Atom-Transfer Radical Polymerization on Zinc Oxide Nanowires

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Atom-transfer radical polymerization (ATRP) has been used to modify the surface of ZnO nanowires with a variety of methacrylate and styrene polymers in a living fashion. The polymers show narrow polydispersities ($M_n/M_w = 1.10-1.19$), and polymerization could be reinitiated after removal of the nanowires from solution. The surface coverage of covalently attached molecules (determined using UV−vis spectroscopy) was found to be 95 ± 0.9 Å/molecule. The polymerization reactions were analyzed using SEM, TEM, size-exclusion chromatography, and elipsometry. Carbon tubes with graphitic domains were isolated from the pyrolysis of polymer-coated wires and were characterized by SEM, TEM, and Raman spectroscopy.

Introduction

Wurzite ZnO nanowires have drawn much attention as building blocks for incorporation into devices because of their novel optical and electronic properties.[1,2] Work in this area has focused on the synthesis and material properties of ZnO nanostuctures,[3] and thus, a wide array of materials are available.[3,4] The properties of these nanostructures, and our ability to assemble them, depend largely on the surface functionalization of such structures. Surface-initiated polymerization promises to be an important tool to further develop their chemical and physical properties in that it provides a potential method for covalently attaching a densely packed array of polymer chains.[5] Such modifications can help tailor important properties including wetting, aggregation, optical emission, electron transport, and chemical stability of the nanostructures.

Following our work on the growth of polymer brushes on SiO_2 surfaces,[5] we have now extended this approach to ZnO nanowire surfaces. In contrast to the large body of work detailing the modification of silica surfaces, we are aware of only a single report of related chemistry with ZnO in which a silane was used to modify the surface.[6]

Here, we report the details of ZnO nanowire elaboration with small molecules and covalently attached polymers. This modification was quantified using a simple experiment designed to estimate the density of surface functionalization. These modifications change the wetting properties of the ZnO nanowires, and the resulting composite materials were then used to create new porous carbon materials. This work demonstrates the growth of a range of polymers from ZnO surfaces. Using ZnO as a template, the polymers reported here also are shown to serve as precursors for carbon tubes via pyrolysis. These carbon tubes are orders of magnitude larger than typical carbon nanotubes and are shown to consist of graphitic and amorphous domains.

Experimental Section

General. All reactions were carried out under an inert atmosphere (N_2) either in a glovebox or using standard Schlenk techniques. Glassware was dried overnight in an oven at 140 °C, unless otherwise noted. Toluene and methylene chloride were dried and purified by passage through activated alumina under a positive pressure of N_2, purged with argon, and stored under an inert atmosphere. Dioxane was distilled from sodium, purged with argon, and stored under an inert atmosphere. All reagents were obtained from Aldrich, except for copper(I) bromide, which was obtained from Strem. Methyl methacrylate, ethylene glycol dimethacrylate, phenyl methacrylate, and styrene were distilled from CaH_2 under a N_2 atmosphere prior to use and stored under an inert atmosphere. All other compounds were used as received. Deuterated benzene was obtained from Cambridge Isotope Laboratories. Surface initiators **1** and **2** were synthesized as previously reported,[5] as was tris(2-(dimethylamino)-ethyl)amine (HMTREN).[7] The synthesis of both the wire arrays[8] and the dispersed wires[9] have also been reported previously. Unless otherwise noted, the experiments were carried out on 0.5−1.0 cm^2 silicon substrates on which the wire arrays were grown.

^{1}H and ^{13}C spectra were recorded on a Bruker DRX-500 (500-MHz) spectrometer. ^{1}H chemical shifts (δ) are reported in parts per million (ppm) relative to residual protonated solvent (C_6D_6, 7.16). Infrared spectra were recorded on a Mattson Genesis Series FTIR spectrometer. UV−vis spectra were recorded on a Varian Cary 50 spectrometer. Mass spectra were recorded on VGProSpec

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(EI) and VG ZAB (FAB) mass spectrometers. Size-exclusion chromatography (SEC) in THF was performed at 35 °C at a nominal flow rate of 1.0 mL/min on a chromatography line calibrated with linear polystyrene standards (162−1 007 000 Da) and fitted with three 5-μm PLgel columns having pore sizes of 10^5, 10^3, and 500 Å. Detection was performed at 25 °C with a Wyatt Optilab DSP interferometric refractometer ($\lambda = 690$ nm). All SEC data were analyzed using Millennium software from Waters. Contact-angle measurements were made using a KSV Instruments Cam100 apparatus. Raman spectra were obtained using a Renishaw micro-Raman system microscope with a green diode-pumped solid-state laser at 532 nm as the excitation source. Scanning electron micrographs were obtained using a field-emission scanning electron microscope (FESEM, JEOL6430) at the National Center for Electron Microscopy (NCEM). Images were obtained with an operating voltage of 5 kV. Transmission electron micrographs were obtained using an analytical electron microscope (AEM, JEOL 200CX) operating at 200 keV located at NCEM. The ZnO nanowire surface area was measured by isothermal nitrogen adsorption using an ASAP 2010 sorptometer from Micromeritics (Norcross, GA); surface area was calculated using the BET model.

