Preparation of ZnO Hybrid Nanoparticles by ATRP

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KEYWORDS: ZnO nanoparticle, SI-ATRP, polymer templates, star templates

GRAPHIC ABSTRACT

ABSTRACT:

Zinc oxide (ZnO) is a wide bandgap semiconductor material that has attracted widespread interest as particle filler in polymer nanocomposite materials. However, its applications have been hindered by the limited dispersibility and surface-modification techniques. Herein, three distinct approaches for the synthesis of polymer-tethered ZnO hybrid materials are compared in terms of uniformity and yield of the particle-brush product: “grafting-from”, “grafting-onto”, and “grafted-copolymer template” methods. In the “grafting-from” method, pristine ZnO nanoparticles (NP) were first functionalized with atom transfer radical polymerization (ATRP) initiators followed by grafting-from process to form poly(methyl methacrylate) (PMMA) or poly(styrene-*co*-acrylonitrile) (PSAN) tethered polymer chains. In the “grafting-onto” method, PMMA-*b*-PAA (poly[acrylic acid]) and PSAN-*b*-PAA diblock copolymers were prepared and attached onto the surface of ZnO NPs using sonication bath. For the “grafted-copolymer template” method, PSAN-*b*-PtBA-Br (poly[*tert*-butyl acrylate]-Br) macroinitiators were crosslinked with divinylbenzene (DVB) to form PSAN-*b*-PtBA-PDVB core-shell star polymers. After hydrolysis to form PSAN-*b*-PAA-PDVB star polymers, the functional stars were used as polymer templates for the synthesis of ZnO NPs within the PAA-core of the stars. Core-shell molecular bottlebrushes with PAA-*b*-PS block-copolymer side chains were also used as anisotropic analogues of star template to prepared worm-like ZnO particles. Several ZnO precursors, zinc nitrite, zinc 2-ethylhexanoate, and zinc acetate were evaluated as precursors of ZnO. Conditions were identified that enable the synthesis of polymer-tethered ZnO with excellent size uniformity and dispersion characteristics using the star-template method.

1. Introduction

ZnO nanoparticles (NP) display high thermal conductivity, UV absorption, high refractive index, and photo-catalytic properties. These unique properties resulted in their evaluation in a number of applications, including cosmetic products, electronic sensors, food products, or cancer theranostics.[1-3] To enable these applications, the development of ligand modification strategies to facilitate the stabilization of particles and their processing into functional material forms, is required. Polymeric ligands have attracted particular attention because of their effectiveness in stabilizing particle dispersions (both in liquid and solid matrix) and to enable the processing of “matrix-free” hybrid materials.[4-9]

Two major routes for tethering of polymer chains to the surface of particles are “grafting-onto” and “grafting-from”.[10-12] The “grafting-onto” process involves the coupling of pre-synthesized polymers to functional groups that are exposed at the surface. The principal advantage of “grafting-onto” modification is the simplicity and scalability of the process; however, the low density of tethered chains limits the overall control of material properties. In contrast, the “grafting-from” of polymer chains involves two steps: the binding of low-molecular-weight initiating groups to the particle surface and subsequent formation of polymers via controlled radical polymerization. Because of the low molecular weight initiating groups, the “grafting-from” process affords higher grafting densities and better control of the physicochemical properties of polymer-tethered particles.[13] One of the most established approaches to form hybrid particles using the “grafting-from” method, is surface-initiated atom transfer radical polymerization (SI-ATRP).[10-12] Advantages of SI-ATRP include excellent control of molecular characteristics as well as the diverse range of accessible monomer compositions.[10, 11, 14-16] Suitable coupling agents are necessary for efficient surface modification of nanoparticles with initiators. However, it is difficult to modify the surface of ZnO NP due to its inert nature and limited functionality at the surface. Modifications of ZnO surfaces through thiol,[17] carboxylic acid,[18] and silane coupling agents[19] were reported, but these methods produce ZnO NPs with limited dispersibility.

An alternative approach to fabricate inorganic/polymer hybrid materials is by templating of grafted-copolymer “nanoreactors”.[20-23] A grafted copolymer molecule contains multiple linear polymer arms connected to a backbone (one-dimensional, also called molecular bottlebrush) or at a central core (zero-dimensional, also called star polymer). Star polymers with block copolymer arms are useful nanoreactors for the synthesis of inorganic materials because they form thermodynamically stable unimolecular micelles that enable high uniformity of particle products. Previous studies demonstrated successful fabrication of star polymer nanoreactors via ATRP of block copolymers from a multifunctional core (“core-first”).[20] A large variety of uniform nanoscale polymer/inorganic hybrid materials were successfully synthesized within the star polymer nanoreactors. These well-defined hybrid materials were demonstrated to be applicable to a broad range of fields.[24-31] One convenient method to form star polymers is to crosslink a functional chain end on pre-existing polymeric chains to form the core of the star (“arm-first”).[32] The “arm-first” approach enabled higher graft density in star polymers, and consequently in the hybrid nanoparticles. In addition to spherical star polymer, molecular bottlebrushes were also used as single-molecule templates for fabricating one-dimensional nanostructures such as nanowires and nanotubes due to their worm-like morphologies.[22, 33-41] Nanoparticles were prepared by *in situ* conversion of the inorganic precursors immobilized within the functional block via a specific bonding.[42] Advantages of the “grafted-copolymer nanoreactor” approach include high achievable particle size uniformity, variability of the resulting ligand composition, and good stability of the particle-polymer bonding. The methodology is particularly interesting for ZnO and other ceramic material systems for which covalent and/or dense tethering of ligands is limited by the particle surface chemistry.

