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Atom transfer radical polymerization (ATRP) initiated by aryl diazonium salts: a new route for surface modification of multiwalled carbon nanotubes by tethered polymer chains

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Abstract

We report for the first time on grafting of poly(*n*-methyl methacrylate), (PMMA), and polystyrene (PS) brushes by ATRP from the surface of aligned multiwalled carbon nanotubes (MWCNT) which were electrochemically treated with brominated aryl groups based on diazonium salts. The polymer brushes formed amorphous coatings, as evidenced by high-resolution transmission electron microscopy, by comparison to the nanotube structure. X-ray photoelectron spectroscopy (XPS) analysis confirmed the presence of PS and PMMA by their characteristic C1s and valence band features. Well-aligned MWCNT network allowed us to sheath individual MWCNTs with polymer brushes while keeping the initial MWCNT alignment structure. This method opens up new avenues for the elaboration of polymer/NT hybrids.

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Keywords: Carbon nanotubes; Diazonium salts; Atom transfer radical polymerization (ATRP)

1. Introduction

Polymer brushes have recently attracted considerable attention because of their novel structures and properties [1,2]. Covalent attachment of polymer chains to the surface can be accomplished by either “grafting to” or “grafting from” techniques. “Grafting to” involves the bonding of a preformed end-functionalized polymer to reactive surface groups on the substrate. The “grafting from” technique involves the immobilization of initiators onto the substrate followed by in situ surface polymerization to generate the tethered polymer chains [2,3]. It has the advantage of preparing polymer brushes with high grafting density (up to 85 mg/m²) as compared to the “grafting to” method (about 1 mg/m²) [4]. Indeed, the attachment of a small number of chains hinders diffusion of additional

macromolecules to the surface, thereby leading to low grafting density. A high polymer chain density is actually of considerable importance when dealing with polymer-based biocompatible materials.

For better control of the molecular weight and the molecular weight distribution of the polymer chains, living radical, anionic, cationic, and ring-opening metathesis polymerizations have been used in “grafting from” methods [2]. Controlled radical polymerization, especially atom transfer radical polymerization (ATRP) [5] is the most used method to graft polymer chains of controlled molecular weight from, e.g. silicon wafers, gold particles, and polymer backbones. ATRP is indeed a versatile method in terms of choice of functional monomers, performance at moderate temperature (100 °C or less), in either aqueous or organic solvents [5]. A variety of polymeric materials can be obtained by ATRP ranging from simple linear macromolecules to more sophisticated architectures such as star brush copolymers [6]. Surface-initiated ATRP (SI-ATRP) [2] allows developing novel thermo-responsive systems [7];

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for the control of cell adhesion [8]; separation materials based on nanofilms of molecularly imprinted polymer brushes [9], and dispersible carbon nanotubes in common solvents [10] to name but a few.

SI-ATRP can be performed using, e.g. initiator-functionalized silanes [5], thiols [11,12], plasma-treated polymers [13], polyelectrolyte macroinitiators [14] and streptavidin–biotin conjugates [15]. Recently, we have proposed that ATRP of vinyl monomers can be initiated by electro-grafted brominated aryl species based on diazonium salts at the surface conductive materials such as iron [16], doped ultrananocrystalline diamond [17] and glassy carbon [18]. The use of aryl diazonium salts is indeed a simple and elegant way of modifying conductive substrates such as metals, semi-conductors and carbon in view of elaborating molecular junctions in electronic circuits, biosensors, and protective layers against corrosion [19]. Particularly, grafting aryl groups was successfully achieved on glassy carbon [20], carbon felts [21], ultrananocrystalline diamond [22] and carbon nanotubes [23,24]. Moreover, they impart controlled interfacial properties to the host substrate such as hydrophilic/hydrophobic character [22], or dispersion in organic solvents [23a].

From the above, it is clear that electrografting halogenated aryl groups based diazonium salts onto carbon nanotubes should be a straightforward way of surface modification as compared to the traditional, harsh chemical attacks. Moreover, this electrochemical surface treatment step can be complemented by SI-ATRP in view of getting carbon nanotube-polymer hybrids. The preliminary nanotube covalent functionalization by aryl groups is thus of major importance to control the nanotube-polymer interface and therefore to get nanocomposites with improved physical properties. It is in this context that this study proposes an efficient way to graft polymer chains through the SI-ATRP method on carbon nanotubes.