Surface Modification of Wire Arrays (4a and 4b). Any residual organic species from the ZnO synthesis were removed by heating the wire arrays to 450 °C for 30 min. Clean wires were then introduced into a small volume of a 10 mM solution of initiator **1** or **2** in anhydrous toluene under N_2 for 8 h at 80 °C with gentle stirring to yield **4a** or **4b**, respectively. The wires were then washed several times with 2-propanol in the air. The modification of the surface of these nanowires was monitored using contact-angle measurements. Before modification, the ZnO arrays had a contact angle of 0°; after modification with **1** or **2**, the arrays had a contact angle of 90−100°.

Surface Modification of Dispersed Wires (5 and 6). The wires were cleaned of any organic residue by being heated to 450 °C for 4 h. A 100-mg sample of the wires was then placed in 4 mL of a 10 mM solution of either initiator **2** or UV tag **3** in anhydrous toluene with gentle stirring for 8 h under N_2 at 80 °C to yield **5** or **6**, respectively. The wires in suspension were washed by increasing the final volume after functionalization to 10 mL in 2-propanol under atmospheric conditions. The wires were transferred to a polyethylene centrifuge tube and spun at 6000 rpm for 30 min. The supernatant was poured off, and the process was repeated two more times by adding 10 mL of 2-propanol and dispersing the wires by sonication for 20 min and subsequent spinning down.

Polymerizations in the Absence of Free Initiator. Under an atmosphere of nitrogen, 4.5 mg (0.031 mmol) of CuBr and 24.5 mg (0.0600 mmol) of 4,4′-dinonyl-2,2′-dipyridine were dissolved in 1.00 mL of dioxane. A surface-initiator-functionalized nanowire array, **4b**, was introduced into the solution, followed by 0.20 mL (0.19 g, 1.8 mmol) of methyl methacrylate or 0.20 mL (0.21 g, 1.1 mmol) of ethylene glycol dimethacrylate, and the reaction mixture was heated to 50 °C for 16 h. After polymerization, the reaction vessel was opened to the atmosphere, and the nanowire array was removed and rinsed thoroughly with acetone.

Methacrylate Polymerizations with Free Initiator. Under an inert atmosphere, 0.750 g (0.725 mL) of a solution 10.0 mM (0.00928 mmol) each in CuBr and 4,4′-dinonyl-2,2′-dipyridine in dioxane was added to a Schlenk flask containing a surface-initiator-functionalized nanowire sample, **4a** or **4b**, followed by 0.250 g (0.242 mL) of a solution of ethyl 2-bromo-2-methylpropionate in dioxane (9.2 mM, 0.00223 mmol, or 14.3 mM, 0.00346 mmol). Then, 1.00 g of methyl methacrylate (9.99 mmol) was added, and the flask was heated to 50 °C for 4−48 h. Alternatively, 1.60 g (9.86 mmol) of phenyl methacrylate was used, and the solution was heated to 50 °C for 24 h. The viscous solution was poured off the substrate through air into 20 mL of stirred hexanes, and the precipitated solids were collected by vacuum filtration. These solids were dried overnight at 65 °C in a vacuum oven, and a 1 mg/mL sample was prepared in THF for characterization by size-exclusion chromatography. The polymer-coated ZnO wire substrate was allowed to stand for 1 h in acetone and then rinsed with several portions of acetone to remove any free polymer from the surface. In cases where the polymerization was reinitiated, the substrate was isolated from the polymerization solution and, after through rinsing, brought into a glove box. Under an inert atmosphere, a fresh solution of catalyst, ligand, and monomer in dioxane was added to the Schlenk flask containing the substrate with polymer.

Styrene Polymerization. Using a procedure adapted from the literature,[10] 0.279 g (0.295 mL) of a DMF solution that was 20.8 mM (0.0644 mmol) in each HMTREN and CuBr was added, under an inert atmosphere, to a Schlenk flask containing 0.205 g (0.217 mL) of a 32.1 mM solution (0.0694 mmol) of 2-bromo-2-methylpropionate in DMF and a surface-initiator-functionalized nanowire sample, **4b**. Styrene (1.50 g, 1.65 mL, 14.4 mmol) was then added, and the solution was heated to 110 °C for 6 h. The substrate and polymer were then isolated and worked up as in the above polymerizations.