Herein, we examined three methods for synthesis ZnO/polymer hybrid NPs: “grafting-from”, “grafting-onto” and use of “grafted-copolymer templates”. Each method was effective for the preparation of stable homogenous dispersions of ZnO NPs of different sizes in both solvents and polymer matrices.

2. Materials and methods

2.1 Materials

All monomers: (2-trimethylsiloxy)ethyl methacrylate (HEMA-TMS, Scientific Polymer Products), *tert*-butyl acrylate (*t*BA, 98% Aldrich), methyl methacrylate (MMA, 99%, Aldrich), styrene (S, 99%, Aldrich), acrylonitrile (AN, 99%, Aldrich), and divinylbenzene (DVB, 80%, Aldrich) were purified by passing through a column filled with basic alumina to remove the inhibitor. Copper (I) bromide (CuBr, 98%, Acros) was purified using literature procedures.[43] Tris[(2-pyridyl)methyl]amine (TPMA) was synthesized according to the previously published procedure.[44] Tri(2-dimethylaminoethyl)amine (Me₆TREN, 99%, Alfa), zinc 2-ethylhexanoate (Zn(EH)₂, 80% in mineral spirits, Alfa), hydrochloric acid (HCl, 36.5-38.0%, Sigma), zinc oxide nanopowder (ZnO, 99.95%, 18nm, US-Nano), zinc nitrate hexahydrate (Zn(NO₃)₂, 98%, Aldrich), sodium hydroxide (NaOH, 98%, Aldrich), trifluoroacetic acid (TFA, 98%, Alfa), anisole (99%, Aldrich), methylene chloride (DCM, 99.5%, Fisher), tetrahydrofuran (THF, 99%, VWR), methanol (99%, VWR), hexane (99%, VWR), acetone (99%, VWR), *N,N*-dimethylformamide (DMF, 99%, VWR), ZnO dispersion(40 wt. % in butyl acetate, Aldrich), α -bromoisobutyryl bromide (2-BiB, Aldrich), ethyl 2-bromoisobutyrate (EBiB, 98%, Aldrich), ethyl 2-bromophenylacetate (EBPA, 97%, Aldrich), *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA, Aldrich), copper(II) bromide (CuBr₂, 99%, Aldrich), triethylamine (TEA, 98%, Aldrich), diphenyl ether (DPE, 99%, Aldrich), zinc acetate (Zn(OAc)₂, 99.99%, Aldrich), tin(II) 2-ethylhexanoate (Sn(EH)₂, 95%, Aldrich), 4,4'-dinonyl-2,2'-bipyridyne (dNbpy, 97%, Aldrich), potassium fluoride (KF, 99%, Aldrich), tetrabutylammonium fluoride (TBAF, 1.0 M in THF, Aldrich), 2,5-di-*tert*-butylphenol (DTBP, 99%), trifluoroacetic acid (TFA, $\geq$ 98%, Aldrich), and 2,2'-azobis(2-methylpropionitrile) (AIBN, 98%, Aldrich) were used as received without further purification.

2.2 Synthesis of polymer grafted ZnO nanoparticles by the “grafting-from” method

2.2.1 Functionalization of ZnO nanoparticles. PMMA and PSAN grafted ZnO nanoparticles were synthesized in two steps. In the initial step initiator functionalized ZnO (ZnO-Br) nanoparticles were synthesized by adding 25 g of ZnO dispersion (40% in butyl acetate) to 200 mL of dry THF in a round bottom flask, then TEA (5.14 mL, 37 mmol) was added to the dispersion. The flask was sealed, transferred to an ice bath and stirred. 2-BiB (4.56 mL, 37 mmol) was added dropwise to the reaction. The flask was stirred for another 48 h at room temperature. The product was washed 3 times with cold methanol and dried in air for 24 h. After removal of all solvents, ZnO-Br NPs were obtained.

2.2.2 General example of surface initiated ATRP procedure. Synthesis of PMMA or PSAN using activators regenerated by electron transfer (ARGET) ATRP from ZnO-Br.[45-47] The polymer brushes were grafted from the surface of initiator-modified zinc oxide nanoparticles using the following procedure: 1.0 g ZnO-Br nanoparticles, Me₆TREN (0.038 g, 0.143 mmol), 30 mM solution of CuBr₂ in DMF (1 mL, 0.030 mmol), anisole (10 mL), and, either MMA (10 mL, 95 mmol) or St (10.5 mL, 95 mmol) and AN (3.7 mL, 57 mmol), were added to a 50 mL Schlenk flask equipped with a magnetic stir bar. The flask was sealed, and the resulting solution was bubbled with N₂ for 30 minutes. 15 mM of a solution of Sn(EH)₂ in anisole (1 mL, 0.015 mmol) was added to the flask to reduce a fraction of the CuBr₂/L to the activator complex. The flask was then immersed in an oil bath set at 70 °C, and the reaction mixture was kept under these conditions for the desired time, MMA system for 1 h while the SAN system for 24 h. The reaction mixture was exposed to air to stop the reaction. Products were precipitated by addition of the solution to cold methanol. The samples were then centrifuged, and the products were redissolved in THF. The resulting suspension was cloudy and unstable. The samples were then centrifuged again to remove the insoluble impurities, which were non-functionalized pristine ZnO nanoparticles. The resulted solution of the polymer functionalized ZnO nanoparticles was concentrated and the particles precipitated by addition of the solution into methanol. Solid products were dried in air for further characterizations.

2.2.2.1 General procedure for cleavage of polymer brushes from nanoparticles. 2 mL of 36.5-38.0% HCl (aq.) solution were added to a 2 mL of solution of the particles in THF (*ca.* 10 mg mL⁻¹), and the reaction was allowed to stir at room temperature for 30 min. The cleaved polymer was isolated by precipitation in cold methanol to remove the zinc salt and acid. After filtration, the remaining methanol was evaporated into the air.

