

Poly(Glycidyl Methacrylates)-grafted Zinc Oxide Nanowire by Surface-initiated Atom Transfer Radical Polymerization

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Poly(glycidyl methacrylates) (PGMA) was grafted from zinc oxide (ZnO) nanowires via surface-initiated atom transfer radical polymerization (SI-ATRP) technique. Firstly, the ZnO nanowires were synthesized by the one-pot hydrothermal technique. Subsequently, the ZnO was functionalized with 3-aminopropyl triethoxysilane, which was converted to macroinitiator by the esterification of them with 2-bromopropionyl bromide. PGMA grafted ZnO nanowires (PGMA-ZnO) were then synthesized in an ATRP of the GMA with CuCl₂, 2'-bipyridine as the catalyst system. Kinetics studies revealed an approximate linear increase in weight of polymer with reaction time, indicating that the polymerization process owned some "living" character. The structure and composition of PGMA-ZnO were characterized with scanning electron microscope (SEM), energy-dispersive X-ray (EDX) spectrometer, fourier transform infrared spectroscopy (FT-IR) and thermogravimetric analysis (TGA).

Keywords: ATRP; Glycidyl methacrylates; Surface-initiated; Zinc oxide nanowires

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ZnO nanowires are one of the most promising materials for optoelectronic applications due to their wide band gap of 3.37 eV and large exciton binding energy of 60 meV [1]. It has been recognized as one of the promising nanomaterials in a broad range of high-technology applications, such as photodetector [2], light-emitting diode [3], gas sensor [4], solar cell [5], and optical modulator waveguide [6], etc. Work in this area has focused on the synthesis and material properties of ZnO nanostructures, and thus, a wide array of materials are available [7, 8]. The properties of these nanostructures, and our ability to assemble them, depend largely on the surface functionalization of such structures.

Surface-initiated polymerization, generally called "grafting from", is an important tool to further develop their chemical and physical properties by covalently graft a wide range of polymer chains onto curved or flat surfaces [9-12]. In comparison with

traditional processes used to prepare polymer coatings, surface-initiated polymerization methods provide numerous advantages, including chemical attachment of the polymer to the surface, [13] preparation of conformal coatings on objects of various shapes [14], and good control over film thickness and composition [15].

One of the most successful processes is ATRP [16-18], which offers efficient, well-controlled grafting and narrow molecular weight distributions of the polymers grown from the surfaces. The radical reactions involved in the ATRP process enable a wide range of monomers to be used, leading to polymer-modified surfaces with new functionality [16]. This, together with the halogen end-groups, can significantly enhance the physicochemical compatibility of the resulting composites, making the design and preparation of novel materials with

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tailorable structures and properties accessible. ATRP reactions have already been used effectively to modify the surfaces of many nanostructured, such as silica surfaces [19], the surfaces of gold [20], magnetic nanoparticles [21], and carbon nanotubes [22], in each case, providing stability and/or other desirable surface properties. In contrast to the large body of work detailing the modification of silica surfaces, we are aware of only a few reports of related chemistry with ZnO in which a silane was used to modify the surface [23, 24].

In this work, the PGMA was grafted from the initiating groups modified ZnO nanowires via the SI-ATRP for the first time. The grafted organic layer composed of PGMA could provide a platform for further surface modification by functionalization of the epoxy groups. The template wires from these inorganic-organic hybrid structures can then be etched away to leave polymers.

Experiment section

Materials

ZnCl₂ and Na₂CO₃ were provided by Shanghai Chemical Co. and used without further purification. 3-aminopropyl triethoxysilane (99.0%) (Aldrich), CuBr₂ (99%) (Aldrich) and 2-bromopropionyl bromide (2-BPB) (97.0%) (Fluka) were all used as received. Glycidyl methacrylate (GMA, Aldrich, 97%) was obtained from Aldrich Chemical Co. and purified over calcium hydride (CaH₂) under vacuum distillation. CuCl (Beijing Chemical Co.) was purified by precipitation from acetic acid to remove Cu²⁺ and then dried. 2,2'-Bipyridine (bpy, Beijing Chemical Co.) was used without further purification. N, N'-dimethylformamide (DMF) was dried with CaH₂ and distilled under vacuum. Triethylamine (Beijing Chemical Co.) was refluxed for 12 h in the presence of CaH₂ and distilled. All the reagents used in this study were of analytic grade.

