Polymer assisted colloidal nanocrystal framework synthesis: sol-gel approach

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Abstract
The porous colloidal nanocrystal framework material was synthesized by sol-gel assembly followed by a self-propagation procedure. The characteristics of the synthesized nanocrystal were confirmed by advanced instruments. From the DTG analysis, the poly (vinyl alcohol) was completely degraded at 400 °C. The XRD pattern and TEM image confirmed the nanoscale crystallite size of the material. BET and SEM analysis showed the mesoporous type pore size distribution. The predictable compositional analysis was confirmed from EDX, SAED, and XPS compositional analysis. Using the HSAB theory and HRTEM image analysis the formation of local heterojunction between metal oxides was approved.

1. Introduction

Colloidal nanocrystal frameworks, which are directed by the presence of polymer, are ordered arrangements of porous (micro-, meso-, and macroporous) colloidal nanocrystals material containing both matter and void space [1, 2]. The frameworks can be prepared either from molecular precursors or from pre-formed nanocrystalline colloids, using the polymer architecture-directing agent (ADA) as nanocrystal tethering and a pore generating domain [3]. The interfacial interaction, commonly electrostatics and ionophobic interactions between the nanocrystals and the polymer ADA led to the formation of a ligand-coated organic–organic interface hybrid. The residual surface charge on molecular precursors (metal cation or hydroxyl-terminated metal oxide nanocrystals) was reported [2] to be generated by solvothermal or sol-gel methods. During colloidal nanocrystal frameworks (CNFs) growth, first, the molecular precursors were decomposed through stepwise heating at moderate temperatures to form nanocrystals (scheme 1(a)). Direct calcination of the pre-formed nanocrystals without using surfactant provides disordered nanoparticles and ordered nanoparticles if the template generating surfactant is used (scheme 1(b)). Subsequent aging, evaporation, and crystallization of the nanocrystals yield a porous inorganic nanocrystals framework (schemes 1(c)–(e)) [4].

Moreover, the colloidal nanocrystal frameworks are also tuned to particular applications by doping or forming a composite as an impurity [5, 6]. During doping, the host dopant reactivity is balanced depending on Pearson’s hard and soft acids and bases (HSAB) principles [7]. According to the HSAB theory, hard acids favor hard bases, while soft acids favor soft bases to bind and yield ionic and covalent complexes, respectively. Besides, hard Lewis acids such as Zn(II) ion can be easily exchanged by soft acids such as Cu(I) and Ag(I) when hard base solvents such as alcohols and water are used [8–10]. However, if host hard Lewis acids such as Zn(II) ion mixed with the dopant hard Lewis acids such as Fe(III) and Mn(III) ion, the surface adsorption occurred rather than doping. After adsorption of the dopant on the surface of the host, it can be easily oxidized by thermal treatments to form a local heterojunction [11, 12]. Fast photoinduced electron–hole recombination is a critical problem for several applications. Creating a binary or ternary composite can diminish the recombination problem and enhance the catalytic application of single materials [13–16].

Here, iron and manganese oxides doped ZnO porous crystal framework were synthesized by sol-gel, followed by a self-propagation approach. Based on the HSAB theory, the formation of a local heterojunction...
rather than doping was confirmed. Advanced instruments were also employed to understand the mesoporous nature and the overall physical properties of the material.

2. Method

The sol-gel-based ternary colloidal nanocrystal framework (TCC) was synthesized by using the PVA as an architecture-directing agent. The zinc nitrate hexahydrate as hard Lewis acid host and iron nitrate nonahydrate and manganese sulfate monohydrate as hard Lewis acid dopant was used to synthesize TCC. First, the polymer was dissolved in distilled water while continually stirring and heating for about 15 min. On the pre-cooled polymer, the Zn, Mn, and Fe precursors were added, to follow the nucleation-doping approach synthesis procedure as described by Buonsanti and Milliron [7]. The synthesized polymer-assisted colloidal particles were then kept for about 2 days to assemble the framework. During heating of the sample at 110 °C, the self-propagation process took place and a porous type product formed, and further calcined at 400 °C for 3 h.

3. Results and discussion

The thermal stability of TCC before calcination was analyzed by differential thermal analysis (TGA) and thermogravimetric analysis (DTA) analytical technique in a nitrogen atmosphere at 20.0 ml min⁻¹ flow rate and 50 °C min⁻¹ ramp time. The change in mass as a function of the temperature for the TCC nanocomposite was given in figure 1(a). Four mass losses corresponding to the adsorbed water evaporation, PVA intramolecular decomposition, crystal water dehydration or/and PVA side chains degradation, and PVA main chain decomposition were observed. The rough temperature ranges for aforementioned mass losses are 30 °C–100 °C, 100 °C–140 °C, 140 °C–230 °C, and 230 °C–400 °C, respectively [18, 19]. The two endothermic peaks corresponding to adsorbed water evaporation or/and PVA intramolecular decomposition and the other two major exothermic peaks corresponding to precursors or/and PVA side-chain decomposition were also confirmed from the DTA analysis [20]. Thus, 400 °C was selected as an optimum poly (vinyl alcohol) (PVA) disintegration temperature after serving as an ADA.