2.3 Synthesis of polymer grafted ZnO nanoparticles by “grafting-onto” method

2.3.1 Synthesis of PMMA-*b*-PAA diblock copolymer.

2.3.1.1 The initial PMMA-Br macroinitiator was synthesized using ARGET ATRP. EBPA (0.20 mL, 1.1 mmol), MMA (12.2 mL, 114 mmol), CuBr₂ (1.3 mg, 0.0057 mmol), Me₆TREN (30 mg, 1.1 mmol) and DMF (0.4 mL) were mixed in a Schlenk flask. The reaction mixture was degassed by N₂ bubbling for 25 min. Meanwhile, a solution of Sn(EH)₂ (28 mg, 0.069 mmol) in anisole (4.1 mL) was degassed. Half of the Sn(EH)₂ solution was injected into the reaction and the mixture was heated to 60 °C in oil bath. After 2.5 h, the other half of the Sn(EH)₂ solution was injected into the reaction. The progress of reaction was monitored with size exclusion chromatography (SEC) and ¹H nuclear magnetic resonance (NMR). At the desired conversion, the reaction was quenched by exposure to air and dilution with 10 mL THF. The PMMA-Br macroinitiator was isolated by precipitation in methanol.

2.3.1.2 Chain extension of PMMA-Br macroinitiator. PMMA-Br (2.0 g, 0.34 mmol), *t*BA (1.5 mL, 10 mmol), CuBr₂ (0.4 mg, 0.002 mmol), Me₆TREN (0.005 mL, 0.02 mmol), and anisole (6.0 mL) were mixed in a Schlenk flask. The reaction mixture was degassed by N₂ bubbling for 15 min and then transferred to an oil bath set at 60 °C. The reaction was stirred for 2 h and quenched by addition of 5 mL THF and exposure to air. The mixture was passed through a flash column filled with neutral alumina to remove all traces of catalyst.

2.3.1.3 Hydrolysis of the *Pt*BA segment. 2.0 g of PMMA-*b*-*Pt*BA diblock copolymer was dissolved in 20 mL DCM. 2.0 mL of TFA was added slowly to the reaction while the solution was vigorously

stirred. The reaction was then stirred at room temperature for 48 h. PMMA-*b*-PAA was isolated as a translucent solid after removal of solvent and acids *in vacuo*.

2.3.2 Synthesis of PAA-*b*-PSAN diblock copolymer.

2.3.2.1 Preparation of PtBA macroinitiator. EBiB (1.0 g, 6.8 mmol), *t*BA (10.0 mL, 68.2 mmol), CuBr₂ (7.6 mg, 0.03 mmol), Me₆TREN (0.091 mL, 0.34 mmol), and anisole (10 mL) were mixed in a Schlenk flask. The reaction mixture was degassed by N₂ bubbling for 40 min and was then transferred to an oil bath set at 60 °C. The reaction was stirred for 2 h and quenched by additional 30 mL THF and exposure to air. The mixture was passed through a flash column filled with neutral alumina to remove residual catalyst.

2.3.2.2 Chain extension of the PtBA-Br macroinitiator with SAN copolymer. PtBA-Br (2.0 g, 0.95 mmol), S (16.4 mL, 142 mmol), AN (3.6 mL, 9.5 mmol), CuBr₂ (5.3 mg, 0.024 mmol), Me₆TREN (6.3 mg, 0.24 mmol) were mixed in a Schlenk flask. The reaction mixture was degassed by N₂ bubbling for 30 min. Meanwhile, a solution of Sn(EH)₂ (58 mg, 0.24 mmol) in anisole (5.5 mL) was degassed. The Sn(EH)₂ solution was injected into the reaction and the mixture was heated to 60 °C in an oil bath. The progress of the reaction was monitored with SEC and ¹H NMR. At the desired conversion, the reaction was quenched by exposure to air and dilution with 15 mL THF. The mixture was passed through a flash column filled with neutral alumina to remove catalyst.

2.3.2.3 Hydrolysis of the PtBA segment. 2.0 g of PtBA-*b*-PSAN diblock copolymer were dissolved in 20 mL DCM. The solution was vigorously stirred and 2.0 mL of TFA was added slowly to the reaction. The reaction mixture was stirred at room temperature for 48 h. The PAA-*b*-PSAN diblock copolymer was obtained as a translucent solid after removal of solvent and acids *in vacuo*.

2.3.3 “Grafting-onto” ZnO nanoparticles. 2.0 g ZnO nanopowder (US-Nano, 18 nm) and 2.0 g PAA-based diblock copolymer were dissolved in 20 mL THF. The mixture was predispersed with a Misonic S-4000 ultrasonic liquid processor with a #419 Microtip probe at amplitude = 70 for 5 min with 1 s interval every second of sonication in an ice bath. The predispersed mixture was then sonicated in a Branson CPX1800H bath sonicator at 50 °C for 48 h. The polymer modified ZnO nanoparticles were

obtained by centrifuging the white dispersion at 14,000 rpm for 5 min. The nanoparticles were redispersed into THF with a Vortex mixer and centrifuged for 3 cycles to remove untethered polymer.

