Photopolymerization of metal nanoparticles on multiwall carbon nanotubes†

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A facile method for the functionalization of multiwall carbon nanotubes (MWCNT) by photopolymerization of 5-mercapto-2,2′-bithiophene modified metal (Au or Ag) nanoparticles on the surface of the MWCNT is developed.

Several strategies for functionalizing carbon nanotubes (CNTs) in order to improve their solubility in common solvents have been reported.[1] Wrapping polymers on a CNT surface through π–π or CH–π interactions can enhance their dispersion within a polymer matrix and their solubility in solvents,[1–5] while direct polymerization of monomers by functionalization of CNTs has also been used to prepare polymer wrapped CNTs.[3,6–8] Soluble poly(3-hexylthiophene)/multiwall carbon nanotube (MWCNT) nanocomposites are reported to give increased conductivity,[3] while polythiophene/CNTs have been tested as sensors for chemical warfare agents.[9] Alternatively the preparation of composite metal nanoparticles inside or outside CNTs has been reported,[10–17] and these are expected to produce novel nanomaterials combining the properties of two independently functional nanoscale materials. Small organic bridging molecules,[18,19] polyelectrolytes,[11,20] and even DNA[21] have been used to achieve adhesion of nanoparticles on CNTs. Au, Ag, Pb and Pt nanoparticles have been spontaneously synthesized on CNTs by redox reactions of the corresponding metal ions.[14,15] However, it is difficult to control the size of the metal nanoparticle and its distribution using this method. Connecting pre-formed nanoparticles with CNTs has advantages of size and shape selectivity. However, the procedure is more complicated and usually more than one reaction is needed.[10]

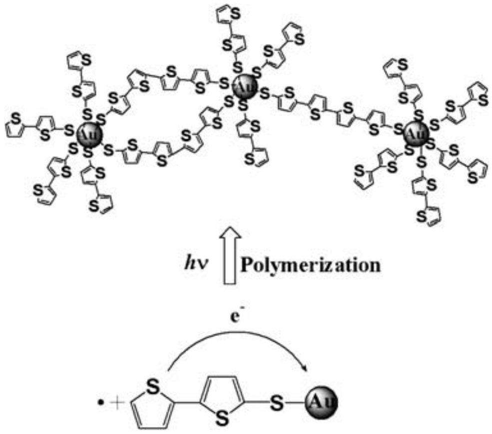
In this paper, we report a facile method for the functionalization of MWCNT by photopolymerization of 5-mercapto-2,2′-bithiophene (BTSH) modified metal (Au or Ag) nanoparticles on their surfaces. Neither prior chemical treatment nor conventional photoinitiators are needed for this new, photochemically initiated procedure.

BTSH functionalized metal nanoparticles [BTSM (M: Au or Ag)] with diameters in the range of 2–6 nm were prepared using a modified Brust method.[22,23] Energy dispersive X-ray (EDX) spectroscopy confirmed the elemental composition of the nanocomposites (see also ESI†) and transmission electron microscopy (TEM) as well as scanning electron microscopy (SEM) were used to determine the size distribution of the nanoparticles and investigate CNT functionalization.

We recently reported the photopolymerization of BTSAu nanoparticles following intramolecular electron transfer formation of the charge separated state ($^{\bullet +}$BTSAu(e)).[24] With positive charge localized on the thiophene ring, the thiophene radical cation initiates the polymerization, Scheme 1.[24,25] Photopolymerization of BTSAg was also observed. Fig. 1 shows the UV absorption changes before and after 350-nm light irradiation in toluene. An SEM image confirms formation of the three-dimensional network of polymerized 4-nm BTSAg formed following irradiation.

Functionalized MWCNT are obtained without prior chemical modification so it seems likely that photopolymerization occurs on the surface. Since thiophene is π electron rich, it is expected that BTSM attaches to the surface of MWCNT through π–π interactions.[1,10]

The experiments were carried out at room temperature with commercial MWCNT (O.D. 10–30 nm, I.D. 5–10 nm, length 0.5–50 μm). A MWCNT solution in toluene was mixed with a BTSAu or BTSAg also in toluene until a UV absorption value of ∼1.0 at 350 nm was obtained, Fig. 2. The samples were sonicated for 30 min to ensure good dispersion of the MWCNT and metal nanoparticles and then separated into two parts. One solution was kept in the dark as a control, while the other was irradiated using a UV lamp at 350 nm for



Scheme 1 Schematic mechanism for the photopolymerization of BTSH-functionalized Au nanoparticles.