Synthesis of ZnO nanowires

The synthesis of ZnO nanowires were performed according to the report described previously [25]. 0.3 g ZnCl₂ and 30 g Na₂CO₃ were successively added into a 100 mL Teflon-lined stainless steel autoclave, which was then filled with distilled water up to 90% of the total volume. The obtained reaction mixture was stirred for an additional 30 min. The autoclave was sealed and maintained at 140°C for 12 h. After the reaction was completed, the resulting white products were filtered off, washed with ethanol and hot distilled water for several times, and then dried in a vacuum at 60°C for 4 h.

Immobilization of the initiator on ZnO surface

1 g ZnO nanowires were put into the solution of 1 ml of 3-aminopropyltriethoxysilane in 5 ml of dry toluene for 24 h at room temperature, then the ZnO nanowires were cleaned under ultrasonic treatment in dry toluene and absolute ethanol successively, finally dried under vacuum. Subsequently, 1 g ZnO nanowires were immersed into the solution of 2 mL of triethylamine in 5 mL dry toluene and then cooled in an ice bath (0°C). After 5 min of stirring, 5 mL of a dichloromethane containing 2-BPB (1.5 mL) was added dropwise to the solution over a period of 1 h. The reaction was carried out at 0°C for 2 h and then at room temperature for 22 h. The ZnO nanowires were purified with toluene and absolute ethanol, respectively, and then dried under vacuum. The initiator-immobilized ZnO nanowires were either used immediately for polymerization or stored in a dry box at room temperature.

Synthesis of PGMA brushes on the ZnO surface

A dry flask equipped with a magnetic stirrer was charged with CuCl (0.036 g, 3.6×10⁻⁴ mol), bpy (0.168 g, 1.08×10⁻³ mol), and ZnO nanowires initiator (0.2 g). The reaction vial was sealed and degassed three times by freeze-pump-thaw cycles. Pre-degassed solvent DMF (3 ml) and monomer GMA (4 g, 2×10⁻² mol) by argon were introduced into the flask via an Ar-washed syringe. Subsequently, the reaction flask was immersed in a constant temperature (90°C) oil bath for the given time. Aliquots (about 0.8 mL of reaction mixture) were removed from the reaction mixture at selected time intervals to monitor the reaction progress. The reaction was rapidly terminated in an ice bath. The crude polymer was precipitated in methanol three times, and then dried under vacuum overnight.

The removing of ZnO nanowires from PGMA-ZnO nanowires by the hydrolysis

0.3 g PGMA-ZnO nanowires were dispersed in a 10 ml of hydrochloric acid (1 mol/L). The mixture was stayed for 48 h at room temperature. After hydrolysis, the powder was centrifuged for 5 min at 4000 rpm/min. The crude polymer was washed with water three times, and then dried under vacuum overnight.

Techniques and measurement

The morphology and structure of the samples were inspected using a field emission scanning electron microscopy (FE-SEM, XL 30, Philips) equipped with energy-dispersive X-ray (EDX) spectrometer and a transmission electron microscope. The infrared spectra (IR) of polymers were recorded on a NICOLET Impact 410 at room temperature. Dried samples (20 mg) were mixed with 100 mg of dry KBr and pressed into

disk ($100 \text{ kg}\cdot\text{cm}^{-2}$). Thermogravimetric analysis (TGA) was performed with a Perkin-Elmer TGA-7 system (Perkin-Elmer Corporation, USA) at a scan rate of $10^\circ\text{C min}^{-1}$ to 800°C at a N_2 atmosphere.

