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Carbon Nanotube and Gold-Based Materials: A Symbiosis

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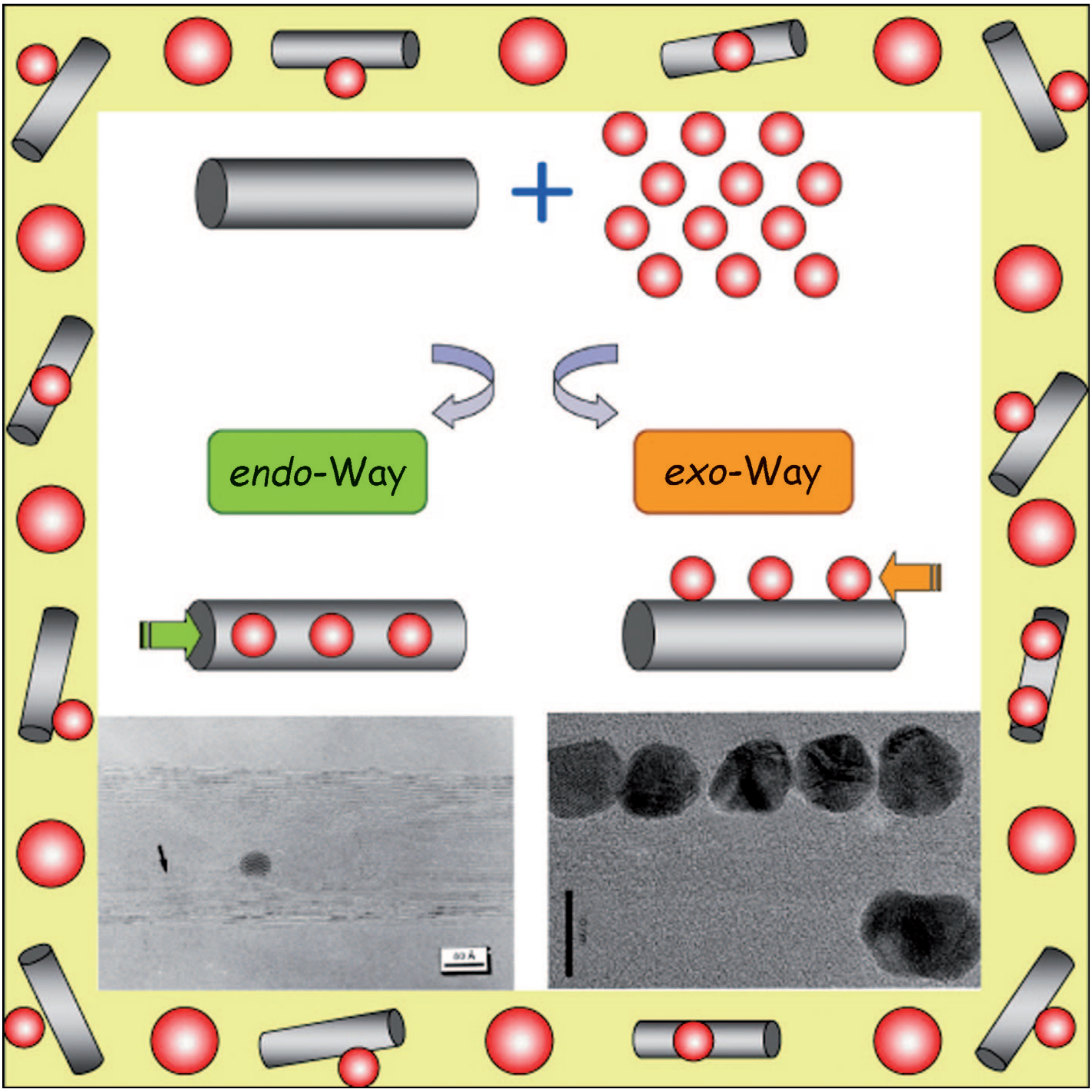

Abstract: Carbon nanotubes constitute a novel class of nanomaterials with potential applications in many areas. The attachment of metal nanoparticles to carbon nanotubes is new way to obtain novel hybrid materials with interesting properties for various applications such as catalysts and gas sensors as well as electronic and magnetic devices. Their unique properties such as excellent electronic properties, a good chemical stability, and a large surface area make carbon nanotubes very useful as a support for gold nanoparticles in many potential applications, ranging from advanced catalytic systems through very sensitive electrochemical sensors and biosensors to highly efficient fuel cells. Here we give an overview on the recent progress in this area by exploring the various synthesis approaches and types of assemblies, in which nanotubes can be decorated with gold nanoparticles and explore the diverse applications of the resulting composites.

Keywords: carbon · composites · gold · nanomaterials · nanotubes

Introduction

Gold (Au) is one of the most ancient discoveries in science. The extraction of gold started in the 5th Millennium B.C. near Varna, Bulgaria and around 1200–1300 B.C. in Egypt. The soluble blue gold appeared in the 4th or 5th century B.C. in Egypt and China. The first book on colloidal gold was published by the philosopher and medical doctor Antonii.[1] This book describes the considerable information on the formation of colloidal gold sol, their medical uses, and successful practical cases. In 1676, Kunckles[2] published another book, in which "drinkable gold" that contains neutral metallic gold in the form of a slightly pinkish solution is described and it also exerts curative properties for several diseases. In addition, it is described that gold is present to such a degree of combination that it is not visible to the human eyes. A complete treatise on colloidal gold was published in 1718 by Helcher.[3] The renaissance of gold now leads to exponentially increasing publications, especially in the context of emerging nanoscience and nanotechnology with nanoparticles and self-assembled monolayers. The gold nanoparticles (AuNPs) are the most stable metal nanoparticles and are expected to be key materials and building blocks for nanomaterials and nanodevices in the 21st century, because of their fascinating aspects in materials science, size-related electronics, magnetic and optical properties (quantum size effect), and their applications in catalysis and biology.

