Synthesis of Nanocomposite Hybrids

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Abstract: Controllable synthesis of zinc sulfide (ZnS) nanocrystals (NCs)/polymer transparent nanocomposite hybrids in situ based on the catalytic chain transfer polymerization (CCTP) technique. Firstly, a polymeric ligand PMAA [PMAA = poly(acrylic acid)] with controllable low-molecular-weight and a terminal double bond was synthesized through CCTP Catalytic chain transfer polymerization (CCTP) has emerged as an efficacious method to produce low-molecular weight polymers. In this paper, we reported the first controllable synthesis of nanosilica surface-grafted poly(methyl methacrylate) (PMMA) (SI-PMMA) macromonomers by using bis(aqua)bis((difluoroboryl)-dimethylglyoximato)cobalt(II) (CoBF) as a chain transfer catalyst via CCTP.

Keywords: Synthesis, Hybrids, ZnS, Nanocomposite, CCTP

I. INTRODUCTION

he photoluminescence measurements present that ZnS NCs, Mn-doped ZnS NCs, and ZnS/PMMA hybrid show good optical properties. roperties [1], such as the potential in lasers, biological labeling, light-emitting diodes (LEDs), and devices. Because of their unique and sizedependent properties arising from quantum confinement and surface effect, ZnS NCs have been extensively studied. In particular, ZnS NCs are often employed to be new luminescence center via doping different ions due to its large band-gap energy. By now, a large number of techniques for preparing ZnS NCs, such as sol–gel, template, vapor deposition , micelles , and solvent growth , have been applied. Among them, the solvent growth technique is very effective in yielding a narrow size distribution and optimization of the properties in preparation of NCs. To this end, a variety of efforts have been carried out via arrested precipitation to synthesize quantum dots (QDs) ZnS NCs, including simple inorganic ions by aid of cysteine stabilizer or low molecular weight thiols stabilizers, and zinc ethylxanthate in trioctyl phosphine by aid of hexadecylamine as a stabilizer [2].

n principle, a functional ligand consists of an anchor group, an outer functionality, and a spacer between them. Up to now, much effort has been devoted to the surface modification of NCs for improving their inherent stability and the luminescence intensity. For example, possible organic anchor groups for semiconductors are provided by amines, oxides, and thiols, which have different affinities to the NC surface and alter the fluorescence properties to a different degree. However, a major problem in linker chemistry is that the stability of the complex relies on the strength of only one chemical bond. If either the anchor to the NC surface or the functional docking bond breaks, the whole complex would dissociate. Therefore, the incorporation of fluorescent NCs with various functional polymer ligands containing many anchor points, such as diblock ionomers homopolymers, block copolymers , polymer micelles, or dendronized polymers, would be extremely useful to improve the interaction between the polymer ligands and NCs. Still, it is essential that the polymer ligands can form strong chemical bonds with polymers as to improve the compatibility between NCs

and polymer matrices. For these purposes we are focused on addressing this problem by introducing a new versatile polymer ligand prepared by catalytic chain transfer polymerization (CCTP) technique, where the interaction between the polymer ligands and NCs is increased by the presence of multiple anchor groups and outer double bond functionality. Metal-based nanoparticles, such as palladium, platinum, or their alloys, have been frequently used as electrocatalysts by anchoring them on carbon-based support [1], [2] and [3]. The performance of such a hybrid catalyst depends on two main issues: (i) the properties of the catalyst – involving the activity of the metal catalyst and the overall electroactive area; (ii) the properties of the support – involving processes such as fuel diffusion (for fuel cell application), good anchoring of catalysts to the support ensuring both long-term stability and efficient electron conductivity, and finally a good electron bulk conductivity of the support to efficiently transfer the electrons to the electrode. Over the last years, a variety of supports, such as carbon nanotubes , graphene , carbon fibers,, and conductive polymers have been tested in electrocatalytic applications such as fuel cells and biosensors. C60 is a less studied support, as explained by the lack of a "one-dimensional" structure and a relatively low conductivity. However, the low conductivity of C60 originates solely from a low concentration of charge carriers, due to its large bandgap of 1.6 eV. In fact, the electron mobility of crystalline C60 is rather high, making it popular in, for example, solar cell and and field effect transistor (FET) applications.

