DNA-Mediated Copper Nanoparticle Formation on Dispersed Single-Walled Carbon Nanotubes

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A new and facile method for the preparation of single-walled carbon nanotubes (SWCNTs) decorated with Cu nanoparticles (CuNPs) formed on a double-stranded DNA template in aqueous solution has been developed. A specially designed synthetic DNA sequence, containing a single-stranded domain for the dispersion of carbon nanotubes and double-stranded domains for the selective growth of CuNPs, was utilized. The final SWCNT/CuNP hybrids were characterized using fluorescence spectroscopy and transmission electron microscopy. The analyses clearly demonstrated the selective formation of uniform CuNPs on the carbon nanotube scaffold.

Introduction. – Novel 1D single-walled carbon nanotubes (SWCNTs)/nanoparticle hybrid materials, in which SWCNTs are often used as scaffolds for the assembly of nanoparticles, are of great importance due to their considerable hardness and toughness [1]. SWCNT/metal nanoparticle hybrids, especially transition metal nanoparticle-decorated SWCNTs, have aroused great interest because of their vast applications in sensor devices [2], photoelectrochemical cells [3], as catalytic supporters [4], and in surface-enhanced *Raman* spectroscopy [5]. Controlled decoration of SWCNTs with metal nanoparticles modifies their electronic structure resulting in better electroanalytical performance due to the synergetic effect of the two materials compared to bare metal nanoparticles [6], making important not only fundamental studies of the interactions between the carbon matrix and the metallic nanoparticles, but also the aspects of their broad potential applications.

Currently, various methods are being explored, generally being divided into covalent or noncovalent attachment of certain metal nanoparticles onto carbon nanotubes [7–12]. Covalent deposition requires prefunctionalization of the nanotubes by modifying their surface. In many cases, it involves acid treatment to create COOH, C=O, or OH groups for subsequent anchoring of metal nanoparticles [8]. The harsh acidic treatment of SWCNTs may introduce many extensive defects in the sidewall, thus considerably perturbing the mechanical and electronic performance of the tubes. On the other hand, the noncovalent approach maintains the properties of the nanotube, the carbon scaffold being minimally perturbed by utilizing functional compounds, such as organic molecules [9], polyelectrolytes [10], and single-stranded DNA (ssDNA)

sequences of different length [11][12], to disperse and functionalize carbon nanotubes for the subsequent anchoring of metal nanoparticles. In this regard, due to the very specific molecular recognition between complementary strands, the high affinity of double-stranded DNA (dsDNA) to a variety of metal ions, and the carbon nanotube-stabilizing property of ssDNA, DNA represents the material of choice for functionalization and metal deposition on SWCNTs. DNA-directed dispersion and functionalization of SWCNTs with a subsequent strand displacement program for the precise addressability of nanotubes on the 2D DNA nanostructures has recently been reported [13]. It would be of great interest to probe the selective functionalization of SWCNTs with a DNA sequence containing both a ssDNA domain for SWCNT dispersion and a dsDNA domain for the decoration with metal nanoparticles.

Mokhir and co-workers [14] reported for the first time that dsDNA can act as an efficient template for the formation of fluorescent Cu nanoparticles (CuNPs) utilizing Cu^{2+} and subsequently sodium ascorbate as reducing agent, whereas random ssDNA does not support nanoparticle formation. Later, *Wang* and co-workers [15] also reported that only very specific ssDNA sequences could also serve as templates for CuNP formation in aqueous buffer solution under the same conditions.

Results and Discussion. – Herein, we report a new mild and facile method for the DNA-mediated dispersion and decoration of SWCNTs with CuNPs in buffer solution exploiting low concentration of Cu^{2+} and sodium ascorbate as reducing agent. We employed a specially designed synthetic DNA sequence containing a single-stranded region for noncovalent SWCNT dispersion and specifically designed dsDNA domains as substrate for CuNP growth (*Fig. 1*).

Under these mild experimental conditions, the SWCNT surface is left largely unperturbed thus preserving the inherent and desirable properties of the underlying nanotube. Several high performance analytical techniques including emission spectroscopy, transmission electron microscopy (TEM), and atomic force microscopy (AFM) were used to confirm the structure of the SWCNT/DNA/CuNP hybrids.