On the nanoscale size (1–100 nm) many materials show interesting quantum effects. The observed strong plasmon absorption bands, arising from the collective oscillation of "roving" electrons on the particle surface, often serve as a probe to monitor the interaction with surface-bound molecules. The nanoparticles in the diameter range of 1–10 nm would display electronic structures, reflecting electronic band structure of the nanoparticles, owing to quantum-mechanical rules.[4] The resulting physical properties are neither of the bulk metal nor of the molecular compounds but they strongly depend on the particle size, interparticle distance, and nature of the protecting organic shell and shape of the nanoparticle.[5]

Since their discovery in 1991,[6] carbon nanotubes (CNTs) have attracted increasing attention, as they belong to a family of nano-objects with remarkable physical, chemical, mechanical, and electronic properties.[7,8] Macroscopic quantities of nanotubes are routinely produced by three different methods, the arc discharge method,[9] the laser vaporization at elevated temperatures,[10] or by the catalytic decomposition of small hydrocarbon molecules.[11] Recently, there is a rapidly growing interest in the understanding of their growth mechanisms and electronic properties.[12] Numerous novel applications of single-walled and multi-walled carbon nanotubes (SWNTs and MWNTs, respectively) have been investigated including their use as field emitters,[13,14] nanoelectronic devices,[15–18] nanotube aquators,[19] batteries,[20] probe tips for scanning probe microscopy[21,22] and nanotube-reinforced materials.

Theoretical studies on CNTs suggest that the introduction of extraneous materials into the hollow nanotube cavities may have interesting effects on the physical and electronic properties of the encapsulated materials.[23–25] It is predicted that filled nanotubes may find practical uses as nanowires, composites, and novel catalysts. By changing the size and concentration of the metal nanoparticles incorporated the electronic properties of the CNTs can be controlled. Early work on bismuth and lead relied upon capillary action to pull liquids into the hollow nanotube cavities.[26,27] Lanthanides and transition-metal carbides have been trapped in nanotube cavities by the arc evaporation of metal-doped

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carbon rods.[28–33] This new type of composite is important not only for fundamental studies of the interactions between the matrix and the metallic nanoparticles but also for various applications such as catalysts as well as electronic and magnetic devices. Though considerable work has been described on CNTs and metal nanoparticles (either particles coated on the surface of the CNTs or trapped in the nanotube cavities), analogous reports have not extensively reviewed the subject precisely and concisely to date. Further, the combination of carbon-based materials such as CNTs, carbon films, and carbon nanoparticles with gold and AuNPs have not been consolidated well. It is important and informative that the consolidated remarks of carbon-based materials such as CNTs, with metals, in general, with gold and AuNPs in particular, are reviewed. Considering the benefits to the scientific community in general, and to the nanomaterials scientists in particular, herein we describe the endohedral and exohedral approaches for CNTs in conjunction with AuNPs and the subsequent characterization of the nanotube nanocomposites. Despite the considerable variety of contributions, we will focus on the synthesis, various types of assemblies, applications, and finally the future prospective.

Synthesis and Assembly

In order to be able to synthesize nanotubes with predetermined characteristics, that is, for the "engineering" of these nanostructures, it is very important to understand and control the mechanisms, which govern the growth of CNTs. The composites of CNTs with gold-based materials may be attained through either AuNPs are grown and/or incorporated into the CNTs hollow cavities (endohedral approach) or gold/AuNPs are interacted and/or deposited on the outer part of the CNTs (exohedral approach).

Preparation of AuNP-filled CNTs

Wet chemistry techniques: In this approach, CNTs are exposed to a solution of $AuCl_3$ under stirring for four days and then $AuCl_3$ is decomposed to AuCl at ~150 °C where the latex dissociates into elements at higher temperatures.[34,35] The filled CNT sample is characterized by high-resolution transmission electron microscopy (HR-TEM), analytical energy-dispersive spectroscopy (EDS) and X-ray powder diffraction (XRD). Figure 1a shows the HR-TEM image where a gold crystal is encapsulated within the CNTs. The observed d spacing of the lattice plane was 2.325 ± 0.05 Å, which corresponds to the (111) planes of gold.[36] The gold was characterized to be in the form of spherical crystallites in the range of 1–5 nm of diameter. Moreover, a few CNTs were found to be filled with small amount of AuCl, which reflects the incomplete reduction of the gold(III) chloride.

Selective attachment of AuNPs: A facile procedure has been introduced to obtain a hybrid material, where MWNTs were filled with AuNPs by mixing an aqueous citric acid