Undec-10-enyl 1-Naphthoate. 1-Naphthoyl chloride (3.20 mL, 4.05 g, 21.2 mmol) was added slowly via syringe to a stirred solution of 4.00 mL (3.40 g, 19.9 mmol) of 10-undecen-1-ol and 3.00 mL (2.18 g, 21.5 mmol) of triethylamine in 100 mL of anhydrous methylene chloride that was chilled on an ice bath. The solution was stirred for 0.5 h in the ice bath and then overnight at room temperature. Fifty milliliters of hexanes was then added, and the copious precipitate was filtered off. The solvent was then removed by rotary evaporation, and the resulting pale yellow oil was taken up in 50 mL of methylene chloride. The solution was washed with dilute HCl, dilute NaOH, and deionized water and then dried with $MgSO_4$, which was then removed by vacuum filtration. Rotary evaporation yielded 5.74 g (88.9%) of a pale yellow oil. ^{1}H NMR (500 MHz, C_6D_6): δ 9.35 (1H, d, $J = 8.5$ Hz), 8.27 (1H, d, $J = 7$ Hz), 7.62 (1H, d, $J = 8$ Hz), 7.56 (1H, d, $J = 8$ Hz), 7.41 (1H, dd, $J = 7, 7$ Hz), 7.23 (1H, dd, $J = 6.5, 8.5$ Hz), 7.22 (1H, dd, $J = 6.5, 7$ Hz), 5.77 (1H, m), 5.08−4.99 (2H, overlapping peaks), 4.29 (2H, t, $J = 7$ Hz), 2.00 (2H, m), 1.58 (2H, m), 1.34−1.19 (12H, overlapping peaks). ^{13}C (125 MHz, C_6D_6): δ 167.68, 139.58, 134.73, 133.80, 132.56, 130.80, 129.13, 126.97, 126.78, 114.90, 34.56, 30.18, 30.13, 29.97, 29.82, 29.67, 29.46, 26.76. MS (HREI): m/z found 324.209084, calculated 324.208930. IR (cm^{-1}, neat): ν 3082 (w), 3052 (w), 2925 (s), 2853 (s), 1715 (s), 1640 (w), 1593 (w), 1577 (w), 1510 (m), 1465 (m), 1438 (w), 1278 (s), 1243 (s), 1197 (s), 1135 (s), 1075 (m), 1052 (m), 1011 (m), 909 (m), 885 (w), 813 (w), 782 (s), 741 (w), 656 (w), 510 (w).

11-(Triethoxysilyl)undecyl 1-Naphthoate (3). Undec-10-enyl 1-naphthoate (3.01 g, 9.28 mmol) and triethoxysilane (1.76 g, 10.7 mmol) were combined in a 25-mL Schlenk tube under N_2. The mixture was heated to 85 °C, and 3.5 mg (0.015 mmol) of PtO_2 was added. The solution was stirred at 85 °C for 10 min, after which time a deep brown color had developed, and then at room temperature overnight. The dark, slightly viscous solution was diluted with 10 mL of hexanes and filtered through florisil and a frit. Rotary evaporation afforded a yellow oil, which was purified by column chromatography (10:1 ethyl acetate/hexanes). The product was isolated as a pale yellow oil (2.36 g, 52.0%). ^{1}H NMR (500 MHz, C_6D_6): δ 9.45 (1H, d, $J = 9$ Hz), 8.27 (1H, d, $J = 7$

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Hz), 7.63 (1H, d, $J = 8$ Hz), 7.57 (1H, d, $J = 8$ Hz), 7.41 (1H, dd, $J = 9$, 10 Hz), 7.23 (1H, dd, $J = 9$,10 Hz), 7.13 (1H, dd, $J = 7$, 8 Hz), 4.29 (2H, t, $J = 7$ Hz), 3.84 (6H, q, $J = 7$ Hz), 1.65 (2H, m), 1.59 (2H, m), 1.37−1.19 (23H, overlapping peaks), 0.83 (2H, m). ^{13}C (125 MHz, C_6D_6): δ 167.67, 134.74, 133.78, 132.58, 130.81, 129.13, 126.99, 126.77, 125.01, 65.53, 58.83, 33.99, 30.38, 30.36, 30.28, 30.17, 29.48, 26.79, 23.86, 19.01, 18.75, 11.57. MS (FAB, NBA + LiCl): m/z 495 $[(M + Li)^+]$, 443 $[(M-OCH_2CH_3)^+]$, 397 $[(M-2\{OCH_2CH_3\}-H)^+]$. IR (cm^{-1}, neat): ν 3051 (w), 2974 (s), 2926 (s), 2854 (s), 1716 (s), 1594 (w), 1577 (w), 1510 (m), 1462 (m), 1442 (m), 1389 (m), 1367 (w), 1346 (w), 1278 (s), 1244 (s), 1197 (s), 1167 (m), 1133 (s), 1104 (s), 1076 (s), 1013 (m), 957 (m), 884 (w), 782 (s), 656 (w), 509 (w). UV−vis: λ_{max} 296, ϵ 6266.

Measurements of Density of UV Tag on the Surface of ZnO Nanowires. Approximately 50 mg of UV-tag-modified wires, **6**, was dissolved in 20 mL of a solution consisting of 10% by volume of concentrated HCl in 2-propanol. After dissolution was complete, the solution was diluted to 25.00 ± 0.03 mL. Three samples were prepared: A 0.500 wt % solution of **3** in acidic 2-propanol was prepared to use in the standard addition. Absorption measurements were made on the as-prepared dissolved nanowire sample and on samples consisting of 3.00 ± 0.01 mL of this solution plus approximately 8, 16, 24 and 32 mg (see Supporting Information) of the standard addition solution. Each measurement was made three times, and the 10 vol % HCl in 2-propanol solution was used as a background. Linear regression of added **3** vs absorption was performed in Excel using the LSFit macro to take uncertainty in volumes and weights into account. From the original concentration of **3** in solution, the volume of solution, weight of ZnO used, and surface area per gram of ZnO, the density of functionalization of **3** could be calculated (see Supporting Information).

