contrast from the center to the edge, as evident from TEM, Fig1b, implicates their uniform self-organization within the volume of bigger ones along with retention of the certain degree of nanoporosity. The higher density of primary particles at the surface implicates the particles predominantly aroused through the mechanism of surface precipitation when starting from nitrate precursors (Fig.1a,b). Based on the elemental analysis (Fig. 1c) it is evident a very homogeneous distribution of the constitutive elements: Y (Lα, 1.9226 keV), Er (Lα 6.9488keV), Yb (Mα 1.5215 keV) which represents one of the basic advantage of the aerosol route showing no compositional segregation at the selected particle agglomerate presented in STEM image (Fig 1c left). Moreover, a uniform distribution of the Yb^{3+} and Er^{3+} ions into a host yttria matrix implicates high up-converting luminescence efficiency to be obtained. FESEM reveals as-synthesized TiO_2 particles from colloidal precursor (Fig.1d) are highly spherical in shape, have smooth surfaces and are non-agglomerated with a fairly narrow size distribution. The particles derived at 150°C are mainly composed from anatase crystal phase and a metastable TiO_2(B) monoclinic structure which gradually convert to rutile phase with temperature increase up to 800°C. The inner structure revealed by TEM (Fig 1e) implied the spherical particles (1st structural level) are assemblies of much smaller building units (2nd structural level) with sizes comparable with the crystallite sizes determined by XRPD analysis (2.5nm at 150°C, 53nm at 800°C). Such structure hierarchy associated with a high curvature of primary nano particles and undercoordinated-five coordinated defect Ti sites, caused selective reactivity towards bidendate ligand binding and functionalization of primary nano particles by forming hybrid TiO_2-Cathechol surface (3rd structural level) (Fig1f). This cause a significant red shift of optical absorption and a decrease of the effective band gap (1.86 eV) in cathechole-modified TiO_2 nanoparticles compared to the band gap of bulk material (3.2 eV), nominating this hybrid structure as a promising material for use in solar cell applications.

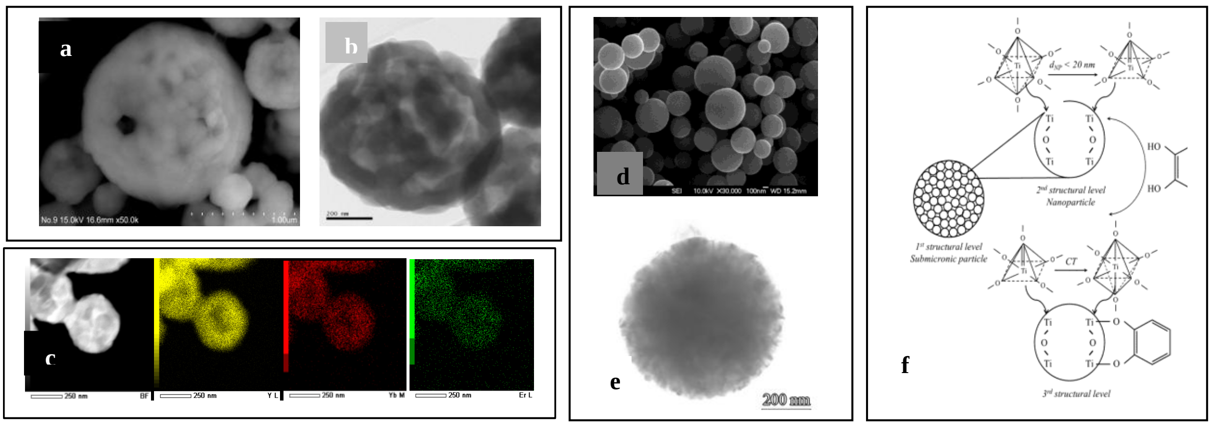

Figure 1. FE-SEM (a, d) and TEM (b,e) images of the particles derived from nitrates (Y_2O_3:Yb,Er) and colloids (TiO_2), respectively; EDS mapping (c); the corresponding structure hierarchy of TiO_2-organic ligand hybrid particles (f)

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References
1) I. Dugandžić, D. J. Jovanović, L. Mančić, N. Zheng, S. P. Ahrenkiel, O. Milošević, Z. V. Šaponjić, J. M. Nedeljković, Surface modification of submicronic TiO_2 particles prepared by ultrasonic spray pyrolysis for visible light absorption, J Nanopart Res (2012), 14:1157, 3
2) V. Lojpur, L.Mancic, M.E. Rabanal, M.D. Dramicanin, Z. Tan, T. Hashishin, S. Ohara, O. Milosevic, Structural, morphological and luminescence properties of nanocrystalline up-converting $Y_{1.89}Yb_{0.1}Er_{0.01}O_3$ phosphor particles synthesized through aerosol route, Journal of Alloys and Compounds, 580 (2013)584

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