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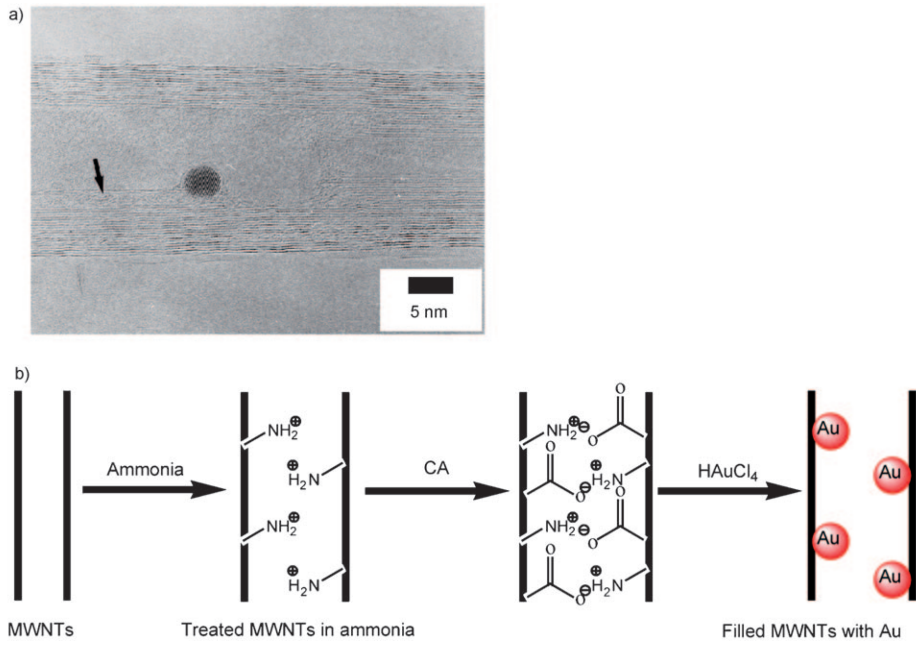


Figure 1. a) HRTEM image of a CNT filled with a spherical Au crystal. The observed fringes of 2.325 ± 0.05 Å correspond to the (111) planes of Au (lit. value = 2.355 Å). The solid arrow indicates where there has been intercalation into the gaps where carbon layers are missing. Reproduced with permission from *Chem. Mater.* **1996**, *8*, 2751–2754. b) Illustration of the process for attaching AuNPs to NH_3-treated CNTs.

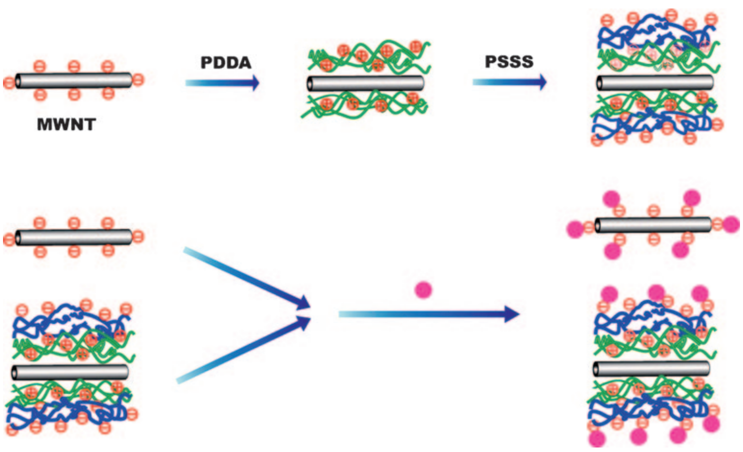
(CA) solution containing NH_3-treated MWNTs and aqueous auric chloride solution.[37] Heat treatment in ammonia was used to change the nanotube properties, caused most nanotubes to open and provided a critical prerequisite for attaching the AuNPs inside the nanotubes. The heat treatment with NH_3 generated basic groups on the inner walls of the CNTs. Figure 1 b shows the illustration of the nanotube surface modification and AuNPs attachment on inside the nanotubes. It indicates that the CNTs modified by heat treatment in NH_3 could adsorb citric acid via electrostatic interactions, thus facilitating the in situ reduction of the AuNPs on the inner walls of the nanotubes.

Interaction between AuNPs and the outer part of CNTs: There is a variety of ingenious approaches described to obtain CNT–AuNP composites, usually, the deposition of AuNPs onto the terrace of the CNT substrate. Many reports have been published in these areas over the years and we will overview only the major developments.

Assembly of the AuNPs on the functionalized CNTs: The functionalization of CNT by chemical methods to enhance its solubility has been reported for the first time in 1998;[38] later the effect of the functionalization time on the functionalized MWNTs (fMWNTs) was discussed by Kim and Sigmund.[39] Positively charged AuNPs were anchored on negatively charged fMWNTs prepared by the layer-by-layer self-assembly technique using polyelectrolytes. Positively charged AuNPs were also attached onto raw fMWNTs, because of the negatively charged carboxylic acid groups produced by the chemical oxidation process during ultrasonication, followed by deprotonation on immersion in water. The fMWNTs were coated with poly(diallyldimethylammonium chloride) (PDDA) by dispersing the fMWNTs in its solution. To obtain a PDDA/PSSS [poly(sodium 4-styrene sulfonate)] bilayer coating, the fMWNTs coated with PDDA were mixed with the PSSS solution under sonication. Finally, the positively charged nanoparticles were added to the dispersion of the polyelectrolyte-coated fMWNTs (Scheme 1).

Zannella et al.[40] developed a direct solvent-free functionalization scheme for pristine MWNTs with aliphatic bifunctional thiols (1,4-butanedithiol, 1,6-hexanedithiol, 1,8-octanedithiol, and 2-aminoethanethiol), aiming at the preparation of chemically modified nanotube surfaces capable of binding AuNPs. Their additional goal was to avoid the use of organic solvents and the thionyl chloride-based activation, which are ecologically unfriendly. In this solvent-free procedure, MWNTs and the dithiol/aminothiol were reacted in a reactor at 130–150 °C for 2 h. Then, $HAuCl_4$ and citric acid were simultaneously added dropwise to the derivatized MWNTs during ultrasonication for 3 min. The resulting MWNTs were dried under vacuum and characterized.