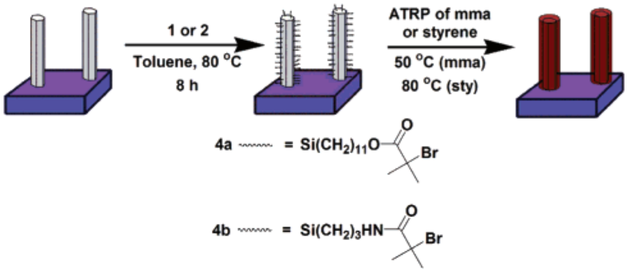
Pyrolysis. The pyrolysis of the polymers on ZnO substrates was performed in a tube furnace at 700 °C for 4 h under a flow of H_2/Ar. Experiments were also conducted in the absence of H_2 in N_2 and Ar. Substrates for pyrolysis were prepared using both dip-coating and ATRP methods. Arrays prepared by dip-coating were immersed in a 5% solution by weight of polyacrylonitrile (PAN) in DMSO. These substrates were then allowed to dry under a flow of N_2, before being placed in the tube furnace. Substrates prepared by ATRP were used as isolated from the polymerization reactions.

Results and Discussion

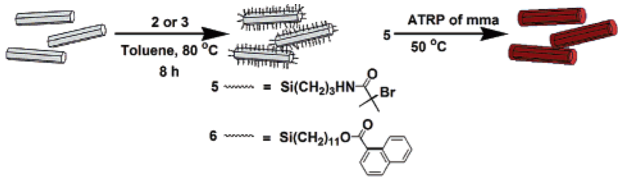
Surface Modification of ZnO. The modifications of both ZnO arrays (grown from Si wafers in aqueous conditions)[8] and solutions of nanowires (synthesized at high temperatures in trioctylamine)[9] were carried out in similar fashions. For the condensation of our modified silanes to occur at the surface, all residual organics had to be removed from the wire surfaces. This was accomplished using a thermal treatment at 450 °C in ambient atmosphere for at least 30 min. The bare ZnO wires were then introduced into a dilute solution of initiator **1** or **2** or UV tag **3** in anhydrous toluene under N_2 for 8 h at 80 °C. It was found that using anhydrous toluene and gentle stirring prevented overcondensation of initiator. When wet toluene was used, a relatively thick coating, which could be seen by TEM to be several nanometers thick, was sometimes found.

In the case of the wire arrays, the modification of the surface was monitored using contact-angle measurements. Before modification, the ZnO arrays had a contact angle of 0°; after modification with **1**, **2**, or **3**, the arrays had a contact angle of 90−100°. The modification of the wires in solution could be qualitatively observed by the change in their suspension behavior. After modification of ZnO in solution with small molecules, the time needed for them to make a homogeneous suspension in 2-propanol was dramatically shorter than that for bare ZnO nanowires. After polymer was grown from the surface, the wires immediately formed a suspension upon addition of 2-propanol. This suspension persisted for hours before the nanowires started to gradually begin to settle, unlike the unmodified wires, which rapidly settled out of a suspension.

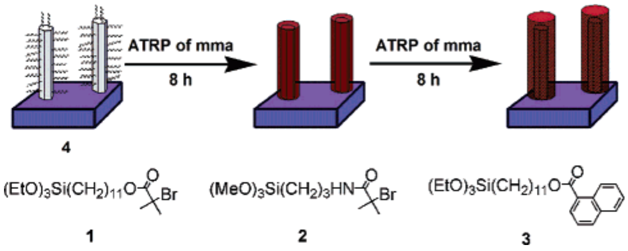
Scheme 1. Surface Functionalization of ZnO Nanowires Grown from Si Surfaces with Polymer Initiator Groups Followed by Polymerization



Scheme 2. Surface Functionalization of Dispersed ZnO Nanowires and Polymerization of the Initiator-Functionalized Wires



Scheme 3. Reinitialization of an Isolated Polymer-Coated Nanowire Sample



Initiator and UV Probe Synthesis. Derivatives of 2-bromo-2-methylpropanoate have been shown to be good initiators for ATRP both in solution and from surfaces.[10−12] Although carboxylic acids have been used as the anchoring functionality for dyes, the attachment can fail under aqueous conditions or at elevated temperatures. In contrast, condensation of the hydroxylated ZnO surface with a silane produces a more robust anchor. Matyjaszewski and co-workers have used a trichlorosilane group to modify silica for ATRP;[13] however, this is not feasible with ZnO, as even the small amount of acid produced in the condensation reaction causes significant

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damage to the nanostructures. For this reason, the trialkoxysilyl functionality was preferred. Details of the synthesis of **1** and **2** have been given previously.[5]

To estimate the density of surface functionalization, a quantifiable tagging scheme based on the high sensitivity of UV−vis spectroscopy was chosen. We sought to label the initiator molecule with a UV tag in as minimal a manner as possible so that the functionalization density measurements were still valid for comparison to our polymerization system. For these reasons, the triethoxysilane anchor and undecyl chain linker in initiator **1** were retained, whereas the initiating head group was replaced with a naphthalene unit. This new UV-active tag was made by the condensation of 1-naphthoyl chloride with 10-undecen-1-ol, followed by hydrosilation with PtO_2 to yield the desired product, **3**, after purification by column chromatography.