2.4 Synthesis of polymer grafted ZnO nanoparticles by the “grafted-copolymer template” method

2.4.1 Synthesis of PSAN-*b*-PAA-PDVB star polymers. The process for synthesis of PSAN-*b*-PAA-PDVB star polymers consists of four steps: synthesis of PSAN-Br macroinitiators (MIs), synthesis of PSAN-*b*-PtBA-Br block copolymer MIs, synthesis of PSAN-*b*-PtBA-PDVB star polymers, and hydrolysis of PSAN-*b*-PtBA-PDVB star polymers. (**Scheme 1**)

Scheme 1. Synthesis of PSAN-*b*-PAA-PDVB star polymer templates

2.4.1.1 PSAN-Br MIs were synthesized first via ARGET ATRP. A clean dry 200 mL Schlenk flask was charged with CuBr_2 (9.6 mg, 0.43 mmol), TPMA (627.2 mg, 2.1 mmol), S (60 mL, 540 mmol),

AN (20 mL, 324 mmol) and anisole (20 mL). The flask was subjected to sonication and was then bubbled with N₂ for 30 min to remove O₂. EBiB initiator (1.05 mL, 5.4 mmol) was then added to the flask. A mixture of Sn(EH)₂ (0.17 mL) and anisole (10 mL) was deoxygenated by bubbling N₂ for 5-10 min, and 1 mL of the mixture was added to the reaction flask to reduce some of the Cu(II) catalyst complex and initiate polymerization. Then the flask was immersed into an oil bath set at 70 °C. At timed intervals, samples were withdrawn and diluted with THF for SEC (calibrated to PS standards) and with CDCl₃ for ¹H NMR analysis. The reaction mixture was kept under these conditions for the desired time and then it was exposed to air to stop the reaction. The product was precipitated by addition of the reaction mixture to cold methanol to remove catalyst, and dried in air.

2.4.1.2 Chain extension of the PSAN-Br macroinitiator and synthesis of a PSAN-*b*-PtBA-Br block copolymer. The PSAN₇₀-Br initiator (*M*_n=5800 g/mol, 10g, 1.8 mmol), *t*BA (60 mL, 545 mmol), CuBr₂ (23.1 mg, 0.14 mmol), TPMA (150.5 mg, 0.68 mmol), and anisole (25 mL) were added to a clean dry 50 mL Schlenk flask. The flask was sealed with a glass stopper and bubbled with N₂ for 30 min. A mixture of Sn(EH)₂ (0.59 mL) and anisole (10 mL) was deoxygenated by bubbling N₂ for 5-10 min, and 0.1 mL of the solution was added to the reaction flask to reduce some of the Cu(II) catalyst complex and initiate polymerization. The flask was immersed in an oil bath set at 70 °C. At timed intervals, samples were withdrawn and diluted with THF for SEC and with CDCl₃ for NMR analysis. The reaction mixture was kept under these conditions for the desired time and then it was exposed to air to stop the reaction. The product was precipitated by addition of the reaction mixture to a cold mixture of methanol/water (volume ratio=1:1) to remove catalyst, and dried under vacuum.

2.4.1.3 Synthesis of PSAN-PtBA-PDVB star copolymer by ARGET ATRP. A clean dry 100 mL Schlenk flask was charged with PSAN₇₀-*b*-PtBA₄₀-Br MI (*M*_n=11000 g/mol, 12 g, 1.09 mmol), DVB (2.18 mL, 15.2 mmol), CuBr₂ (2.4 mg, 0.01 mmol), TPMA (31.6 mg, 0.11 mmol), and anisole (80 mL). The flask was subjected to sonication and then was bubbled with N₂ for 30 min. The flask was sealed with a glass stopper and immersed in an oil bath set at 110 °C. A solution of Sn(EH)₂ (0.7 mL) in degassed anisole (10 mL) was deoxygenated by bubbling N₂ for 5-10 min, and 0.1 mL of the solution

was added to the reaction flask at different timed intervals – 0, 5, 10, 20, 40, and 50 h to maintain a low concentration of the Cu^I/L complex. At timed intervals, samples were withdrawn via a syringe fitted with stainless steel needle and diluted with THF. The samples were used to measure the monomer conversion and polymer molecular weight by SEC and ¹H NMR, respectively. After 20 h the reaction mixture was exposed to air to stop the polymerization, the unreacted MIs were removed by precipitation of the product in cold methanol, and product was dried under vacuum.

2.4.1.4 Hydrolysis of PSAN-*b*-PtBA-PDVB star polymers 2.0 g of PSAN-*b*-PtBA-PDVB star polymers were dissolved in 20 mL DCM. 2.0 mL of TFA was added slowly to the reaction while the solution was vigorously stirred. The reaction was stirred at room temperature for 48 h. The PSAN-*b*-PAA-PDVB star polymer was obtained as a white solid after precipitation in hexane and removal of solvent and acids under vacuum.

2.4.2 Synthesis of PSAN capped ZnO nanoparticles from star polymer templates. The PSAN-*b*-PAA-PDVB star polymers were used as templates for formation of ZnO nanoparticles. 100 mg PSAN-*b*-PAA-PDVB star polymer was dissolved in a 10 ml DMF followed by addition of appropriate amounts of ZnO precursors [Zn(NO₃)₂, Zn(OAc)₂, Zn(EH)₂], that were selectively incorporated into the inner PAA blocks. The molar ratio of AA units in the PAA blocks to precursors was set at 1:10 to ensure the complete loading of precursors into the PAA domains. The mixture solutions were stirred at room temperature overnight. Then the mixture was refluxed at 180 °C for 5h. A transparent ZnO nanocomposites DMF dispersion was obtained after removing the remaining solids from the reaction.