As stabilizing DNA sequence for the dispersion of SWCNTs, we used a long 130-mer synthetic oligonucleotide sequence (Poly-T) consisting of an interior domain of 100-mer poly[d(T)] and marginal binding domains, consisting of 15-mer sequences each at both 3′- and 5′-ends. Prior to stabilization of SWCNTs, the ends of the Poly-T

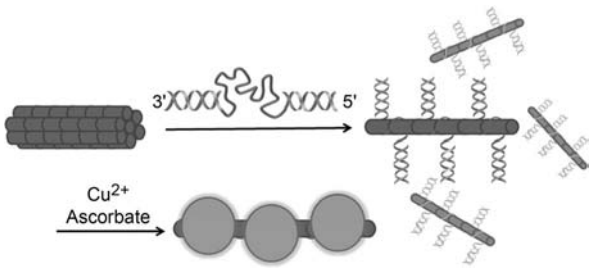

Fig. 1. *Dispersion of SWCNT bundle by ssDNA containing short dsDNA regions to form SWCNT/CuNP hybrids in solution of Cu^{2+} and sodium ascorbate*

sequence were hybridized on marginal domains at 3′- and 5′-ends with short, 10-mer oligonucleotides by annealing the mixture of the three sequences from 90 to 4° in the course of 10 h. This mixture of DNA was then used for the dispersion of SWCNTs by sonication in H_2O/ice bath for 60 min. The resulting black suspension was then subjected to ultracentrifugation at 4° for 30 min to afford the final brownish solution of suspended DNA-stabilized SWCNTs.

To confirm the dispersion of SWCNTs, we analyzed the prepared sample by AFM in air and under liquid on a mica surface, and by TEM on carbon-coated grids (*Fig. 2*). Both analyses revealed the presence of dispersed individual nanotubes and thin bundles of different size in the sample.

A purification step was introduced prior to CuNP growth on SWCNTs in order to prevent the unspecific formation of CuNPs in solution on free Poly-T sequence not associated with SWCNTs. For this purpose, after the sonication step, the sample was filtered through a *Microcon* centrifugal filter (100,000 Da NMWL) followed by washing with buffer solution to get rid of the unbound Poly-T DNA sequence.

To perform CuNP growth on DNA-dispersed SWCNTs, we implemented and then compared the results of two separate ways of proceeding. First, we mixed the filtered sample of DNA-stabilized SWCNTs with tenfold excess of sodium ascorbate and incubated the solution for 15 min at room temperature. A solution of $CuSO_4$ was then added and the mixture was studied using fluorescence spectroscopy (*Fig. 3*).

The fluorescence spectra clearly indicated the formation of CuNPs with an emission maximum of λ_{em} 475 – 490 nm. These data are in accordance with previously published results [14]. By fluorescence spectroscopy, we could observe that the formation of CuNPs is finished after 15 min of incubation at room temperature. Addition of a higher amount of $CuSO_4$ (twice the initial amount) did not change the shape or the maximum intensity of the emission spectra.

The resulting solution was subsequently studied by TEM. High contrast TEM images of SWCNTs with almost uniformly-sized CuNPs (average size 309 nm) deposited on them were obtained (*Fig. 4*).

It can be observed that in most cases, the nanoparticles are organized in rows on single or multiple SWCNT templates. Probably, in solution, when nucleation of Cu^0 is taking place, several long SWCNTs are merged together to form several nanotubes

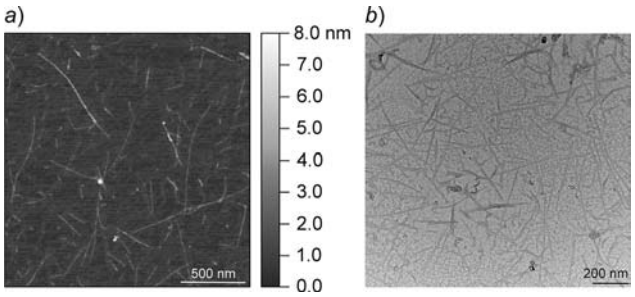

Fig. 2. *AFM and TEM images of DNA-stabilized SWCNTs. a*) AFM Image on mica surface after drying and washing of the surface with dist. H_2O (scale bar, 500 nm). *b*) TEM Image of DNA-dispersed SWCNTs (scale bar, 200 nm).