Functionalization Density Determination. Modification of the surface was analyzed by anchoring of the UV-tagged initiator mimic **3** to the nanowire surface, followed by dissolution of the ZnO wires and measurement (in solution) of the quantity of **3** liberated. These measurements were carried out on the bulk "free" wires, as these were available in larger quantities (and therefore larger total surface areas) than wafer-grown wires.

Three samples of ZnO wires were treated with a dilute solution of **3** as described above. The wires were then dissolved with 2-propanol/HCl (95/5 vol %), and the concentration of **3** was determined by measuring the absorbance at $\lambda_{max} = 296$ nm. (Full experimental and calibration curve data are available in the Supporting Information.)

Surface area measurements made on premodified wires using BET nitrogen adsorption isotherms gave a specific surface area of 10.7 ± 0.1 m^2/g. This value is close to the value of 18 m^2/g that was calculated from the average wire dimensions of 40 nm × 2.5 μm. After the total surface area and total number of molecules of **3** in each sample have been measured, the surface density can be found, which is usefully expressed as Å^2/molecule. Averaged data for all three samples show a density of 95.0 ± 0.9 Å^2/molecule. Although this value represents a slightly less dense packing than has been found for long-chain alkylsilanes on other metal oxide surfaces (SiO_2, TiO_2, ZrO_2; typically in the range of 25−45 Å^2/molecule),[14,15] we note that El Harrak and co-workers found the density of mercaptopropyl triethoxysilane on silica nanoparticles to be in the range of 20−100 Å^2/molecule, depending on the reaction conditions. El Harrak et al. found that densities of 100 Å^2/molecule were optimal for further functionalization and surface-initiated ATRP.[10]

Surface Initiation of Methacrylate-type Polymers. Polymerizations of methacrylic monomers using several catalyst and solvent systems were studied. First, two literature methods were investigated. These employed a copper(I) catalyst with a bipyridyl-type ligand at or near room temperature, with water and either ethanol[16] or DMF[17] as the cosolvent. Neither system gave reproducible polymer coatings, and furthermore, SEM images showed that the ZnO nanowires were damaged under these conditions. We found that more promising results were obtained using anhydrous conditions with a catalyst and solvent combination developed earlier in our laboratory.[5]

Copper amine complexes have been the most successful and widely used ATRP catalysts to date. In the case of methacrylate polymers, bipyridyl-type ligands (particularly 4,4′-bis-(1-butyl-pentyl)-[2,2′]bipyridinyl, dNbpy) have been employed in low-polarity solvents where solubility can be an issue. We have found that 4,4′-dinonyl-[2,2′]bipridinyl is a reasonable (and commercially available) alternative to dNbpy. Although these types of ligands are often used with copper(I) chloride, we have found that copper(I) bromide can be used at lower temperatures to give good control of the polymerization. Under these conditions, dioxane was found to give better control than more polar solvents, such as acetonitrile.

Methyl methacrylate-type polymers were reproducibly grown from ZnO nanowire surfaces functionalized with 1 and **2** to give materials **4a**,**b** and **5** (Schemes 1 and 2) using essentially the same procedure as in our previous work with Si/SiO_2 wires.[5] The two initiators gave indistinguishable results.

Approximately 10-nm layers of both cross-linked (ethylene glycol dimethacrylate) and non-cross-linked PMMA-type polymers were grown from ZnO arrays by introducing surface-initiator-modified arrays into a solution of dinonylbipyridine, CuBr, and monomer in dioxane at 50 °C overnight. These solutions did not include any free initiator. The catalyst system was found to be quite oxygen-sensitive, and when proper precautions were not taken, the characteristic yellow-brown color of the dilute Cu(I) solution was replaced with a rich green indicative of Cu(II) formation.

Thicker layers of PMMA were obtained by adding ethyl 2-bromo-2-methylpropionate to the polymerization solution as free initiator (Figure 1); this increased the copper(II) concentration in solution, leading to a more controlled polymerization reaction. This is a common practice in surface-initiated ATRP, and the effects of added free initiator have been well studied.[11] All polymerizations, except in the previously mentioned experiments, were carried out in the presence of free initiator. By varying the polymerization time, polymer layers of controlled thicknesses, from approximately 3 to 14 nm, could be obtained, as shown in Figure 2. The 14-nm upper limit of the thickness was dictated by the spacing between the wires on the silicon substrate. Contact-angle measurements of the polymer-coated wires showed an increased contact angle compared to the surface-initiator-functionalized arrays on the order of 105−110°. Phenyl methacrylate was also grown from ZnO surfaces, yielding results similar to those obtained with the MMA system. Specifically, after 8 h, 4.7 ± 1.7 nm of polymer was obtained on the wire surface.