2.4.3 Synthesis of one-dimensional ZnO hybrids. One-dimensional ZnO hybrids were synthesized following previously reported procedures for synthesis of one-dimensional TiO₂ hybrids, with ZnO precursors.[33]

2.5 Characterization

Number average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were determined by SEC, conducted with a Waters 515 pump and Waters 2414 differential refractometer using PSS columns

(Styrogel 105,103, 102 A) in THF as an eluent (35 °C, flow rate of 1 mL min⁻¹). Linear PS and PMMA standards were used for calibration. Conversion was calculated by detecting the decrease of the monomer peak area relative to the peak area of the internal standards. ¹H NMR spectroscopy used for polymerization monitoring was performed using a Bruker Advance 300 MHz NMR spectroscope with CDCl₃ as a solvent.

Transmission electron microscopy (TEM) was performed using a JEOL 2000 EX electron microscope operated at 200kV. The size of the particles was determined from statistical analysis of the TEM micrographs using ImageJ software. Dynamic light scattering (DLS) using a Malvern Zetasizer Nano ZS was also employed to determine volume-weighted average hydrodynamic radius and distribution to confirm the results obtained from TEM. The particles were suspended in filtered THF or DMF (220 nm PTFE filter) at micro concentrations. To characterize the structure and crystallinity, a Philips X'Pert (Philips Analytical, Netherlands) X-ray diffractometer (XRD) (Cu-K α radiation) was operated at 45 kV and 40 mA in grazing incidence mode. The fraction of ZnO in the nanocomposite was measured by thermogravimetric analysis (TGA), TA Instrument 2950, and the data was analyzed with TA Universal Analysis. The heating procedure involved 4 steps: 1) samples were placed on a Platinum pan and the temperature jumped to 120 °C in air atmosphere; 2) the temperature was held at 120 °C for 10 mins; 3) ramp up at a rate of 20 °C/min to 800 °C; 4) hold for 5 mins. The TGA plots were normalized to the total weight of the sample after holding at 120 °C. The grafting densities of hybrid particles were calculated using the following equation:

$$\sigma_{\text{TGA}} = \frac{(1 - f_{\text{ZnO}})N_{\text{A}} \rho_{\text{ZnO}}d}{6 f_{\text{ZnO}} M_{\text{n}}} \quad (1)$$

where is f_{ZnO} the ZnO fraction measured by TGA after exclusion of any residual solvent; N_{A} is the Avogadro number; ρ_{ZnO} is the density of zinc oxide NPs; d is the average diameter of ZnO NPs; M_{n} is the overall number average molecular weight of polymer brushes.

3. Results and Discussion

3.1 Synthesis of polymer grafted ZnO NPs by “grafting from” method

The selection of a suitable coupling agent is important for a successful “grafting-from” method. Herein, 2-BiB was chosen as surface modifier for pristine ZnO NPs (~25 nm in diameter) to introduce active -Br onto the surface of NPs which were then used as ATRP initiators.ARGET ATRP with low concentration of copper was employed instead of conventional ATRP, owing to the facile setup and simplified catalyst removal process.[48] Two kinds of particle brushes: PMMA-g-ZnO and PSAN-g-ZnO NPs, were prepared, as illustrated in **Scheme 2**. During the polymerization, a large amount of unmodified pristine ZnO NPs precipitated from the solution. Only ca. 30 wt% ZnO NPs were successfully functionalized by 2-BiB, due to the poor functionalization of the inert ZnO surface with ATRP initiators.

Scheme 2. Synthesis of polymer brush grafted ZnO NPs by "grafting-from" method

Table 1. PMMA/PSAN-g-ZnO nanoparticles prepared by "grafting-from" method

Sample Identity	M_n (polymer brush) ^a	Inorganic fraction ^b	Grafting density (nm ⁻²) ^c	Average diameter (nm) ^d
PMMA-g-ZnO	169,700	34%	0.16	260
PSAN-g-ZnO	98,100	44%	0.18	180

^a Determined by SEC; ^b determined by TGA; ^c calculated from inorganic fraction and polymer molar mass assuming all nanoparticles are spherical; ^d z-average hydrodynamic diameter in THF determined by DLS

Both of the hybrid particle products, PMMA-g-ZnO and PSAN-g-ZnO NPs, were dispersed in THF to form stable and transparent solutions. However, DLS showed that these ZnO/polymer nanoparticles

formed aggregates with diameter of 150-300 nm (PMMA-*g*-ZnO 260 nm, PSAN-*g*-ZnO 180 nm) As shown in Table 1, the inorganic content of ZnO/polymer hybrids are 34 and 44 wt% for PMMA-*g*-ZnO and PSAN-*g*-ZnO measured by TGA corresponding to grafting densities of 0.16 nm⁻² for PMMA-*g*-ZnO and 0.18 nm⁻² for PSAN-*g*-ZnO, respectively. Grafting density >0.15 nm⁻² would be sufficient to stabilize these clusters in solutions.[49]

Figure 1. (a and b) TEM images with different magnifications of the PMMA-*g*-ZnO NPs, which showed the ZnO/polymer composites uniform clusters morphology; (c) TGA trace indicating *ca.* 65 wt% polymers in this PMMA-*g*-ZnO composite; (d) hydrodynamic size distribution measured by DLS in THF.

Figure 2. (a and b) TEM images with different magnifications of the PSAN-*g*-ZnO NPs, which showed the ZnO/polymer composites uniform clusters morphology; (c) TGA trace indicating *ca.* 55 wt% polymers in this PMMA-*g*-ZnO composite; (d) hydrodynamic size distribution measured by DLS in

Figure 1 and **Figure 2** show that the hybrid particles formed uniform cluster structures with gaps in between, which were distinct from pristine ZnO NPs (Figure S1). The relatively broadly dispersed particle brush samples were observed by DLS. This probably results from the fact that unmodified surface of the NPs tended to agglomerate and form clusters and polymer brushes are grafted from the surface of the agglomerate to form the shell and prevent further aggregation of the NPs.