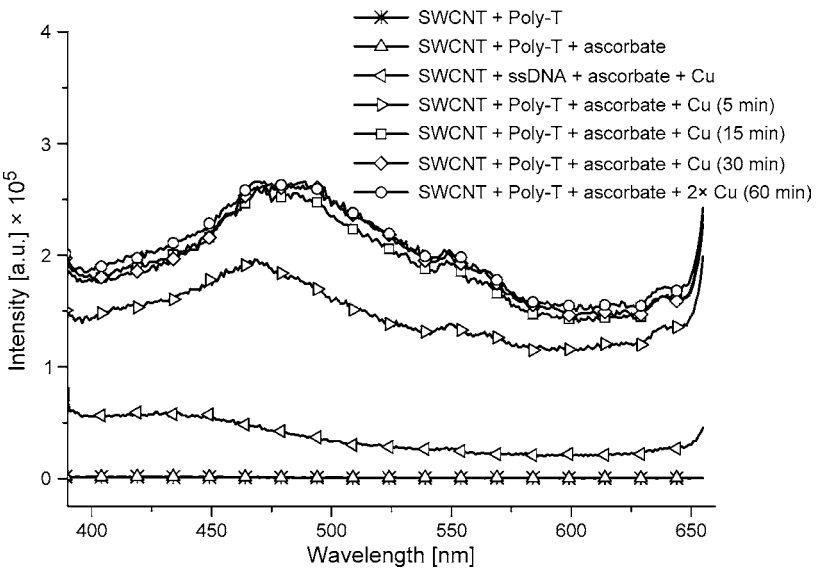

Fig. 3. *Fluorescence spectra* (λ_{ex} 335 nm) *obtained 5, 15, and 30 min after addition of* $CuSO_4$ (200 μM) *to the mixture containing 3-(*N*-morpholino)propanesulfonic acid* (MOPS; pH 7.5, 1 mM), Mg^{2+} (12.5 mM), *and sodium ascorbate* (2 mM). Curve with circles, 60 min after addition of $CuSO_4$ (400 μM).

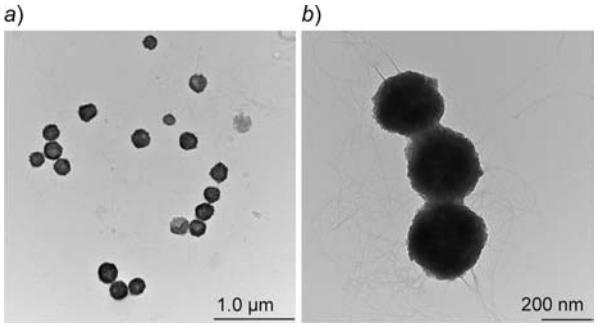

Fig. 4. a) *TEM Images of SWCNT/CuNP hybrids showing positioning of CuNP along one or several individual SWCNTs;* b) *Zoom in image of an individual SWCNT/CuNP hybrid showing several nanotubes covered with CuNPs.*

with common CuNPs. Individual CuNPs observed in the TEM images most probably result when CuNPs grow on short DNA-stabilized SWCNTs.

Also, we could observe dispersed SWCNTs without any sign of metal particles on them. We explain this by the fact that probably the formed dsDNA domains extending from the Poly-T sequence were disturbed during sonication leading to the formation of dispersed SWCNTs containing only single-stranded Poly-T wrapped around them.

A reversed way of proceeding, *i.e.*, when sodium ascorbate was added to the sample subsequently after the addition of $CuSO_4$ for the deposition of Cu on the DNA-

dispersed SWCNTs, was also tested. Fluorescence data did not show the specific emission band characteristic for the formation of CuNPs in solution (data not presented), we could only investigate the sample by TEM. We could observe that, in comparison to bare DNA-stabilized SWCNTs, the obtained structures represent carbon nanotubes covered with a thin and uneven layer of metal without clear formation of nanoparticles. This result is in accordance with the previously reported data where the initial binding of Cu^{2+} to dsDNA is disturbing rather than facilitating the transformation of Cu^{2+} to Cu^{0} due to the stabilization of Cu^{2+} by the N- and O-atoms of the nucleobases [14].

In summary, we have developed a new and facile method for the preparation of SWCNTs decorated with CuNPs in buffer solution. It is based on the very selective growth of CuNPs on the double-stranded regions of the DNA template while the single-stranded region provides a perfect dispersion and stabilizing agent for the SWCNTs. This approach is easy and avoids the chemical modification of the SWCNT scaffold thus preserving the mechanical and electronic performance of the nanotubes. Future work will focus firstly on optimization of the conditions for the control of the length of dispersed SWCNTs and the size of the formed CuNPs and, secondly, on exploring new advanced sensors and catalytic applications of the SWCNT/CuNP hybrids [16].

Experimental details and supplementary AFM and TEM figures are available in the Supporting Information[1]).

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