In cases where free initiator was added to the reaction solutions, polymer grown in solution could be isolated and

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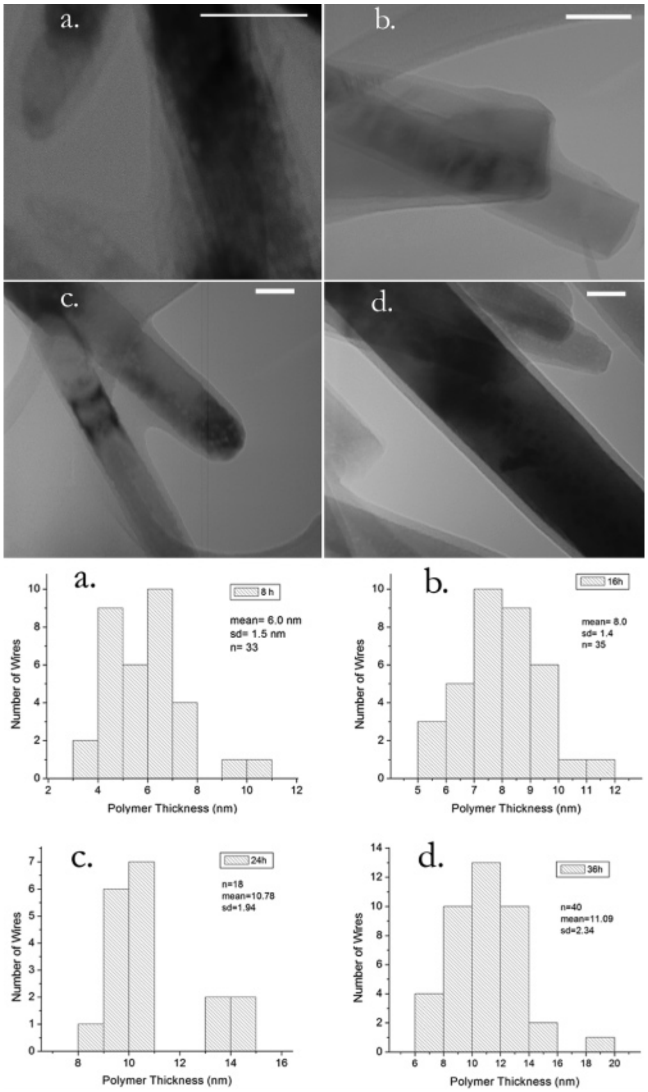

Figure 1. Representative TEM micrographs of ZnO nanowires coated with poly(methyl methacrylate) (PMMA). All scale bars represent 50 nm. The various images were recorded for samples subjected to polymerization conditions for (a) 8, (b) 16, (c) 24, and (d) 36 h. Below the images are included the thickness distributions for the polymer at each of these polymerization times.

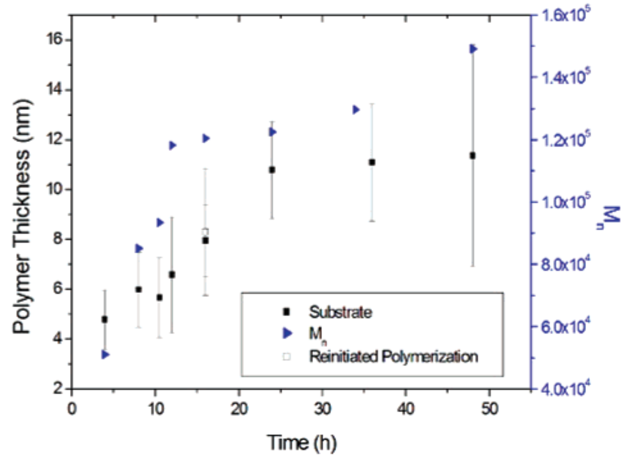

Figure 2. Change in polymer thickness as a function of time (squares), which can be seen to increase with time (error bars are drawn at one standard deviation). As expected, the M_n value of the polymer formed in solution (triangles) follows the same trend as the thickness.

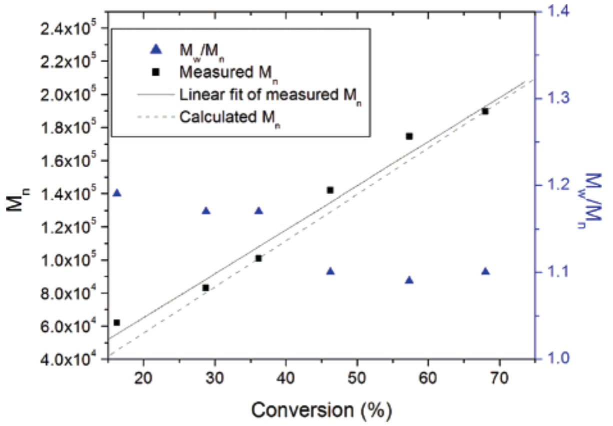

Figure 3. Dependence of M_n on percent conversion (squares), which follows very close to the predicted trend (dashed line). PDI (triangles) as a function of percent conversion, which decreases slightly with increasing conversion, as expected for ATRP.

analyzed. For example, in a polymerization with a monomer-to-initiator ratio of 2790:1 (assuming one polymer chain for each initiator molecule), the theoretical number-average molecular weight, M_n, is 279 299 for PMMA. The amount of initiator present on the surface of the ZnO substrate was negligible compared to the amount of initiator in solution. As can be seen in Figure 3, the measured M_n agrees well with the calculated M_n at each conversion point recorded. The polydispersity fell from 1.19 at low conversion to 1.10 at 68% conversion. These characteristics, along with the ability to reinitiate polymerization with added monomer, indicate a living polymerization. The rate, however, was somewhat low, as 48 h was required to achieve this degree of conversion.