3.2 Synthesis of PSAN/PMMA capped ZnO by “grafting-onto” method

The “grafting-onto” approach is a widely used method to fabricate polymer grafted NPs. The grafting of PMMA or PSAN brushes onto ZnO NPs was accomplished via exploitation of the strong affinity of carboxylates to the ZnO surfaces (**Scheme 3**).[50]

Scheme 3. Synthesis of PSAN/PMMA-*b*-PAA capped ZnO by "grafting-onto" method

Table 2. PSAN/PMMA capped ZnO by "grafting-onto" method

Inorganic filler	Polymer ^a	Inorganic fraction ^b	Grafting density (nm ⁻²) ^c	Average diameter (nm) ^d
ZnO ^e	PAA ₁₂ - <i>b</i> -PSAN ₆₂	93%	0.11	160
	PAA ₁₂ - <i>b</i> -PMMA ₅₉	92%	0.13	122

^a Determined by SEC before hydrolysis; ^b determined by TGA; ^c calculated from inorganic fraction and polymer molar mass assuming all nanoparticles are spherical; ^d z-average hydrodynamic diameter in THF determined by DLS; ^e supplied by US Research Nanomaterials as dry powders, diameter 18 nm as claimed by the supplier.

As shown in **Table 2**, two diblock copolymers each with a short poly(acrylic acid) (PAA) block were synthesized via ATRP and hydrolysis of the *Pt*BA segments. In order to synthesize PAA-*b*-PSAN, and prevent distinction of reactivity of S-Br and AN-Br chain ends,[51] a short *Pt*BA block was initially synthesized via initiator for continuous activator regeneration (ICAR) ATRP followed by chain extension with an azeotropic mixture of S and AN.[52] In the case of the PAA-*b*-PMMA, a PMMA-Br macroinitiator was synthesized first to avoid inefficient initiation from acrylate chain end.[53] The *tert*-butyl group was hydrolyzed with 10 vol% TFA in DCM.

In both cases, the NPs were first dispersed in THF with a sonicating probe to sufficiently expose the surface of the particles to the carboxylic acids. After that, the reaction mixture was sonicated in a bath at 50 °C for 48 h. No sediment was observed in the resulting dispersion. However, the two samples

displayed distinctly different results. A low level of aggregation of PSAN-*g*-ZnO NPs, of ca. 150 nm, was observed by both DLS and TEM (**Figure 3** and **Figure 4**). In contrast, PMMA-*g*-ZnO displayed an insignificant degree of aggregation. The difference in polarity between PSAN and PMMA may contribute to such difference.

Figure 3. DLS hydrodynamic size distributions. 1 mg/mL dispersion in THF: (a) PMMA-*b*-PAA capped ZnO NPs showing $\langle D_h \rangle = 122$ nm with narrow size distribution peak at *ca.* 20 nm and slight aggregation signal at *ca.* 50-300 nm, (b) PSAN-*b*-PAA capped ZnO NPs showing $\langle D_h \rangle = 160$ nm with size distribution ranging from 60-300 nm.

Figure 4. TEM images of PMMA-*g*-ZnO NPs via “grafting-onto” approach. Negligible aggregation was observed. Inset: magnified TEM image.

3.3 Synthesis of PSAN capped ZnO by “star template” method

As illustrated in **Scheme 4**, an “arm-first” method was applied to the synthesis of PSAN-*b*-PAA-PDVB star polymers, which can be used as a soft template for the fabrication of ZnO hybrid nanomaterials.[54-56] ARGET ATRP was used for both the preparation of the multifunctional macroinitiator (MI) and linkage of the arms by chain extension with DVB. Initially, a highly

functionalized, PSAN-Br macroinitiator, with $M_n = 5,800$ and $M_w/M_n = 1.12$ was synthesized via ARGET ATRP. The macroinitiator was chain extended with a second monomer, *t*BA, to form PSAN-*b*-P*t*BA-Br diblock copolymer. During the chain extension polymerization, the SEC traces of the product shifted to higher molecular weight, indicating the formation of diblock copolymers (Figure S4). Finally, DVB was employed to simultaneously chain extend and cross-link the PSAN-*b*-P*t*BA-Br MIs to form the PSAN-*b*-P*t*BA-PDVB star copolymer. A timed-feeding method was used in the reaction to control the concentration of activator in the system forming PSAN-*b*-P*t*BA-PDVB star block polymers ($M_n = 67,800$, $M_w/M_n = 1.88$). After deprotection of the P*t*BA segments with TFA, the PSAN-*b*-PAA-PDVB star polymers were obtained. The SEC traces in Figure S4 showing decreasing signal corresponding to the unreacted MIs and increasing peak at higher molecular weight region suggests the formation of star polymers.

Zn(EH)₂ is an appropriate precursor for in situ synthesis of ZnO particles because it is cost-effective, air-stable, and non-toxic.[57] Zn(EH)₂ precursors were loaded into PSAN-*b*-PAA-PDVB star polymer templates. The hydrophilic PAA blocked inside the core impart preferential incorporation of Zn(EH)₂ into the interior space of the star via a strong coordination bonding between the metal moiety and the carboxylic groups of PAA segments whereas the outer PSAN corona did not complex with Zn(EH)₂ and remained unloaded. Excess Zn(EH)₂ was loaded into the star template solutions to ensure saturation of PAA cores with precursors. The hybrid nanomaterials were then refluxed in DMF at 180 °C for complete hydrolysis of Zn(EH)₂ to form ZnO NPs within star templates. The shell of the nanoparticles was intimately and permanently connected with hydrophobic PSAN blocks. PSAN coronas prevented intermolecular cross-linking during hybrid formation and solubilize the ZnO hybrid NPs in organic solvents (e.g. toluene, THF, chloroform, DCM, DMF, etc.) to form stable and transparent solutions. Unbound ZnO NPs formed from excess precursors in the solution were removed by centrifugation. A summary of the synthetic route is illustrated in Scheme 4.