II. SYNTHESIS OF HYDROXYL-COATED MANGANESE-DOPED ZNS NCS

Nanostructural magnetic materials have the potential to revolutionize current data storage technologies, magnetoelectronics, and biotechnology. Recently, the surface and size effects in magnetic nanoparticles have been
one of the main topics among scientists . The core/shell systems,in which both of the core and shell are magnetic, are gaining increasing attention due to their appealing novel properties and promising application. Especially, the

research about ferromagnetic (FM)/antiferromagnetic (AFM) core/shell structures has become a focus. Many valuable phenomena, such as giant magnetoresistance and interfacial exchange bias effect, have been found in the structures. Basically, nanosized transition group metal particles are usually chosen to be the magnetic cores. Compared with Feand Co, the synthesized Ni particles are especially commended due to the antioxidant ability. So far, several physical and chemical composite methods, such as sonochemical deposition, colloidal chemistry method [15], mechanical milling, polyol method and chemical reduction have been applied to fabricate the nanosized Ni particles. As exemplified in the polyol method which is a typical chemically composite route, Ni(NO) was dissolved in an organic solvent like polyethylene glycol (PEG) and then heated to a certain temperature. An organic surfactant like oleic acid or oleyl amine was used to prevent the Ni nanoparticles from agglomeration. In this case, small and uniform nanoparticles can be manufactured [3]. A series of CV measurements was performed to investigate the electrocatalytic performance of the prepared Pd-decorated C60 NRs in a blank nitrogen-bubbled KOH solution to determine the electrocatalytic area (non-decorated C60 NRs showed no catalytic activity in agreement with previous reports. A classic reduction peak was observed in the potential region from −0.1 to −0.5 V for three modified electrodes, ascribed to the electroreduction of Pd oxide. The peak potential of Pd reduction are 0.270, 0.265, and 0.261 V for polymerized (curve a), as-grown (curve b), and porous (curve c) Pd-C60NRs, respectively. The peak current density of Pd reduction on polymerized Pd-C60NRs is significantly higher than that of as-grown and porous Pd-C60NRs. This is rationalized by the excellent stability of polymerized C60 NRs in ethanol solution which gives an efficient process for the self-assembly of Pd nanoparticles at the photo-transformed C60 NR surface. ZnS:Mn) In a typical procedure, 5 mmol of zinc chloride in 56 ml of DMF was continuously stirred and mixed with 3.2 ml of aqueous solution of manganese chloride (MnCl 2 mmol). In the second step, 4 ml of aqueous solution of ME (10 mmol) was slowly added dropwise into the above solution under stirring. Then, sodium sulfide (NaS:3 mmol), which was dissolved in 4 ml deionized water, was added dropwise into the resulting complex (the molar ratio between the total amount of salt and sulfur is controlled to be 10:6). Once added, the color of the above solution turned white immediately. The reaction was carried out for additional 6 h at room temperature. Finally, the white solution gradually turned to be transparent.

III. SYNTHESIS OF PMAA MACROMONOMERS

In a typical reaction, 0.3 g of azo initiator VA-044 and 13 mg of CoBF dissolved in 2 mL acetone were added to DI water (150 mL). The mixture was heated under nitrogen atmospheres at 55 C after degassing using six alternating cycles of evacuation and pressurization with high purity nitrogen (starting with evacuation). Polymerization carried out after the injection of a CoBF/MAA mixture (7.5 mg CoBF dissolved in 74.0 g MAA). The reaction was allowed to proceed for 2 h with continuous stirring under nitrogen atmosphere and then quenched with an ice-water bath. The as-prepared PMAA was precipitated in diethyl ether, and then redissolved in DI water and reprecipitated in diethyl ether for several times. UV-vis absorption spectra were taken with a Perkin–Elmer Lambda 900 UV-vis spectrometer with the scan rang from 260 to 450 nm using DMF as solvent. The powder X-ray diffraction (XRD) patterns were conducted on a Bruker-AXS D8 ADVANCE X-ray diffractometer at a scanning rate of 6°/min in 2θ ranging from 10° to 80° with CuKα radiation (λ=0.1542 nm). Fourier transform infrared (FT-IR) spectra were recorded on a NICOLET-NEXUS 670 spectrometer. The samples were grounded with KBr crystal and the mixture of them was pressed into a flake for IR measurement [4]. A high-resolution transmission electron microscope (HRTEM; Model JEOL JEM-2100 electron microscope) was conducted on JEOL JEM-2010 TEM at an acceleration of 200 kV and used to observe the morphology of the NC and the nanocomposites. The samples were dispersed in DMF, and a drop of the solution was placed on a copper grid that was left to dry before transferring into the TEM sample chamber. Molecular weight distributions were analyzed by gel permeation chromatography (GPC) using a Waters 1515 isocratic pump, a Waters 717 plus autosampler, a column set consisting of three Waters Styragel columns (7.8 9 300 mm 2) HR4, HR3, HR1, and a Waters 2414 differential refractive index detector. Tetrahydrofuran (TEDIA, HPLC grade) was used as eluent at 0.6 mL/min. Calibration of the GPC equipment was carried out with narrow polystyrene standards (molecular weight range 1,200–538,000 g/mol).