Functionalized CNTs with thiol groups were synthesized in an efficient way and AuNPs were successfully self-assembled onto them.[41] For the self-assembling of AuNPs to the functionalized CNTs, the thiol-functionalized CNTs (HS-



Scheme 1. Schematic representation of the experimental procedure for the preparation of MWNT/AuNPs composites.

CNTs) were sonicated in toluene to a homogenous dispersion to which AuNP/toluene was added and stirred at room temperature. The black AuNPs–CNTs were obtained after centrifugation. In another method, HS–CNTs were dispersed in aqueous $HAuCl_4·4H_2O$, where $NaBH_4$ was added to this suspension. The CNTs with AuNPs were obtained during 30 min stirring at room temperature. The TEM images (Figure 2) show the self-assembly of the AuNPs on the fMWNTs, where the AuNPs (Figure 2a) of 25 nm were dispersed on the HS–CNTs. Due to the soft chemical character of both the AuNPs and S, the thiol groups could strongly bind the AuNPs through ligand exchange with tetraoctylammonium bromide (TOAB).[42] More AuNPs at the bend of the CNTs are also visible, which indicates more functional groups there. The shape and size of the AuNPs are different in Figure 2b, which may be explained by that the thiol groups are surrounded by $AuCl_4^-$ that turned into the AuNPs when meeting the reducing agents. These AuNPs are the cores for further growth, as the thiol groups do not cover the whole particles. Additional evidence of AuNPs on the surface of the fCNTs is shown by EDS. According to the EDS pattern, Au, S, O, and C are present on the surface of the in situ AuNPs–CNTs, while the Cu and C signals should belong to the copper-hole carbon support grid. Therefore, it is concluded that the visible black dots in the TEM images are AuNPs.

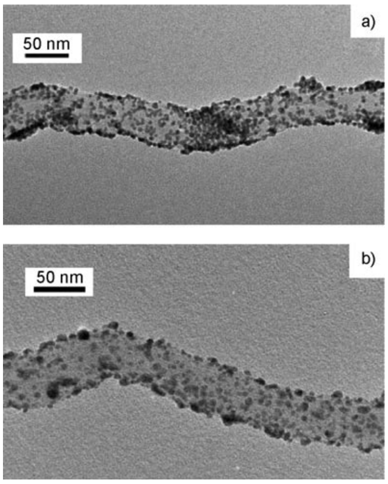


Figure 2. TEM images of a) AuNPs-CNTs, and b) in situ-AuNPs-CNTs. Reproduced with permission from *Chem. Phys. Lett.* **2005**, *401*, 352–356.

Smorodin and co-workers[43] discovered a method to deposit and to chemically bond SWNT perpendicularly to prepatterned gold electrodes. In their method, thiol end groups were produced chemically on the SWNT ends and defects, and then by surface acoustic waves to a SWNT suspension, the SWNT were oriented with respect to the electrodes.[44] Thus, the AuNPs were tethered to the thiolated SWNTs. The SWNTs and AuNPs were characterized by SEM images.

A novel strategy of combining microwave radiation with polyol reduction of a metal salt to derivatize CNTs with AuNPs in a single processing step was demonstrated by Raghuveer and co-workers.[45] Exposing CNTs to microwaves results in defect creation and formation of functional groups on the CNT surface. The functional groups serve as preferred nucleation points for reducing metal ions in solutions by microwave-assisted reduction reactions, yielding CNTs that are uniformly decorated with AuNPs. The typical roots to functionalize CNTs include the acid-based wet chemical oxidation, esterification, diimide activation, electrochemical modification or the hydrophobic adsorption of aromatic derivatives,[46–49] however, a new ecofriendly approach by using microwaves to rapidly functionalize MWNTs with carboxyl, carbonyl, hydroxyl and allyl termini without using the above-mentioned aggressive oxidants or ultrasonication has also been described.[45] The CNTs derivatized with nanoparticles synthesized by in situ metal-ion reduction during functionalization, all in a single-processing step. The other functional groups such as amines and thiols can also be generated on CNTs by microwave exposure in a controlled gas environments (e.g., NH_3, H_2S). The TEM examination revealed that the functionalized MWNTs are derivatized with AuNPs, when ethylene glycol is present (Figure 3a). A representative bright-field micrograph at a slightly higher magnification is shown in Figure 3b. The AuNPs are equi-axed and the MWNT surface is uniformly decorate along its length. The nanoparticle size ranges from 3 to10 nm, with an average of ~6 nm (Figure 3c). The overall tubular structure of the MWNTs remained intact in contrast to rupture and tube breakage, which is observed during functionalization by aggressive sonication and acid treatment.[50]