Figure 1(b), inset label (A) shows the XRD pattern of PVA, and figure 1(b), inset label (B) is for TCC. The XRD pattern crystal planes (ICSD: 00–036–1451, P63mc (#186-1)) support the hexagonal structure of ZnO NPs with an approximate average crystallite size of 7 nm. The fitting of 2θ values and corresponding crystal planes was also reported in Kotresh et al study [21]. The absence of crystal plane for iron (5%) and manganese (5%) oxides is due to the percent domination of ZnO (90%). The exact fitting of the crystal plane for ZnO may also indicate the non-existence of structural alteration on the ZnO lattice ascribed to Fe(III) and Mn(III) ion diffusion into the Zn host crystal.
Actually, according to Pearson’s hard and soft acid–base principle, the iron and manganese ion hard Lewis acids dopant does not diffuse into hard Lewis acids zinc ion in water solvent \[8–10\]. Therefore, during thermal treatment the surface adsorbed dopant ion oxidized to Fe$_2$O$_3$ and Mn$_2$O$_3$ NPs (see TEM analysis) and withstand as separate phases by forming a local heterojunction with wurtzite ZnO, a consistent result was also reported \[11\]. The non-existence of the PVA XRD pattern on the TCC shows the complete decompositions of PVA at 400 °C as confirmed from the DTG analysis. The inset structure in figure 1(b), shows the stable ZnO crystals structure developed from VESTA 3D software with help of AMCSDF cif data. The BET plot of the TCC (figure 1(c)) looks to have cylindrical shapes \[22\]. The TCC also has type IV matching adsorption isotherm and H3 hysteresis loops. The calculated average specific surface area and pore sizes are 23.9 m$^2$ g$^{-1}$ and 25.7 nm, respectively, which indicates the domination of the mesoporous pore size distribution (see figure 1(c) inset) \[23, 24\].

The mesoporous framework porous TCC morphology was also further confirmed from the HR-SEM image (figure 1(e)). The Mn, Zn, Fe, and O elemental compositions have existed at binding energy values of 0.5, 1, and 6.5 keV, respectively (see the EDX spectra, figure S1(a) (available online at stacks.iop.org/MRX/8/125005/mmedia)). The existence of S as an impurity is probably from the MnSO$_4$.H$_2$O precursor, which needs a high melting temperature. The crystallite size obtained from the TEM image (figure 1(e)) was between 5–30 nm, which is consistent with the XRD pattern. From the HRTEM image (figure 1(f)), the lattice fringes value of TCC, 0.28,0.34, and 0.368 are consistent with (002), (221), and (012) plane of ZnO, α-Mn$_2$O$_3$, and α-Fe$_2$O$_3$, respectively \[25–27\]. The measured interplanar spacing of diffraction rings from fast Fourier transform SAED patterns matches with the hexagonal wurtzite ZnO structure as detected on the XRD pattern (figure 1(d) inset). The nonexistence of spots on the ring/or and out of the ring show less crystallinity of the TCC materials \[28\]. The zinc (Zn 2p, 3s, 3p), iron (Fe 2p, 3p), manganese (Mn 2p, 3p), and oxygen (O 1s, 2s) are expected from XPS spectra from ZnO, Fe$_2$O$_3$, and Mn$_2$O$_3$ composite materials, respectively. The typical wide scan survey x-ray photoelectron spectroscopy spectrum of TCC (figure 1S(b)) also confirms the presence of Zn 2p, Mn 2p, Fe 2p, O 1s chemical states in the TCC \[29–31\].

4. Conclusions

The TCC material was grown by the sol-gel-thermal treatment route at DTG optimized PVA decomposition temperature. As confirmed from advanced analytical techniques, the synthesized TCC material has a nanometer-scale size and mesoporous type pore size distribution. Besides, the formation of local heterojunction between the metal oxides rather than doping was confirmed. This is also consistent with the HSAB hardness theory and HRTEM analysis. Herein, somewhat disordered porous material was found, thus the authors...
recommend selecting a proper architecture-directing agent for obtaining a more ordered framework assembly as future perspective.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Declaration of interests

The authors declare no competing financial interest.

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