Result and discussion

Synthesis of ZnO nanowires

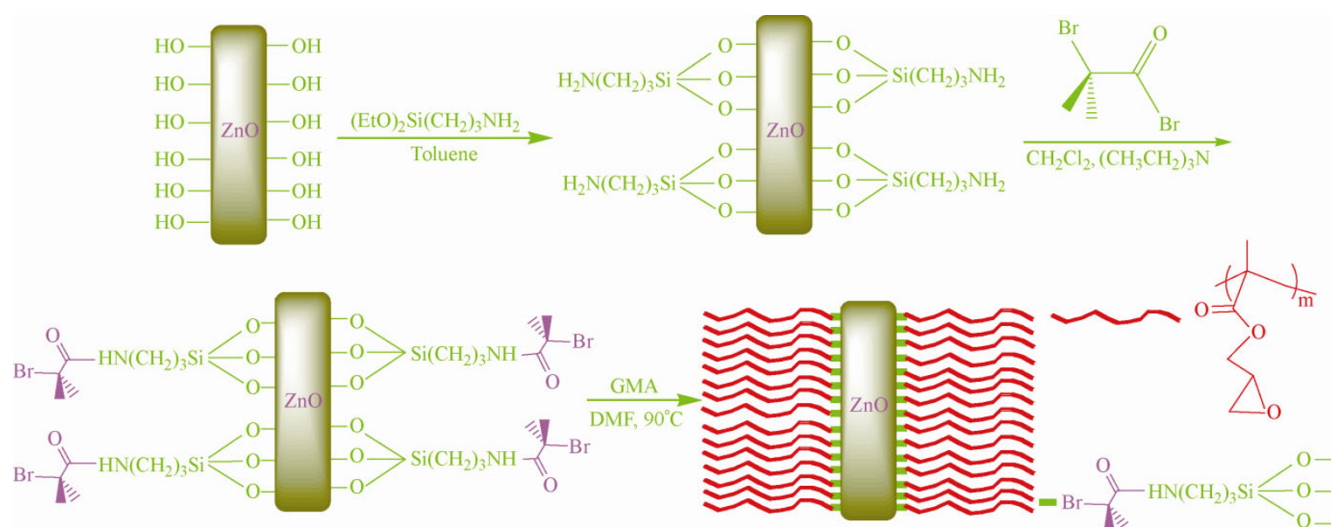
The synthesis route of the ZnO nanowires was shown in scheme 1. Figure 1(A) shows the high-magnification FESEM image of the obtained sample, which indicates that the as-synthesized ZnO products were wire-like nanostructures, and their lengths are up to $20 \mu\text{m}$. The diameters of ZnO nanowires are about 60-100 nm. Further structural characterizations of the ZnO nanowires were performed by EDX. The elements of Zn and O can be detected in the EDX pattern and their atomic percent is shown in the inset. It indicates that the atomic ratio of Zn to O is approximately 1:1. According to EDX patterns, it can be deduced that ZnO nanowires were synthesized successfully and have a high purity.

Immobilization of the initiator on ZnO surface

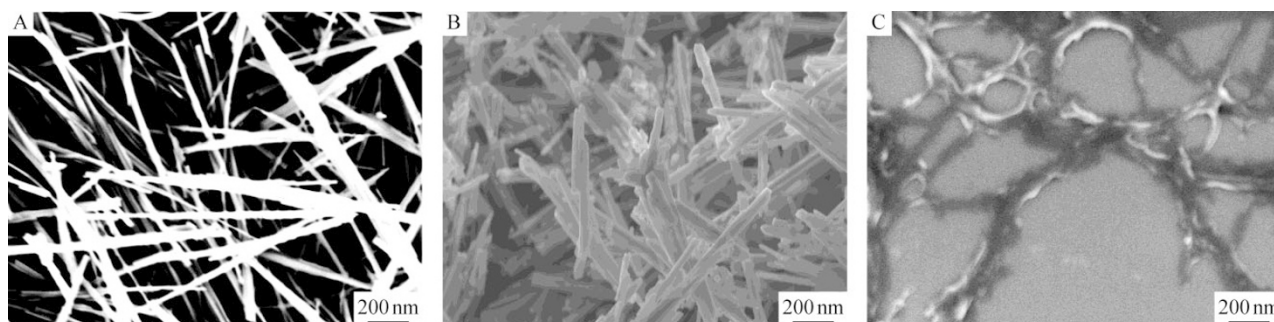
To prepare the polymer brush on the ZnO surface, a