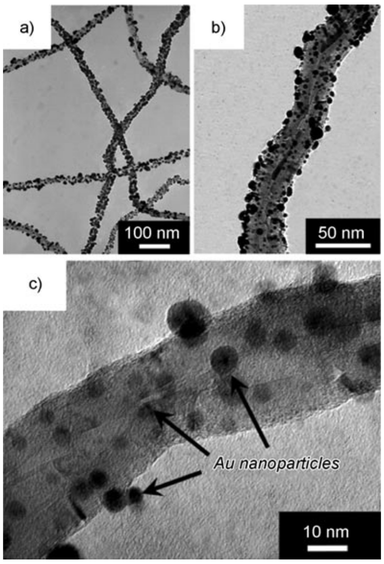
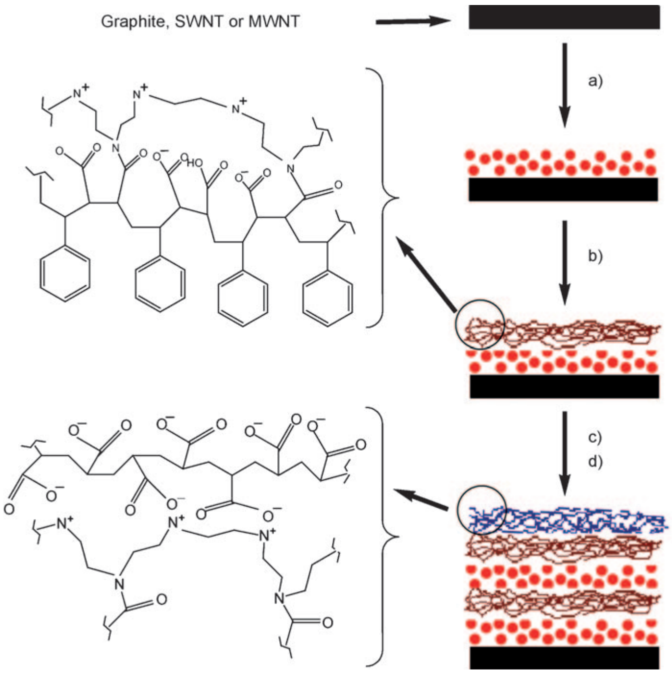


Figure 3. a), b) Low- and c) high-magnification bright-field TEM images showing the decoration of MWNTs with 3–10 nm diameter AuNPs. Reproduced with permission *Chem. Mater.* **2006**, *18*, 1390–1393.

Noncovalent functionalization of CNTs with polymer multilayers and AuNPs: Carrillo et al.[51] functionalized hydrophobic graphite and CNT surfaces[52] to form polymer multilayers on methyl-terminated self-assembled monolayers of hexadecanethiolate on gold (Scheme 2). The hydrolyzed poly(styrene-*alt*-maleic anhydride (hPSMA) adsorbed noncovalently onto graphite or CNT surfaces from aqueous solutions via hydrophobic interactions. This noncovalently attached layer of hPSMA contained carboxylic groups, which were used to attach poly(ethylenimine) covalently and a cross-linked polymer bilayer was formed, which increased the stability of the polymer layer. These steps are repeated to build a multi-layered polymeric film, consisting of alternate polyanionic and polycationic layers. The noncovalent method of functionalization is important for preserving the mechanical and electrical properties of CNTs. Functionalization with polymer multilayers allows the introduction of reactive groups, for example, carboxyl acid or amine groups onto the nanotube surface, and these groups may be utilized to attach biospecific ligands[53] and other groups as well. Thus, nonspecific adsorption of biomolecules[54] have been used for applications in biosensors.



Scheme 2. Schematic showing the procedure used to prepare multilayered polymer films. a) Deposit a layer of h-PSMA and rinse with deionized water; b) covalently attach a layer of PEI and rinse with deionized water; c) repeat steps a) and b) to deposit a second bilayer, and d) deposit a layer of PAA.

Ellis et al.[55] connected monolayer-protected AuNPs to non-oxidized CNTs by means of relatively weak (~0.1 eV) hydrophobic interactions, rather than covalent interactions. The anchorage was done by interdigitation of alkyl chains of self-assembled molecular layers (SAMLs) by capping the nanoclusters and molecular moieties adsorbed onto nanotubes. Due to the similarity of the SAMLs to many biomolecules (e.g., proteins), the cluster attachment through SAMLs will enable the design and creation of new bio-inspired hybrid nanodevices. The MWNTs synthesized by the arc-discharge method were treated with acetone for 1 h in an ultrasonic bath and then dried in air for 15 h to remove traces of acetone. These activated tubes were dispersed in toluene by agitation in an ultrasonic bath and then mixed with octanethiol-capped gold nanoclusters, which were prepared by the Brust method.[56] The gold nanoclusters were attached to the MWNT surface by mixing the octanethiols-capped nanoclusters with the acetone-reacted MWNTs dissolved in toluene. The attachment of the gold nanoclusters to nanotubes was confirmed by UV-visible, FTIR spectroscopy and HR-TEM images.

The polymer-wrapping technique, which allows the noncovalent attachment of silica-coated, AuNP mono- and multilayers onto CNT templates was also used.[57] Such composite nanowires were optically labeled and have potential applications as components of nanoelectronic circuits and waveguides. The MWNTs were dispersed in water by sonication in the presence of poly(styrene sulfonate) (PSS), which acts as the wrapping polymer, yielding a stable dispersion of individual CNTs. PSS has negatively charged sulfonate groups, which serve as primer for the homogeneous adsorption of the cationic polyelectrolyte poly(diallyldimethylammonium chloride) (PDDA).[58] In the layer-by-layer (LBL) technique, the interactions responsible for the assembly are mainly electrostatic[59] and allow the exploitation of the surface properties of silica to obtain close-packed mono- and multilayers, as shown in Figure 4. It is observed in Figure 4a that very long MWNTs (> 8 µm) are completely covered with