Reinitiation of polymerization from the surface was tested by resubjecting a polymer-coated nanowire sample to the polymerization conditions (Scheme 3) and analyzing the change in polymer thickness. A sample of ZnO wires grown from silicon substrate and coated with initiator was subjected to the standard MMA polymerization conditions for 8 h. The resulting substrate was thoroughly washed with acetone, then placed back into an identical, fresh polymerization solution for 8 h, and again washed thoroughly. Reinitialization yielded a polymer layer 8.3 ± 2.5 nm thick (see Figure 2), whereas the original 8 h sample had a polymer layer of 6.0 ± 1.5 nm. This is essentially the same as the 8.0 ± 1.4 nm found on the substrate surface after a single 16-h polymerization using the same monomer-to-initiator ratio (4500:1). This same experiment was repeated with reaction times of 24 h for both the first and second polymerizations. SEM images of this substrate showed a polymer layer that almost completely filled the voids between the ZnO wires; this is significantly more polymer than was present after the first 24-h polymerization. (See the Supporting Information for the SEM micrograph of the filled sample.) TEM could not be used in this case to measure polymer thickness, because the wires could not be isolated from the continuous polymer matrix. As a control, a sample that had been subjected first to identical polymerization conditions except for the absence of free initiator showed no increase in polymer thickness after a second polymerization.

The same reinitiation procedure was used to obtain block copolymers on the surface of our ZnO wires. A substrate was first polymerized in the presence of methyl methacrylate for 6 h, producing a polymer layer 4.6 ± 1.2 nm thick. After isolation, this substrate was placed into a polymerization solution containing phenyl methacrylate, and the polymerization was allowed to proceed for an additional 6 h, giving a final coating of 14.2 ± 3.4 nm. (See the Supporting Information for the corresponding histograms.)

Polymerization of Styrene. Polystyrene was grown from the ZnO surface using a procedure similar to one published for the polymerization of styrene from a silica nanoparticle surface.[10] In contrast to the published procedure, which used a styrene-to-initiator concentration ratio of 1670:1, we used the slightly higher monomer ratio of 2075:1 and replaced the dimethylacetamide solvent with the more polar dimethylformamide. Although highly polar solvent systems lead in some instances to elimination of the terminal bromine atom[18] (thereby stopping the polymerization prematurely and leading to a high PDI), we observed a well-controlled polymerization under these modified conditions. After 6 h, TEM showed 6.5 ± 2.5 nm of polymer coating the nanowire surface. Polymer formed in solution from the same reaction was found to have an M_n of 163 154 and a PDI of 1.18. After a 24-h polymerization time, the surface was completely filled, and useful TEM samples could not be prepared.

Pyrolysis. Previous work has shown that many polymer precursors, including polyacrylonitrile,[19] pitch,[20] and sucrose,[21] can undergo pyrolysis under an inert atmosphere to give graphitic carbon products. This method is ideally suited for templating and has been used to make mesoporous carbon matrixes from SBA-15.[22] It has also been used to synthesize other nanostructures including dots[19] and graphite-coated nanowires.[23] Using ZnO nanowires as a template, the tubes synthesized would have an inner diameter between 50 and 100 nm.