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† Electronic supplementary information (ESI) available: Synthesis and characterization of BTSAu and BTSAg, SEM images of photopolymerization of 2-nm BTSAg and 2-nm BTSAu on the surface of MWCNT. Thickness distributions of MWCNT before and after irradiation. See DOI: 10.1039/b807407k

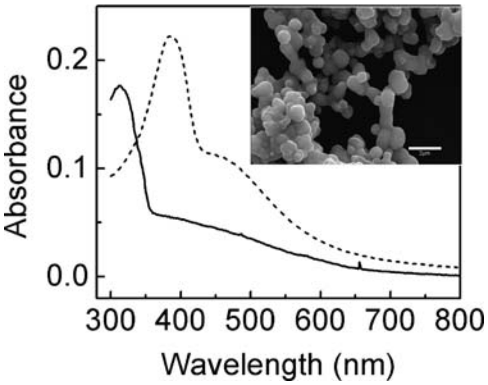

Fig. 1 UV absorption changes before (short dashed line) and after (solid line) 350-nm lamp irradiation of 4-nm BTSAg toluene solutions. Inset shows the SEM image after irradiation. Scale bar represents 2 μm.

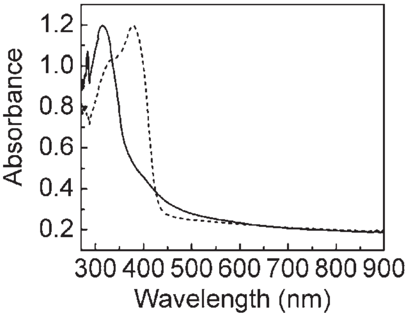

Fig. 2 UV absorption changes before (short dashed line) and after (solid line) 350-nm lamp irradiation of 2-nm BTSAu toluene solutions in the presence of MWCNT.

20 min. As a result of the irradiation, the absorption band around 400 nm decreases and becomes broad, with a tail absorption extending to 600 nm. A new absorption band around 320 nm also appeared. The residual absorption (up to 900 nm) is due to the MWCNT.[1] Because the BTSAu nanoparticles are less than 5 nm in diameter, no plasmon band absorption is observed.[23,24] The non-irradiated and irradiated samples were further analyzed by TEM, SEM and EDX, Fig. 3.

The MWCNT become ragged following UV exposure while EDX analysis of the surface indicated it is covered by BTSAu. In Fig. 3(b), although the Au peaks are less than 10, it is suggested that BTSM attaches to the surface of MWCNT through π–π interactions. However, the modification of CNTs should not be only by the π–π interaction between the thiophene ring and the carbon tubes. The primary photopolymerization of BTSM originates from the surface of the CNTs, which formed the crosslinking-like photopolymerized nanostructure around the CNTs. The thickness distributions of MWCNT before and after irradiation are shown in ESI.† We carried out control experiments in the presence of BTSH with MWCNT without the metal nanoparticles. No obvious photopolymerization on the surface of MWCNT was observed. The density of BTSAu on the surface of MWCNT could be adjusted by increasing or decreasing the concentration of metal nanoparticles in solution. Fig. 4(a) shows the irradiated sample of 2-nm BTSAu nanoparticles with concentrations 100 times greater than the sample used in Fig. 3. At high concentrations of metal nanoparticles, the polymerization of BTSAu not only occurred on the MWCNT, but resulted in aggregation of the particles as well. Given that these self aggregated BTSAu particles were anchored onto the surface of the MWCNT, the primary photopolymerization of BTSAu most likely originates from there. In the case of the 6-nm BTSAu nanoparticles, the attached nanoparticles can be independently identified (Fig. 4(b) and (c)).

The conductivity of the polythiophenes is well known. Oligothiophene linked Au nanoparticles prepared by electrodeposition methods have also been reported.[26,27] Thus metal nanoparticles linked by polythiophenes are expected to provide improved conductivity and this we have observed. It is also expected that

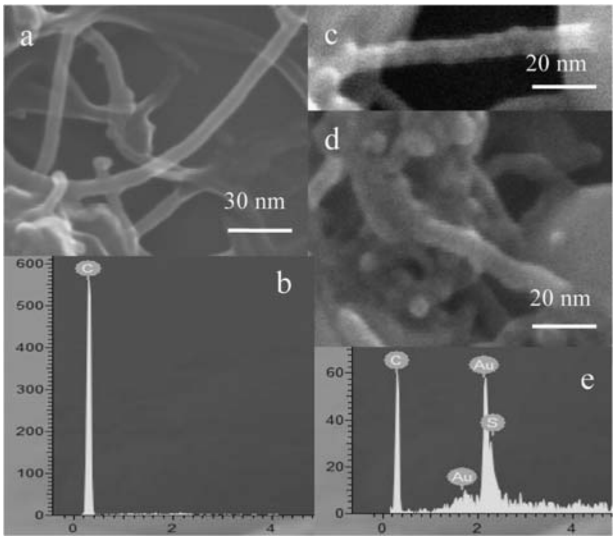

Fig. 3 SEM images and EDX spectra of 2-nm BTSAu in the presence of MWCNT before (a and b) and after (c, d, and e) 350-nm lamp irradiation (x-axis is energy in keV and y-axis is counting numbers).