uniform and dense layer of initiators immobilized on the ZnO surface is indispensable. Scheme 1 outlines the route to generate the ATRP initiator on the ZnO surface. The α -bromoester initiator on the ZnO substrate was prepared by the self-assembly of 3-aminopropyl triethoxysilane, followed by amidization with 2-BPB. FTIR (Fig. 3 A) was used to confirm the formation of the initiator monolayer. The characteristic absorption bands appeared in the wavenumber region of 1450 cm^{-1} was assigned to the methyl of the initiator, which indicated the successful immobilization of the initiator on the ZnO surface.

The ATRP of GMA from initiator ZnO-Br was carried out in DMF at 90°C using CuCl/bpy as the catalyst system. A new absorbance band at 1732 cm^{-1} of the characteristic of the ester groups was appeared in the FT-IR spectrum of the products (Fig. 3B), the characteristic bands at 2950 cm^{-1} were assigned to the stretching of methyl group in the PGMA blocks. These indicated that the PGMA chains had been successfully grafted from the surfaces of the macroinitiator. Further structural characterizations of the functionalized ZnO nanowires were performed by EDX, as shown in Fig. 2B. The elements of Zn and O can be detected in the EDX pattern and their atomic percent is shown in the inset. It indicates that the atomic ratio of Zn to O has been



Scheme 1. Surface functionalization of ZnO Nanowires and polymerization of the initiator-functionalized wires.



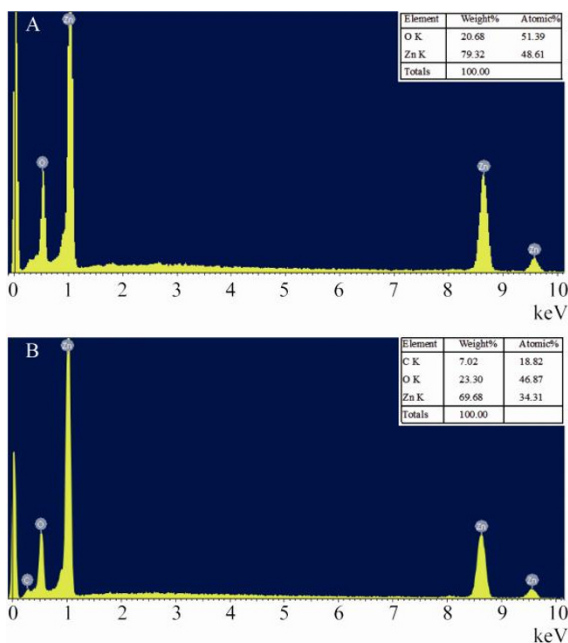


FIG. 2. Energy dispersive X-ray spectroscopy of (A) ZnO nanowires; (B) PGMA-ZnO nanowires.

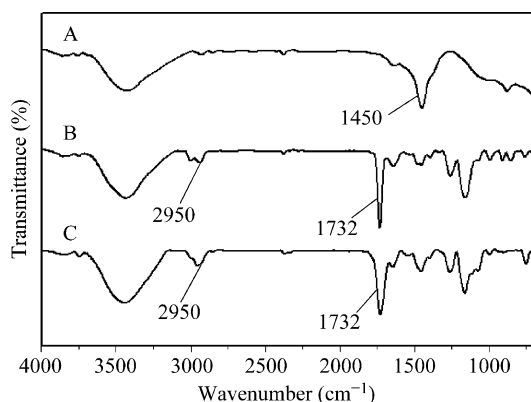


FIG. 3. IR spectra of (A) ZnO-NH₂ nanowires; (B) PGMA-ZnO nanowires; (C) after treatment of PGMA-ZnO nanowires in HCl solution.

marginally changed after ATRP process, which suggests that the functionalization of ZnO nanowires has been successfully achieved.