In this communication, we report on the surface functionalization of multi-walled carbon nanotubes (MWCNT) by phenyl ethyl bromide groups following the electrochemical reduction of the corresponding diazonium salt BF_4^- , $^+\text{N}_2\text{-C}_6\text{H}_4\text{-CH}_2\text{CH}_2\text{-Br}$ (**D1**). Aligned MWCNTs were grown on Si substrate by aerosol-assisted catalytic chemical vapour deposition [25]. MWCNT-modified Si wafers are amenable to electrochemical treatment and the as-obtained $\text{BrCH}_2\text{CH}_2\text{-C}_6\text{H}_4$ -modified MWCNT (MWCNT–Br) served as a platform for the growth of polystyrene and poly(methyl methacrylate) (PS and PMMA, respectively) chains by ATRP. The MWCNT-polymer hybrids were characterized by transmission electron microscopy and X-ray photoelectron spectroscopy (XPS).

2. Experimental

2.1. Preparation of MWCNTs

The MWCNT synthesis has been performed by aerosol-assisted catalytic chemical vapour deposition (CCVD) process which has been described elsewhere [25]. Briefly, this process involves the use of solutions containing both liquid hydrocarbon and metal precursor. This method consists in producing and subsequently pyrolysing mixed liquid aerosols generated from

the solutions. The starting solution is composed of ferrocene (5 wt.%) dissolved in toluene and the aerosol, carried by an argon flow, is pyrolysed at 850 °C during 7 min. Sample was grown on *n*-doped silicon substrate. It is composed of multi-walled carbon nanotubes perpendicularly aligned and attached to the substrate surface and looks like a carpet. The nanotube length reaches 130 μm and the average inter-tube space is around 100 nm. External diameter of carbon nanotubes is varying between 10 and 100 nm.

2.2. Synthesis of the diazonium salt BF_4^- , $^+\text{N}_2\text{-C}_6\text{H}_4\text{-CH}_2\text{-CH}_2\text{-Br}$

The starting diazonium salt was synthesized in one pot from the commercially available 4-aminophenethyl alcohol (1 g) by heating at 150°C in 48% HBr (25 mL) for 4h, then cooling to 0 °C to give a white precipitate. The diazotization is then achieved by the standard method that consists of adding HBF₄ and NaNO₂ (1.1 equivalent). The precipitated brown diazonium tetrafluoroborate was filtered and washed with 5% NaBF₄, methanol, and ether. ¹H NMR, 200 MHz, δ ppm: 3.35 (t, 2H), benzylic protons; 3.47 (t, 2H) ethylic proton; 7.87 (d, 2H, *J*= 8.8 Hz) and 8.59 (d, 2H, *J*= 8.8 Hz), aromatic protons [3 to the diazonium function and to the benzylic carbon, respectively].

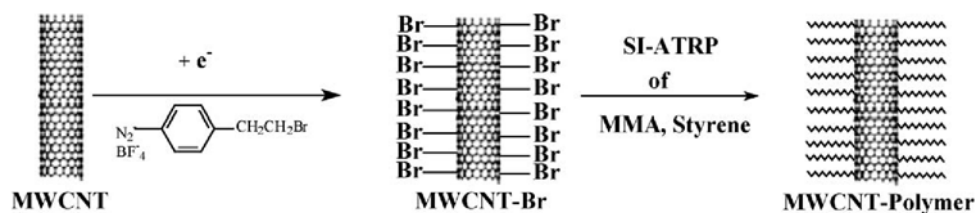
2.3. Electrochemical treatment of multiwalled carbon nanotubes

Electrochemical reduction of the diazonium salt was achieved by chronoamperometry for 300 s, at a potential 300 mV negative to the peak potential (-138 mV/SCE) (measured on glassy carbon). The Si wafer-supported MWCNT were then thoroughly sonicated in de-aerated ethanol. Some of the nanotubes were detached from the Si wafers due to this washing procedure. The as modified nanotubes are abbreviated by MWCNT–Br.

2.4. Surface-Initiated ATRP of vinyl monomers

The MMA, and styrene (Aldrich) were each distilled prior to polymerization. *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA), CuBr, CuCl, and CuCl₂ (Aldrich) were used as received. Surface-initiated ATRP was undertaken on the Si wafer-supported MWCNT–Br specimens.