Scheme 4. Hybrid ZnO nanoparticles formation using PSAN-*b*-PAA-PDVB star copolymer templates.

After infiltration and thermal hydrolysis of $\text{Zn}(\text{EH})_2$ within the star templates, the chains within PAA compartment were stretched. The average diameter of the star increased to 25 ± 2 nm compared to the 18 ± 2 nm of the pristine unloaded star templates as measured by DLS (

Figure 5e). ZnO NPs were homogeneously dispersed in the polymer with no free ZnO NPs in the background as assessed by TEM (Figure 5a-c). The ZnO NPs had good uniformity with diameter of 3-5 nm. TEM images of inorganic particles formed from the precipitates of free ZnO NPs in the solution show aggregation of nanostructures indicating that the presence of hydrophobic PSAN blocks was crucial to ensure the miscibility of NPs with the host matrix by preventing aggregation and encouraging dispersibility.

The XRD patterns (Figure S5 and S6) confirm the formation of crystalline ZnO. The XRD patterns consist of diffraction peaks corresponding to the reflections from (100), (002), (101), (102) and (110) planes of a wurtzite ZnO crystal (JCPDS-36-1451). Peak broadening suggests that the individual crystalline NPs were quite small. TGA determined the weight fraction of ZnO in the star templates with 40 repeating units of PAA to be 11.7 wt%.

Star templates with various degrees of polymerization (DP = 40, 70, and 90, respectively) were used to study the effect of star template size on ZnO NP formation. Retaining an equal DP of PSAN on the star template shell facilitated better comparison of the amount of inorganic loading in the PAA core, as shown in samples 1, 2 and 3 for the ZnO NPs. in Table 3. TGA determined the weight of ZnO in the star templates increased from 11.7 wt% with DP 40 of PAA to 27.5 wt% with DP 90 of PAA. These data suggest that PAA with relatively high DP increased chain mobility, loaded more $\text{Zn}(\text{EH})_2$ precursors into the core, and subsequently increased the loading capacity. Conversely, the diameter of

ZnO NPs ($D_{\text{ZnO-NP}} \sim 3\text{-}5\text{ nm}$) was essentially independent of the DP of PAA DP in the core of star templates. A possible reason for the independence of the ZnO NP size on the PAA block length may be that the longer PAA block results in a lower PAA block density within the compartment partially occupied by PAA chains, thus allowing a larger degree of collapse of PAA blocks.

Figure 5. (a, b, and c) TEM images of PSAN capped ZnO NPs synthesized by different star polymer templates and $\text{Zn}(\text{EH})_2$ precursors: (a) PSAN₇₀-*b*-PAA₄₀-PDVB star copolymer, (b) PSAN₇₀-*b*-PAA₇₀-PDVB star polymer, (c) PSAN₇₀-*b*-PAA₉₀-PDVB star polymer. All TEM images indicated homogeneous dispersion of ZnO NP. (d) TGA traces of PSAN-*b*-PAA-PDVB ZnO NP showing increasing organic content with DP of the PAA blocks; (e) DLS hydrodynamic size distributions of PSAN-*b*-PAA-PDVB ZnO NPs in DMF showing the increase of size with DP of the PAA blocks and after loading.

Table 3. Results of PSAN-*b*-PAA-PDVB star copolymer templates the ZnO NPs.

Entry	Composition	$M_{n, \text{PSAN}}^a$	$M_{n, \text{PAA}}^a$	$M_{n, \text{star}}^a$	M_w/M_n^a	$D_{h, \text{star}}^b$ (nm)	$D_{h, \text{star+ZnO}}^c$ (nm)	ZnO Frac ^d	Diameter of ZnO NP (nm) ^e
1	PSAN ₇₀ - <i>b</i> -PAA ₄₀ -PDVB	5,800	11,000	67,800	1.88	16±1.8	20±2.2	11.7%	3-5
2	PSAN ₇₀ - <i>b</i> -PAA ₇₀ -PDVB	5,300	13,000	60,600	3.0	18±2.0	22±1.8	17.2%	3-5

	A ₇₀ -PDVB								
3	PSAN ₇₀ - <i>b</i> -PA	6,000	17,000	61,300	3.0	20±2.2	24±2.3	27.5%	3-5
	A ₉₀ -PDVB								

a) Molecular weights and molecular weight distributions were measured by THF SEC using linear PS standards as calibration; b) D_h of PSAN-*b*-PAA-PDVB star polymer in DMF measured by DLS; c) D_h of PSAN-PAA-PDVB star polymer loading with ZnO NPs in DMF measured by DLS; d) the amount of inorganic ZnO NPs of hybrid materials measured by TGA; e) the diameter of ZnO NPs measured by TEM.

In order to study the effect of the Zn precursors on the ZnO NPs, three different zinc compounds, Zn(EH)₂, Zn(NO₃)₂, Zn(OAc)₂, were used as ZnO precursors and formed complexes within PSAN₇₀-*b*-PAA₄₀-PDVB templates. The morphology, size and crystallinity of ZnO crystals was assessed by TEM (**Figure 6**). The diameter of ZnO NPs was observed to be approximately 8, 4-5 and 3 nm for the precursors Zn(NO₃)₂, Zn(EH)₂ and Zn(OAc)₂, respectively. ZnO NPs from Zn(NO₃)₂ had a higher contrast than that of Zn(EH)₂ and Zn(OAc)₂, but the yield of the NPs was not as high. It can be seen from TEM images (Figure S7) that there were some free ZnO NPs aggregated in the background. KOH is a strong base and can efficiently react with Zn(NO₃)₂ to form Zn(OH)₂. The decomposition of Zn(OH)₂ is much faster than that of an organic acid based zinc, such as Zn(EH)₂ and Zn(OAc)₂. The base (KOH) more readily forms a complex with Zn²⁺ than the PAA, resulting in the formation of Zn(OH)₂ in the solution. The Zn(OH)₂ in solution formed free ZnO NPs, which is the reason for the low yield of ZnO NPs.