To investigate the content of the polymer on the ZnO nanowires, we carried out the TGA characterization. In the TGA curve of the PGMA-ZnO nanowires (Fig. 4), the weight loss at near 100°C is assigned to the release of moisture adsorbed. And the weight loss at the temperature range of 250–550°C is assigned to the thermal degradation of the grafted PGMA. As far as the ZnO nanowires (Fig. 4A) is concerned, the weight was nearly not changed. As for the PGMA-ZnO nanowires (after the reaction was going on 12 h) (Fig. 4B), the weight decreased to 32%, which means that the content of the polymer in PGMA-ZnO nanowires was 68%. The kinetics of SI-ATRP

of GMA was studied by monitoring the changes in the polymer content of the PGMA-ZnO nanowires by TGA as a function of time. To prove the controlled nature of the polymerization initiated from the surface by the ZnO-Br macroinitiator, the effects of the polymerizing time on the PGMA weight % was investigated (Fig. 5). They increased linear with the increasing of the polymerizing time. It indicated that the ATRP of GMA

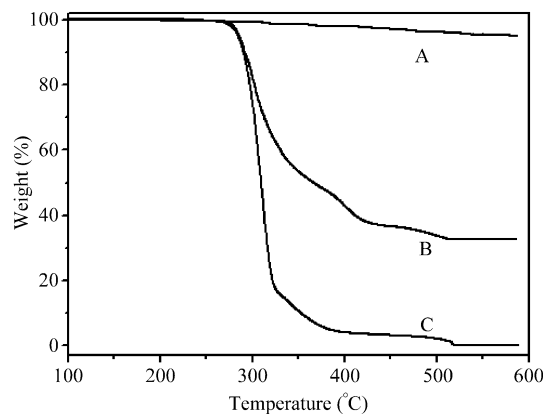


FIG. 4. TGA curve of (A) ZnO nanowires; (B) PGMA-ZnO nanowires; and (C) after PGMA-ZnO nanowires in HCl solution.

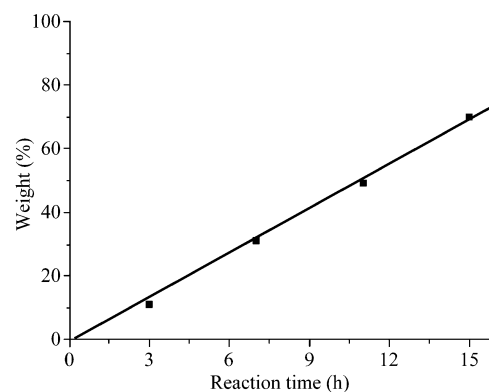


FIG. 5. The effect of the polymerizing time on the polymer weight values.

showed the characteristics of the controlled/“living” radical polymerization.

Attempts were made to prepare polymer nanotube by removing the ZnO nanowires in hydrochloride acid, but polymers failed to make well-formed tubes (Fig. 1C), instead forming disordered polymer thin films. We studied ZnO nanowires with different thickness of polymer, but they are never sufficient to give normal polymer nanotubes. We deduced that the soft polymer will be collapsed and adhered together after the template ZnO was removed. The FTIR spectrum of the products (Fig. 3C) is similar to PGMA-ZnO nanowires (Fig. 3B), which indicated that the polymer component was not changed. To prove the ZnO nanowires were removed completely, the product was investigated by TGA. The result (Fig. 4C) shows that the

product was degraded completely, which proved the product has no ZnO component.

Conclusion

Organic-inorganic hybrid materials were synthesized successfully. PGMA was grafted from the ZnO semiconductor nanowires via the copper-mediated SI-ATRP technique. By controlling the time of polymerization, along with the amount of monomers added, both the amounts and the properties of the polymer can be tailored. The SI-ATRP procedure showed the characteristics of the controlled "living" radical polymerization. The grafted organic layer composed of PGMA could provide a platform for further surface modification by functionalization of the hydroxyl groups. It is also expected to be used for the assembly of the ZnO semiconductor devices.

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