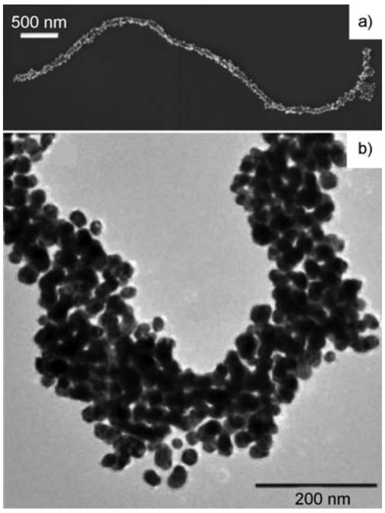
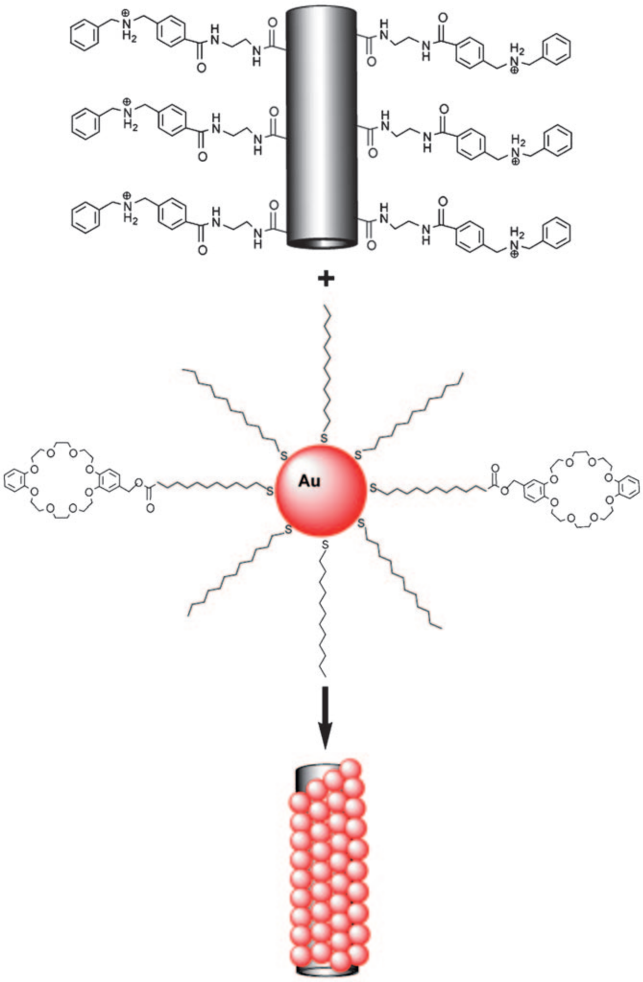


Figure 4. a) SEM image of thin MWNTs (15 nm outer diameter) on which one monolayer of Au@SiO_2 nanoparticles have been assembled using LBL process. b) TEM image of thin MWNTs (15 nm outer diameter), coated with two monolayers of Au@SiO_2 nanoparticles. Note that larger AuNPs (22 nm) were assembled on thin CNTs and the silica-shell thickness is ~3 nm.[57]

dense monolayers of Au@SiO_2 nanoparticles. However, Figure 4b shows that nanotubes are coated with two monolayers, and in both the cases compact packing was achieved. The repetition of the LBL process allows a good control of the thickness of the nanocomposites by increasing the number of layers deposited.

The use of a dibenzylammonium-cation-modified MWNTs to template the noncovalent self-assembly of crown-modified (dibenzo[24]crown) AuNPs was described by Sainsbury and Fitzmaurice.[60] The driving force for the self-assembly was the formation of a surface-combined pseudorotaxane (Scheme 3). The stable dispersion of dodecanethiol-modified AuNPs was prepared by the method described by Brust et al.[44] The nearly size-monodisperse fraction was subsequently modified by the exchange of the adsorbed thiol for thiol-incorporating crown molecules (dodecanethiol incorporating a crown moiety in the terminal position).[61] The MWNTs were modified by two amide-coupling reactions: the first was between the carboxy-modified MWNTs and ethylenediamine, and the second between the remaining amine of the coupled ethylenediamine and the cation precursor [*N*-(4-carboxydibenzylamine)carbamate]. For the templated self-assembly of a gold nanowire in solution, a dispersion of crown-modified AuNPs in chloroform was added to a freshly sonicated suspension of cation-modified MWNTs in chloroform. The gold nanowire formation was confirmed by TEM. The MWNT-templated self -assembly of a solid nanowire was observed only when uncomplexed cations were present on the surface of the MWNTs and uncomplexed crown was present on the surface of the AuNPs. Therefore, it was concluded that the templated self-assembly of nanowires is driven by the formation of the surface confined to pseudorotaxanes (Scheme 3).



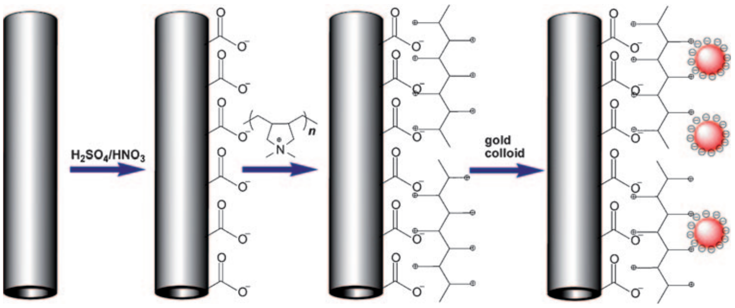
Scheme 3. A cation-modified MWNT template the noncovalent self-assembly in solution of a gold nanowire from crown-modified AuNPs.

Correa-Duarte et al.[62] demonstrated the uniform electrostatic assembly of gold nanorods on MWNTs in such a way that the rods form strings with end-to-end contacts. Such a morphology results in uni-axial plasmon coupling but can be used to monitor the degree of alignment of CNTs within polymer films or other nano-structured systems. The formation of the aligned gold nanorods is based on the polyelectrolyte LBL approach.[63,64] Prior to the assembly of gold nanorods, the MWNTs were wrapped with the negatively charged polyelectrolyte PSS, followed by electrostatic assembly of the positively charged polyelectrolyte PDDA.