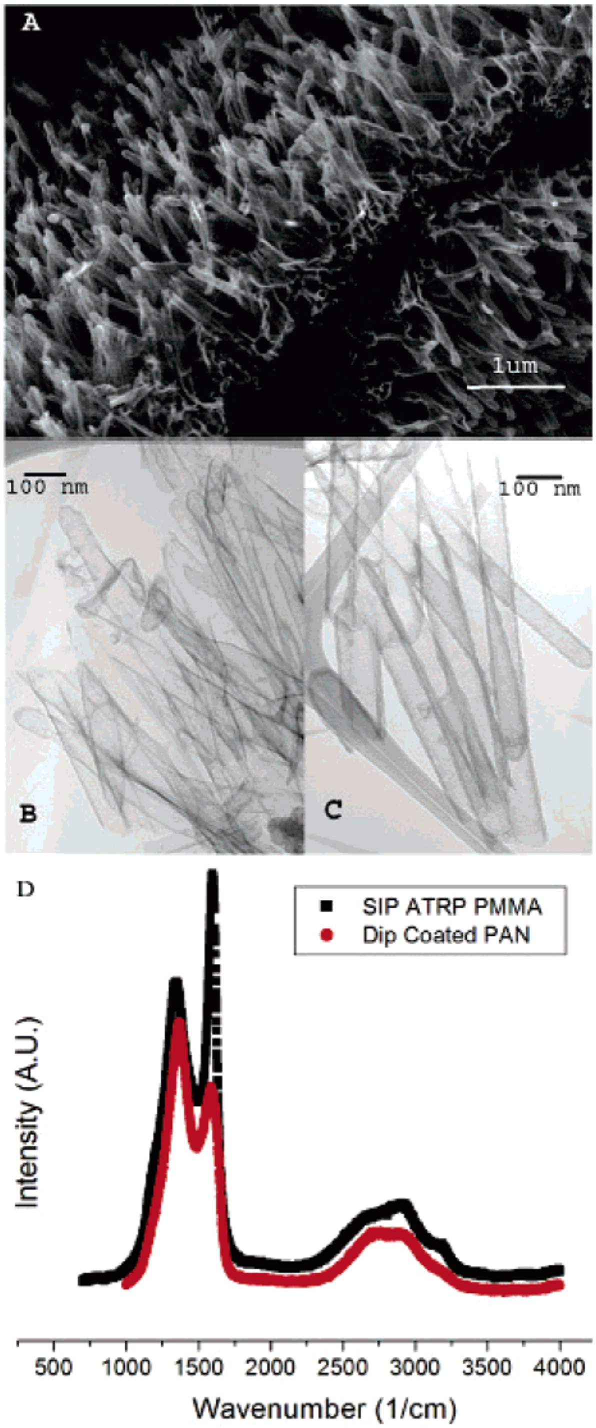

Figure 4. (a) SEM image of the pyrolysis product from a surface-initiated polymerization of PMMA on ZnO. (b) TEM micrograph of the sample in a. (c) TEM micrograph of the pyrolysis product from a sample of dip-coated PAN on ZnO. (d) Raman spectrograph showing the intensities of the ordered and disordered bands of graphite from each of the methods of preparation.

We were successful in forming carbon tubes by the pyrolysis of ZnO nanowires coated with various polymers (Figure 4). Both traditional templating routes using polyacrylonitrile dissolved in DMSO dip-coated onto ZnO arrays and arrays coated with polymer via surface-initiated ATRP were examined. The coated arrays were subjected to pyrolysis conditions at 700 °C in a tube furnace under a flow of Ar/H_2. In cases where only Ar or N_2 was used, no tubes were obtained owing to the carbo-thermal reduction pathway of ZnO in the presence of the polymers at elevated temperatures. Reduction of the ZnO in the presence of Ar/H_2 meant that, over the course of the carbon pyrolysis, the ZnO was reduced and carried away as zinc metal vapor and water, leaving only carbon tubes after 4 h. Each method produced arrays of carbon nanotubes with one end closed. The dip-coating route produced nanotubes with thicker walls but less ordered structures (based on Raman spectroscopy); substrates prepared from surface-initiated polymerization produced much thinner-walled carbon tubes, with a more intense Raman peak corresponding to graphitic ordering. The degree of ordering in graphitic structures can be determined by comparing the relative intensities of the G-band (E_{2g} mode) and D-band (disordered band) signals in the Raman spectrum (Figure 4d). For single-crystalline graphite, only one peak at ~1575 cm^{-1} should be observed; all other graphitic materials, including

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carbon nanotubes, also show the D band at ∼1355 cm^{-1}.[24] The intensity ratio of the G band to the D band in the dip-coated samples was 0.77, whereas in the tubes made from surface-initiated polymer, the ratio was 1.32. Even with the higher degree of ordering seen in the surface-initiated sample, the intensity seen in the C-H stretching region indicated an incomplete pyrolysis.

Unsuccessful attempts were made to increase the degree of ordering in these structures by using higher pyrolysis temperatures. The effect of the polymer on the final quality of the carbon tubes was also briefly studied. We examined the effect of carbon content in the precursor polymer on the final quality of the pyrolyzed carbon and found that both poly(methyl methacrylate) and poly(phenyl methacrylate) produced carbacious material with the same Raman signature when grown off the surface. Attempts were also made to grown polyacrylonitrile from the surface for these pyrolysis experiments, but the thickness of these layers was never sufficient to give free-standing carbon tubes. Methacrylate polymers were also used for the dip-coating experiments, but these polymers failed to make well-formed tubes, instead forming textured carbon thin films with disordered Raman spectra.

Conclusions

By controlling catalyst and reaction conditions, polymerizations of methyl methacrylate, phenyl methacrylate, ethylene glycol dimethacrylate, and styrene on ZnO were all successfully performed. The average thickness for the polymer layers was determined using TEM. By controlling the time of polymerization, along with the amount and type of monomers added, both the thickness and the properties of the polymer can be tailored. In particular, we obtained polymer thicknesses ranging from 3−14 nm, with the upper bounds being dependent on the inner wire spacing. A wide range of homopolymers were grown from the surface, as were block copolymers. The ability to reinitiate and grow block copolymers demonstrates that this is a living polymerization and implies that this method could be extended to the synthesis of different polymer types.

The grafting density of surface initiators was determined spectroscopically using a functionalized derivative incorporating a UV tag. To our knowledge, this is the first time such a density analysis has been carried out for the surface of ZnO. The results indicate that an incomplete monolayer is formed on the surface of ZnO during our functionalization procedure.

Last, these hybrid organic−inorganic materials were used as precursors for graphitic carbon tubes. These tubes could find applications as electrode materials,[25] as catalyst supports,[26] or as a chemically modifiable sheath for other 1D nanostructures.[5]

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Supporting Information Available: Data from BET absorption isotherms, chromophore density measurements, and SEM images of selected samples. This material is available free of charge via the Internet at http://pubs.acs.org.

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