H-NMR spectra were acquired with a BRUKER DAX 500 with TMS as internal standard in deuterate DMF. Fourier transform Raman (FT-Raman) spectroscopy were performed on an NXR FT-Raman Module by sharing interferometer installed in the Fourier transform infrared (FT-IR) bench. The Raman optics system is comprised of Nd:YVO4 laser operating at 1064 nm, sample holders, an InGaAs detector, and a CaF beam splitter.

controllable fabrication of inorganic–organic polymer hybrid composites based on the molecular level has been extensively investigated due to their potential applications, such as electrochemical sensors, drug carriers and nanocomposites materials. However, it seems to be difficult to obtain well-dispersed inorganic–organic nanocomposites owing to the strong tendency of aggregation among inorganic nanoparticles, which may serve to depress properties of nanocomposites. To this end, considerable efforts have been devoted to the design and controlled fabrication of well-defined inorganic–organic polymer hybrids. There are two principle approaches for attaching polymer chains onto surfaces of nanoparticles, involving chemisorptions, covalent attachment of end-functionalized polymers to a reactive surface ("grafting to") and in situ monomer polymerization with monomer growth of polymer chains from immobilized initiators ("grafting from"). Among these methods, the "grafting from" approach offers the

most promising method in the synthesis of inorganic–organic polymer hybrids with high grafting density. Recently, several research groups have reported the synthesis of inorganic–organic polymer hybrids via "grafting from" method, The assumed mechanism on synthesis of SI-PMMA macromonomers via CCTP is shown in Scheme 3. In catalytic chain transfer polymerization, initiation, propagation and termination are thought to occur by a free-radical process. The Co(II) complex abstracts a hydrogen atom from the polymeric radical on the surface of vinyl-functionalized nanosilica, resulting in the formation of dead PMMA chain with terminal unsaturated double bond and a Co(III)–H complex. This Co(III)–H complex is very reactive and can react with a MMA monomer molecule by a hydrogen transfer reaction, resulting in a monomeric radical and the regeneration of the original Co(II) catalyst. As a result, when increasing the concentration of CoBF, the tendency for Co(II) complex abstracting hydrogen atoms from polymeric radical is intensified. It may further restrain the process of polymer chain propagation, thus leading to the reduction of the grafting degree and molecular weight of PMMA grafted onto the surface of nanosilica. These deduce was also confirmed by the results of FT-IR, TGA and GPC [5].

IV. CONCLUSION

modification of C60 NR surface, through a photopolymerization process, we are able to stabilize the surface so that it can be homogeneously decorated by the palladium nanoparticles in a solution process, without any structural damage. This gives a material that exhibits a much more homogeneous and well-distributed decoration of Pd nanoparticles than reference samples of non-polymerized C60 NRs.

Mn-doped ZnS NCs with good luminescence property could be synthesized with the similar method. Then, the hydroxyl-ending alkyl group thus introduced onto the surface of ZnS NCs enhances their dispersity in solvent, allowing the particle size of NCs to be controlled. We have found that the particle size of the ZnS NC characterized by TEM is about 2.6 nm, in agreement with the calculated data from UV-vis absorption spectra according to Brus's model and Debye–Scherrer formula.

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