For SI-ATRP of styrene, a 100-mL Schlenk flask equipped with a magnetic stir bar and sealed with a rubber septum was deoxygenated by a vacuum followed by back-filling with nitrogen three times. The CuBr powder (36.1 mg, 2.52 × 10⁻⁴ mol) and the MWCNT-coated Si wafers were introduced into the flask under a nitrogen flow. A mixture containing styrene (13.5 g, 1.3 × 10⁻¹ mol), and PMDETA (26 mg, 1.55 × 10⁻⁴ mol), previously degassed, was added to the polymerization flask using a double-tipped needle under a nitrogen flow. The flask was placed in an oil bath at 110°C for 16h. The polymerization was stopped by cooling and opening the flask to expose the catalyst to air. For the growth of PMMA, the same procedure has been



Scheme 1. Brominated initiators are attached to Pristine MWCNTs via electrochemical reduction of the corresponding diazonium salts. PS and PMMA chains are grafted by SI-ATRP from the MWCNT-Br platform.

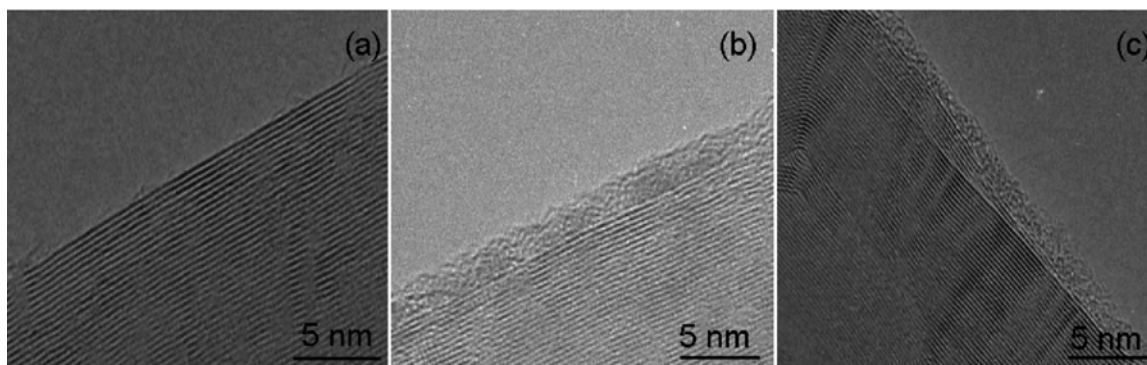


Fig. 1. HRTEM images of untreated MWCNT (a), MWCNT-PMMA (b), MWCNT-PS (c).

(18.0 mg, 1.82×10^{-4} mol), CuCl_2 (2.8 mg, 2.08×10^{-5} mol), methyl methacrylate (14.1 g, 1.41×10^{-1} mol), and PMDETA (34.8 mg, 2.01×10^{-4} mol). The polymerization was carried out at 90°C for 6 h. The target molecular weights of the PS and PMMA chains were 42,500 and 32,500, respectively. The MWCNT-polymer hybrids were sonicated in dichloromethane for five periods of 5 min.

It was observed that during the SI-ATRP process, nanotube bundles were detached from the Si wafer. After the washing procedure following ATRP, almost the majority of nanotubes were detached from the surface. However, this is absolutely not a drawback since the MWCNT were already modified by the grafted initiators (MWCNT-Br) so that SI-ATRP could still progress until completion in suspension rather than at the surface of the Si wafers. Indeed, electrochemical modification by the diazonium salts was effective on each individual nanotube because these were separated by about 100 nm from each other. Such a gap between the MWCNT-Br nanotubes is large enough to allow the growth of polymer brushes by SI-ATRP.

2.5. Characterization

High resolution TEM was performed on a JEOL 2010 microscope at 200 kV. For grid preparation, samples were dispersed in absolute ethanol using an ultrasonic bath. A droplet of solution was deposited on a lacey carbon grid.

XP spectra were recorded using a Thermo VG Scientific ESCALAB 250 system fitted with a micro-focused, monochromatic Al K_{α} X-ray source (1486.6 eV, $650 \mu\text{m}$ spot size) and a magnetic lens which increases the sensitivity. The pass energy was set at 150 and 15 eV for the survey and the narrow regions,

respectively. The detached raw and modified MWCNT were mounted on sample holders.