ZnO templates could be directly obtained from Zn(EH)₂ and Zn(OAc)₂ after reflux in DMF due to the metal-oxygen bond in the organometallic precursors. These ZnO NPs dispersed well in good solvents and selected polymers with good uniformity. The diameter of ZnO NPs from Zn(OAc)₂ was smaller than that of Zn(EH)₂. All samples were identified by XRD as wurtzite ZnO crystals. These results demonstrated that the size of ZnO NPs was dependent on the composition of the zinc precursors.

Figure 6. TEM images of PSAN capped ZnO synthesized by PSAN₇₀-*b*-PAA₄₀-PDVB star copolymer template and different ZnO precursors: (a) Zn(NO₃)₂ and NaOH, (b) Zn(EH)₂, (c) Zn(OAc)₂. All three samples displayed good dispersibility.

Figure 7. (a) TEM image of PSAN capped ZnO NPs synthesized by reloading presynthesized PSAN capped ZnO with Zn(OAc)₂ precursor; (b) TGA traces of PSAN capped ZnO Ns showing increased inorganic content after 2nd loading; (c) DLS hydrodynamic sizes of PSAN capped ZnO nanoparticles in DMF solutions growing with the loading of ZnO.

Dispersions were prepared by dispersing purified hybrid ZnO NPs in DMF and adding Zn(EH)₂ precursors in excess. The hybrid nanomaterials in DMF were then refluxed at 180 °C to ensure complete hydrolysis of the incorporated Zn(EH)₂ precursors. TEM showed the size of ZnO NPs increase greatly from 5 nm to 20 nm after sequential loading. DLS also showed *D_h* of star copolymers containing ZnO NPs increase from 20 nm to 45 nm with increase of inorganic content from 11.7 to 30 wt% measured by TGA, **Figure 7a**. These results demonstrated that the initially encapsulated ZnO NPs could be used as seeds to grow larger NPs through sequential loading of Zn(EH)₂ precursors.

ZnO nanoparticles were also prepared using brush-like templates (PBiBEM₃₇₂-*g*-(PAA₄₇-*b*-PS₉₂)) with poly(acrylic acid)-block-polystyrene (PAA-*b*-PS) side chains, as previously reported [33].

Scheme 5. Hybrid ZnO nanoparticles formation using PAA-PS brush-like templates

Anisotropic nanoparticles with a worm-like structure were observed in the TEM images (Figure 8). The statistical analysis of TEM images indicates that the number-average lengths of the worm-like nano-objects 75 nm with dispersity (L_w/L_n) = 1.08. The length of each repeat unit in backbone is calculated to be 0.16 nm, indicating the backbone of brush-like template does not adapt fully extended conformation. Effective control over the width of nanoparticles is supported by the dispersity of width as low as 1.04.

Figure 8. TEM images of ZnO nanoparticles prepared from brush-like templates.

Table 4. TEM characterization of the length (L_n) and core diameter (W_n) of zinc oxide hybrid nanoparticles prepared from brush template.

Template ID	L_n (nm)	L_w/L_n^a	W_n (nm)	W_w/W_n^a
L ₃₇₂ A ₄₇ S ₉₂	75±1	1.08	15.0±0.3	1.04

^a Dispersity index of zinc oxide nanoparticles length or width obtained from TEM images.

4. Conclusions

ZnO/polymer hybrid materials with different sizes were successfully synthesized by three different methods: “grafting-from”, “grafting-onto” and “grafted-copolymer template”. Both SI-ATRP (using 2-BiB to introduce ATRP initiators onto the surfaces) as well as the “grafting-onto” method (by surface-adsorption of PMMA/PSAN-*b*-PAA diblock polymers) were successfully used to tether PMMA to commercial ZnO nanoparticles and to enable their dispersion in organic solvents. However, gradual aggregation of particles in solution confirms a low grafting density that limits the stabilization of particles. In contrast, polymer tethered ZnO nanoparticles are synthesized in a one-step procedure using PSAN-*b*-PAA-PDVB star polymers and PAA-*b*-PS copolymer brushes as template for particle synthesis. $\text{Zn}(\text{NO}_3)_2$, $\text{Zn}(\text{OAc})_2$, $\text{Zn}(\text{EH})_2$ were studied as precursors of ZnO formed within the PAA-core of the star copolymers, among which $\text{Zn}(\text{EH})_2$ turned out to be the best choice taking cost, yield, and quality into account. Excellent particle size uniformity was obtained using the star template method and dispersions were stable without indication of aggregation. Given the wide range of chemical compositions of possible star-polymer template compositions the technique could conceivably be used to tailor the compatibility of ZnO particles to a wide range of organic media. The development of convenient methods for the synthesis of ZnO-polymer hybrid materials with controlled size and inorganic composition could therefore broaden the future applications of ZnO based materials, including drug delivery, photo catalyst, and electronic sensors.

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ACKNOWLEDGMENT

Funding provided by the following organizations: the National Science Foundation (DMR 1501324, DMR 1436219); DOE (EE 0006702); the National Science Center (2014/14/A/ST5/0020); the Natural Science Foundation of China (NSFC51273022).

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