A new strategy, where the noncovalent functionalization of MWNTs was performed with a surfactant (sodium dodecyl sulfate: SDS) using the LBL assembling of a MWNT multilayer film onto indium tin oxide (ITO)-coated glass plates for attaching the AuNPs onto the MWNTs to fabricate a AuNPs/MWNT nanohybrid was described by Zhang et al.[65] The surfactant interacts with the MWNTs through hydrophobic interactions between the hydrophobic chains of the SDS and the sidewalls of the MWNTs, which leads to the noncovalent adsorption of SDS onto the MWNTs, resulting in an enhanced dispersion of MWNTs in distilled water and providing negative charges to the tube surface. More importantly, the adsorption of the surfactant onto the MWNTs creates a distribution of electronic charges at the tube surface and, thus, makes it possible to uniformly LBL assemble MWNT multilayer films onto the solid substrate and fabricate a AuNPs/MWNT nanohybrid. Due to these properties, the MWNT multi-layer film assembled onto the ITO plate through the alternate adsorption of oppositely charged SDS-functionalized MWNTs and polyelectrolyte (i.e., PDDA), as characterized by SEM, UV/Vis-NIR spectroscopy and cyclic voltammetry (CV). The same properties of the SDS-functionalized MWNTs were also demonstrated to be useful for mediating the attachment of AuNPs onto the surface of the tubes. This strategy[66–68] through a noncovalent approach may be superior to those of using covalent approaches due to the ability to maintain the electrical and structural properties of the CNTs. Further applications of the LBL-assembled CNT multi-layer films and the AuNPs/MWNT nanohybrids are in the development of bio-electronic nanodevices such as biosensors and biofuel cells.

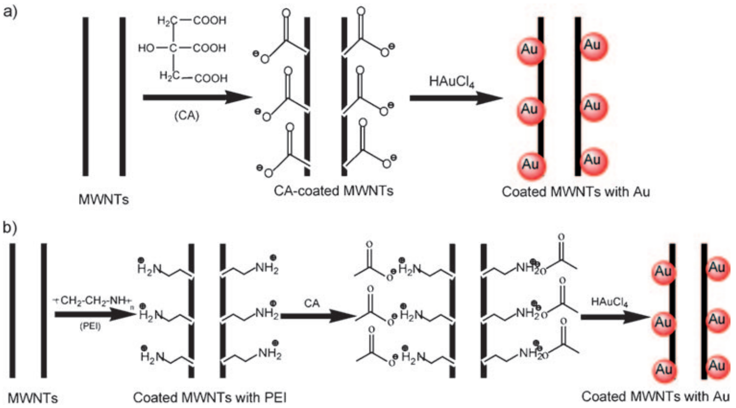
Attachment of AuNPs to CNTs: AuNPs were anchored to the surface of nitrogen-doped multiwalled CNTs

(CN_xMWNT) by Jiang and co-workers[69] by a simple and versatile technique of electrostatic adsorption. The product CN_xMWNT was initially modified/functionalized with a mixture of H_2SO_4 and HNO_3 to result in carboxyl, carbonyl, hydroxyl, and sulfate groups on the surface. Subsequently, the nanotubes were tailored with a cationic polyelectrolyte and exposed to negatively charged AuNPs for selective anchoring of the nanoparticles on the surface through the electrostatic interactions between the polyelectrolyte and the nanoparticles. Thus, a novel hybrid nanostructure with homogeneously distributed AuNPs on the nitrogen-doped CNTs resulted. This method of decorating nanotubes can be also used to identify the location of the functional groups. The procedure for the nanotube surface modification and the AuNPs attachment on the nanotube surface is shown in Scheme 4. The CN_xMWNT consists of carpet-like structures of uniform diameter (10–40 nm) and length (50–60 μm), which was confirmed by high-resolution TEM. These nanoparticle-decorated nanotube heterostructures could be used in catalytic, electronic, optical, and magnetic applications.



Scheme 4. Schematic illustration of the process for anchoring AuNPs to CN*x* nanotubes.

AuNPs were selectively attached onto CNTs by gas treatment, which is more convenient and avoids the introduction of impurities.[37] In this versatile and novel method, they used cationic poly(ethylenimine) (PEI) and anionic citric acid (CA) as dispersing agents to modify the surfaces of CNTs. In the case of CA-coated MWNTs, a layer of about 10 nm consisting of AuNPs was attached to the outer layer of the nanotubes. The citric acid forms an adsorption layer around the outer walls of the CNTs and then reduces in situ the $HAuCl_4$ to produce the AuNPs. The PEI treatment of the nanotubes and the exposure to the $HAuCl_4$ solution generated nitrogen-containing functional groups on the outer walls of the CNTs and has been confirmed from FTIR spectroscopic and Zeta potential measurements.[70,71] Moreover, the electrostatic interaction of PEI and citric acid occurred only at the outer layers of the nanotubes, which is proved by the attachment of AuNPs onto the CNTs, as shown in the Scheme 5. PEI is effective for imparting a positive charge, while citric acid produces a negative charge around the nanotubes.



Scheme 5. Simulative view of the process for attaching AuNPs to a) CA-coated, and b) PEI-coated CNTs.

Goring et al.[72] attached gold onto CNTs by annealing impregnated porous alumina at 200 °C for 2 h and at 350 °C for 1 h. The matrix surrounding the gold crystallites (10 nm diameter) does not show any lattice fringes and, thus, is amorphous only. Alexeyeva and co-workers[73] prepared a AuNPs-MWNT hybrid by adding an aqueous solution of $HAuCl_4{\cdot}3H_2O$ to an aqueous suspension of MWNTs–SDS under stirring, followed by the addition of an aqueous $NaBH_4$ solution. The aqueous dispersion of AuNPs–MWNT was assembled onto the surface of a glassy carbon (GC) electrode by physical adsorption, followed by drying in air. This modified electrode showed a high electrocatalytic activity for the oxygen reduction.