3. Results and discussion

MWCNT-polymer hybrids were obtained in two steps. First, ATRP initiators were grafted on the MWCNT surface, second PS and PMMA chains were grafted by SI-ATRP from the surface of MWCNT-Br specimens. The overall synthesis process is illustrated in Scheme 1.

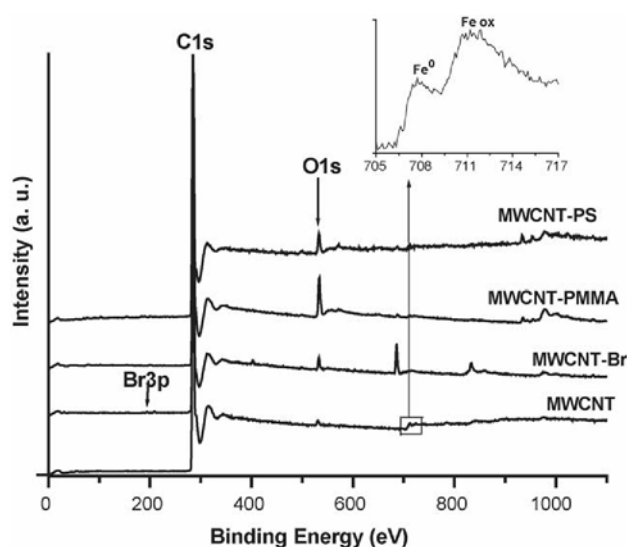


Fig. 2. Survey scans of MWCNT, MWCNT-Br, MWCNT-PS and MWCNT-PMMA.

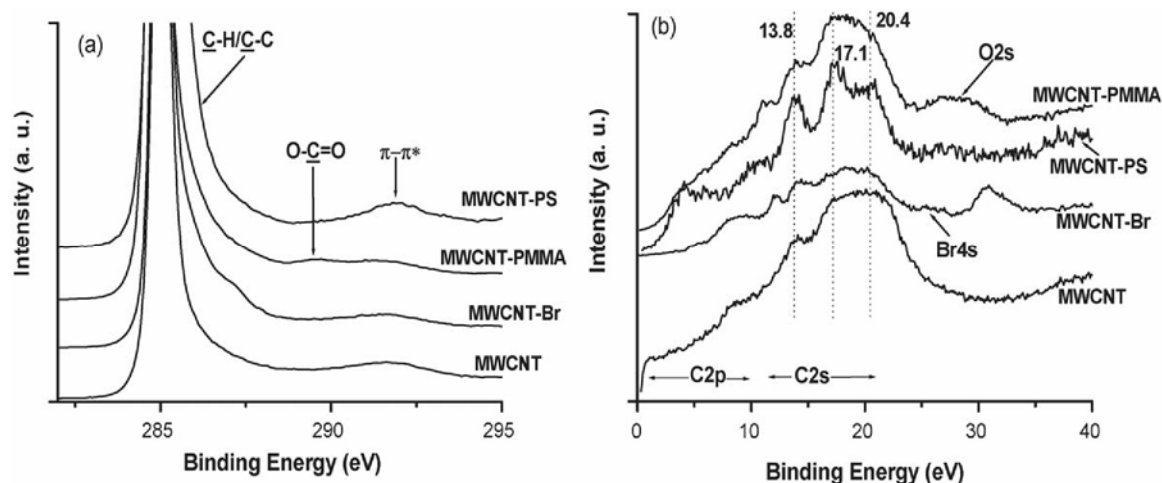


Fig. 3. High-resolution spectra for MWCNT, MWCNT-Br, MWCNT-PMMA and MWCNT-PS. C1s (a), and valence band (b) regions.

The morphology and structure of the pristine and modified MWCNTs was examined by HRTEM and the surface chemical composition by XPS.

In order to compare the surface morphology and structure of the carbon nanotubes before and after growth of polymer chains, raw MWCNT, MWCNT-PS and MWCNT-PMMA were observed (Fig. 1). For raw MWCNTs, the external surface of the nanotubes is well crystallised and corresponds to graphene layers (Fig. 1a). On the contrary, it is obvious that surfaces of MWCNT-PMMA or MWCNT-PS are covered by an amorphous layer exhibiting a thickness between 1 and 2 nm (Fig. 1b and c). These layers correspond to the grafted polymer chains. This result demonstrates the efficient grafting of PS or PMMA by ATRP on each individual MWCNT. When observing several nanotubes, it is important to note that the distribution of polymer layer is homogeneous along the nanotubes for grafted PS. However, the PMMA layer is locally disrupted.