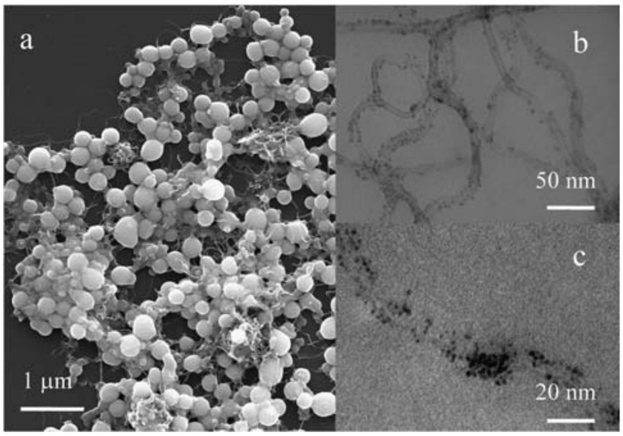

Fig. 4 SEM images of 2-nm BTSAu nanoparticles with concentration 100 times greater than the sample used in Fig. 3 in the presence of MWCNT after 350-nm lamp irradiation (a) and TEM images of 6-nm BTSAu with UV absorption value of $\sim$1.0 at 350 nm in the presence of MWCNT after 350-nm lamp irradiation (b and c).

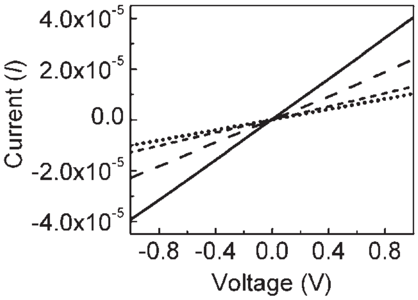

Fig. 5 Current–voltage curves of irradiated (solid line), non-irradiated 2-nm BTSAu/MWCNT (long dashed line) in PEDOT/PSS films, PEDOT/PSS only (dotted line), and the PEDOT/PSS film with non-functionalized MWCNT (short dashed line).

the polymeric BTSM functionalized MWCNT will have novel electronic properties.[28] Since the metal nanocore is bound to at least a α-quaterthiophene (Scheme 1), the adjacent metal nanocores should have strong electronic interactions. On the other hand, MWCNT electrons should also have strong electronic interactions with those of BTSM. Simple experiments were carried out to measure current–voltage curve changes occurring after the non-irradiated samples (~1% by weight) were irradiated (2-nm BTSAu/MWCNT), Fig. 5. Samples were dispersed in poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT/PSS) by sonication. The mixture was then coated onto a glass surface to yield thin films (~200 μm). The conductivity experiments were carried out under conditions in which the sample concentrations in PEDOT/PSS were the same.

The conductivity of PEDOT/PSS film is only slightly enhanced in the presence of MWCNT but the conductivity of PEDOT/PSS is much enhanced in the presence of nanoparticles. The irradiated sample is almost two times more conductive than the non-irradiated sample. We also carried out control experiments using MWCNT in the presence of BTSH and without BTSH. No obvious changes were observed suggesting that the conductivity changes observed in Fig. 5 are due to the polymerization of metal nanoparticles on the surface of MWCNT. It should be noted that Fig. 5 shows just the conductivity changes of PEDOT/PSS film; not the conductivity of the functionalized MWCNT. Though it is expected that the conductivity of BTSM modified MWCNT is substantially enhanced, we could not carry out the conductivity measurements at the nanometer size level owing to instrumental limitations in our laboratory.

In summary, we demonstrate a novel method for the functionalization of MWCNT by photopolymerization of BTSAu or BTSAg on the surface. The process does not involve prior chemical treatment of the nanotubes and no photoinitiators are needed. The experiments can be easily controlled by the photochemical conditions at room temperature. Because the MWCNT were functionalized by conductive polymeric metal nanoparticles, it is expected that such functionalized MWCNT will have potential applications as sensors, electronic and optoelectronic nanodevices.

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