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Review paper

The processing of optically active functional hierarchical nanoparticles

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ABSTRACT

Global climate changes and the aroused environmentally-energy problems categorically moved the research efforts towards programmed processing of a novel class of hierarchical materials having well defined phase, compositional and morphological features. The synthesis based on the principles of the molecular design and integrative chemistry which includes the innovative aerosol and hydro(solvo)thermal nanotechnology routes, the building block assembling and hybridization, represent intelligent platform for the creation of advanced functional materials. Due to exceptional optical properties and a diverse application in electronics, optoelectronics, energy conversion/storage and biomedicine, the examples from some wide band gap oxides for light harvesting and photocatalytic applications as well as both down and up-conversion energy-saving luminescent materials for photonic and biological applications are considered. With the help of various analyzing techniques like XRPD (X-ray powder diffraction), field emission scanning electron microscopy (FE-SEM), energy dispersive spectroscopy (EDS), analytical and high resolution transmission electron microscopy (TEM, HR-TEM), selected area electron diffraction (SAED), scanning tunneling electron microscopy (STEM), Fourier transform infrared (FTIR) and Raman spectroscopy, photocatalytic and fluorescence measurements, the opportunities of the aerosol and hydro(solvo)thermal routes for the synthesis of novel hierarchically and hybrid assembled structures and nanocomposites are reviewed highlighting the recent research activities realized in the Institute of Technical Sciences of SASA, Belgrade, Serbia and University Carlos III, Madrid, Spain. The morphological, structural and functional aspects of the following systems: ZnO, TiO_2, Y_2O_3:Eu,Yb/Er/T/Hm, Y_2O_3:Eu@Ag, $(Y_{1-x}Gd_x)_2O_3$:Eu, (NaYF4:Yb/Er)@EDTA/PEG/PVP, are discussed from the state-of-the art and literature contexts. Controlled growth of 1D and 3D hierarchical structures based on the single-source processing methodology in combination with the homogeneous precipitation of optically active intermediate precursor are especially stressed for the case of yttria based phosphor particles and phase-dependent luminescence efficiency. The obtained results offer possible routes for the synthesis of hierarchically structured nanomaterials with tunable structure, morphology and optical properties.

Contents

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1. Introduction

Tremendous technological and scientific efforts in materials science are nowadays basically focused to the development of next generation of advanced materials with new and improved properties able to solve the aroused energy and environmental problems. The field of nanoscience and nanotechnology thus has had an exciting progress in recent decade, particularly regarding the control building of nanostructured materials that might have a great potential for use in solid-state functional materials and devices, like phosphors, sensors, and catalysts [1–4]. However, besides that nanotechnology will continue to influence materials development through microstructure refinement, the key point for the future progress of advanced materials will be focused on the development of new material forms through controlled assembly and hybridization of atoms and molecules towards desired functionality. It is presumed the 21st century's Science & Technology should provide low carbon and sustainable society through control of materials assembling and creation of the specific structures [5]. The progress in assigned processing with the ability to force the advancement of materials moved the research interest towards controlled synthesis of hierarchical structures using the mechanisms of integrative chemistry and favorable soft chemical techniques [6]. The building block assembling proposed by Mann [7] and materials nanoarchitecturing [8,9] represent the new era in materials creation and modern materials chemistry.

Aerosol route belongs to the family of "bottom-up" chemical approaches for nanomaterials processing. Since that synthesis occurs in a dispersion, the generation of ultrafine, either single or complex particles with controlled stoichiometry, chemical and phase content is favored on the account of a high heating and cooling rates, short residence time and enhanced chemical activity. The particles obtained are with either amorphous, nanocrystalline or metastable structures that might have a huge impact in the processing of advanced functional materials having novel and unique structures and properties [10–12]. The opportunities of the hot wall aerosol synthesis, i.e. spray pyrolysis, has been demonstrated for the generation of highly spherical three-dimensional (3D) nanostructured particles with uniformly distributed components, phases and nano-clustered inner structure [13–15]. When one-dimensional (1D) nanomaterials are considered, the hydro(solvo) thermal method (HT/ST) is shown to be one of the simplest techniques for their obtaining [16]. 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.

During the last decade we explored both methods in the synthesis of different optically active hierarchical structures having well controlled structural and morphological features. The present review covers major aspects of the applied strategies which contribute to the development of advanced oxide and fluoride functional materials useful in optical, catalyst and sensing technologies.

Pure and/or doped hierarchical nanostructures based on semiconducting nonstoichiometric oxides, like ZnO or TiO_2 [17–19] have received considerable attention and importance due to their interesting properties, i.e., large exciton binding energy, high luminescence efficiency, transparence, large piezoelectric coefficient, high electron mobility, non-toxicity, biocompatibility and high isoelectric point ($IEP_{ZnO} \sim 9.5$, etc.). Consequently, they could be used as photocatalysts, solar cells, for the environmental issues i.e. destruction of intractable chemical waste, purification of polluted water, decomposition of offensive atmospheric odors and as transparent conducting layers. However, due to their large band-gaps (3.37 eV-ZnO, 3.2 eV-TiO_2 anatase, 3.0 eV-TiO_2 rutile), these oxides absorbed less than 5% of the available solar photons. Both, dye-sensitization and defect induced doping are the most promising pathways for increasing their photoactivity. Additional improvement of the efficiency of light absorption can be achieved by using submicronic hierarchical/hybrid particles as light scattering centers in photovoltaic technology [20]. Moreover, the ZnO and TiO_2 mesoporous particles with well controlled pore structure and well developed specific surface area, could afford high loading and low mass-transfer resistance, widening their potential application for photonic materials, sensors, absorbents, drug delivery, fuel cells, batteries, etc. [2,3,6]. On the other side, luminescent materials (phosphors) possessing either Down- or Up- conversion (DC or UC) optical properties, have received considerable attention due to their potential applications in luminescent nanodevices including flat-panel displays, solid-state lasers, optical-fiber telecommunication and solar cells [21–23]. Particularly, rare-earth doped hosts, and among them yttria compounds, optically active in the visible range of spectra, are of great interest since that can be used in solid state lasers, screen displays, sensors, optical data storage, fluorescent labels for sensitive detection of bio-molecules and telecommunications. Recently, rare-earth doped up-conversion nanoparticles demonstrated the great potential in biological applications, including bio-labeling, imaging and detection, as fluorescent nanothermometers and phototherapy of the diseased cells [22]. Being excited by near infrared light, rare earth UC phosphors provide deeper, non invasive penetration in tissues, exhibit low toxicity, high chemical stability, high signal-to-noise ratio (due to the absence of auto-fluorescence), sharp absorption and multicolored emission. However, despite to their obvious advantages, their application in biological subjects is still limited due to their low dispersibility in water and up-conversion efficiency.

2. Hierarchical structures

Hierarchical structures (HS), which refers to the materials that have multiple length scale [24] from atomic to macro level, organized as the assemblage of primary units with high surface-to-volume ratio, play an important role in advanced materials design. They are generally divided into three categories: 1D (nanotubes), 2D (nanolayers), 3D (nano particles), but also regards to the hybrid organic-inorganic interfaces and/or porous structures: (nano: $\leqslant$2 nm, meso: 2–50 nm, macro: $\geqslant$50 nm), the latter enabling good incorporation, dispersion and intensive diffusion of active sites, high surface reactivity, intensive interphase transport and solid state diffusion [1,2]. The geometries and sizes are tailored to enhance specific functionalities and performance integration,

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