Structural surface characterization of the modified carbon nanotube surface was undertaken by means of high resolution X-ray photoelectron spectroscopy. Fig. 2 shows the survey scans together with the main peak assignment.

The pristine MWCNT exhibits $\text{Fe}_{2p_{3/2}}$ peak at 710 eV which originates from the ferrocene precursor. The high resolution Fe2p region displayed in inset, indicates the presence of metallic iron confirming published structural results obtained by X-ray scattering measurements performed on individual carbon nanotube carpets [26].

For the MWCNT-Br, the Br_{3d} and $\text{Br}_{3p_{3/2}}$ centred at 70 and 187 eV, respectively, are assigned to the grafted brominated aryl groups. The binding energies (BE) are characteristic of CBr chemical bonds. The F_{1s} peak centred at 685.1 eV is due to BF_4^- from the diazonium salt which could not be removed despite a thorough rinsing.

Interestingly, the O_{1s} peak is more intense for MWCNT-PMMA than for MWCNT-PS since the former polymer contains oxygen atoms but not PS. For MWCNT-PS, the O_{1s} region arises only from the underlying nanotubes.

The high resolution C1s and valence band regions are shown in Fig. 3. MWCNT exhibits a main C1s peak at 285 eV and

a shake-up satellite around 291.5 eV. The oxidized carbon atoms induce a shoulder in the 286–288 eV range. MWCNT-Br exhibits a more localized shake-up satellite peak and an important component at 286 eV partially due to CBr bonds.

For MWCNT-PMMA hybrid the occurrence of the polymer is confirmed by the peak at 289 eV due to the OCO carbon from the repeat units. For MWCNT-PS, the C1s region exhibits a main C1s peak at 285 eV that is slightly broader than that of the carbon nanotube due to the insulating nature of the polymer. In addition, the shake-up satellite at 291.5 eV is very well defined and in line with published data [27].

As far as the valence band regions are concerned (Fig. 3b), the MWCNT are characterized by a broad band around 20 eV BE whereas the MWCNT-Br exhibits a Br_{4s} peak at 26 eV; note also F_{2s} at 30 eV due to BF_4^- . The remarkable resolution available in the valence band reveals subtle molecular structure differences in the C2s and C2p regions between the MWCNT-PMMA and MWCNT-PS reflected in the changes observed in the C1s regions discussed above. For MWCNT-PMMA, the valence band displays a broad band at 27 eV due to O_{2s} from the acrylate groups and another broad and unresolved band centred at ca. 17.5 eV, as currently observed for pure PMMA [28]. MWCNT-PS hybrids exhibits three C2s peaks centred at 13.8, 17.1 and 20.4 eV the BE positions of which match those published for a pure and thick solvent-cast PS film [27,29].

Interestingly, the valence band spectral regions near the Fermi level (about 0.4 eV), show the evolution between a conducting (pristine MWCNT) and an insulating (MWCNT-PMMA) sample characterized by a few eV gap.

4. Conclusion

The present study demonstrates, for the first time, that the “*diazonium salt/ATRP*” process is a simple, efficient and valuable way of surface modification of carbon nanotubes by tethered polymer brushes. This process involves two steps. First, the surface of MWCNTs is modified by electrochemical reduction of brominated aryl diazonium salts within a few minutes at room temperature. Second, we gave evidences that such modified

face provides a valuable platform for the surface grafting of polymers, namely PS and PMMA, by ATRP. The tethered polymer chains constitute dense organic adlayers at the surface of MWCNTs.

This communication highlights aryl diazonium salts as versatile building blocks for the development of novel hybrid carbon nanotube-polymer interfaces. Such assemblies are potentially interesting for numerous carbon nanotube applications such as electronic devices and sensors, but also for the preparation of novel composite materials. In the latter application, the grafted polymer brushes would serve as conversion layers for improving the dispersion of the as-modified carbon nanotubes (discontinuous phase) in the host organic polymer matrices (continuous phase).

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