A high-density assembly of AuNPs on the sidewalls of MWNTs using 1-pyrenemethylamine as the interlinker has been also demonstrated.[74] The alkylamine substituent of the pyrene derivative binds to a AuNPs, while the pyrene fluorophone is in contact with the sidewalls of the CNTs via π–π stacking interactions. A significant quenching of the luminescence of 1-pyrenemethylamine upon binding to the AuNPs was also recorded, which is a result of energy transfer and/or electron transfer from the excited pyrene fluorophore to the AuNPs. This strategy of the high-density assembly of AuNPs onto the surface of CNTs may be applied to other linking molecules such as *N*-(1-naphthyl) ethylenediamine and phenethylamine, which demonstrates that the molecules of similar structures can also serve as effective interlinker in producing MWNT–Au nanostructure composites.

Kim et al.[75] prepared a water-soluble CNT–AuNPs hybrid material in the homogeneous phase by using the reduction reaction of a gold salt with surfactant-suspended SWNTs in water by using the solution-phase dispersion technique (Figure 5).[76] The average size of the AuNPs was 2.94 ± 0.75 nm as measured from high-resolution TEM image (Figure 5b). It was calculated that 7.5×10^{-17} g of Au was coated on one individual nanotube and one tube contained about 300 AuNPs. In contrast to previous studies, a reductant was not used and not needed in this approach. The well-dispersed AuNPs were formed quite uniformly on the sidewalls of SWNTs (Figure 6). This process is easy to scale up and the size also can be controlled. In addition, water-soluble and processable products are formed.

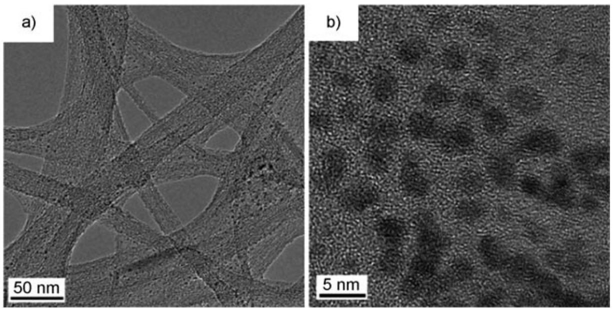


Figure 5. TEM images of the CNT/AuNPs hybrid a), and high-resolution TEM image of the CNT/AuNPs hybrid b) obtained from a solution of CNTs suspended in Tween 80 (0.46 mM of $KAuCl_4$; focusing on the AuNPs prevents visibility of the SWNTs, b).[75]

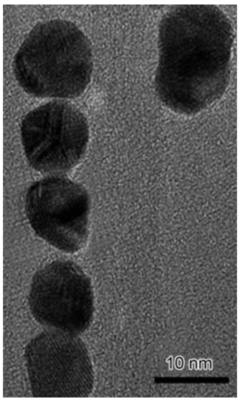


Figure 6. High-resolution TEM image of the CNT/AuNPs hybrid obtained from a solution of CNTs suspended in Tween 80 (3.5 mM of $KAuCl_4$).[75]

Sonication-assisted deposition of AuNPs: The gold deposition onto nanotubes is not an easy task, as the well-graphitized CNTs have normally a very regular structure, not allowing the attachment of AuNPs. A detailed survey of formation of AuNPs–CNTs hybrid materials including the diameter of AuNPs is presented in Table 1. If the regular structure is damaged, the chances for a successful deposition increase. An efficient way of breaking the regularities of the structure by ultrasonication cavitation has been reported and deposited AuNPs onto the outer surface of CNTs deposited.[77] They prepared a gold colloid from $HAuCl_4$ solution, which was decomposed and stabilized with a solution of sodium hydroxide or tetrakis(hydroxymethyl)phosphonium chloride (THPC). The gold dispersion occurred by adding the gold colloid to the CNT suspension during sonication. Both, the sonication upon gold deposition and the stabilizer of the gold colloid (THPC) were equally important in the preparation.

The gram-negative bacteria *Acidothiobacillus ferrooxidans* has also been reported for the electroporation of AuNPs via CNTs.[78] The bacterial suspensions were prepared by the dispersion of pellet cells from a culture in a colloidal gold solution containing hydrophilic CNTs. The filtered bacterial suspension was centrifuged and the supernatant discarded. The cell viability and cell growth provided insight into the stability of cell in microwave exposure, the reversibility of electroporation via CNTs, and the ability of the cells to withstand a high intake of AuNPs. Upon random addition to a bacteria–AuNPs solution, CNTs, and the AuNPs remained uniformly suspended without a strong tendency to accumulate on the cells. However, upon exposure to microwaves, a large fraction of CNTs and AuNPs accumulated on the cell surface (Figure 7). Some of them even penetrated the cell walls, which may be due to the oscillating dipole moments of the metallic particles. These charges (dipole–dipole moment), in turn, induce effective opposite image charges in the metallic CNTs and AuNPs, consequently leading to the observed mutual attraction of AuNPs and CNTs. This effect is clearly visible (in Figure 7 a, b) and the actual transport of AuNPs across the cell wall is seen in Figure 7 c. This novel technique has a great potential for applications in cell biology and medicine.[79]

AuNPs were used to immobilize $HS\text{-}(CH_2)_{11}\text{-}CH_3$ on the surfaces of SWNTs and MWNTs through dispersion, which creates novel hybrid materials.[80]

Biju et al.[81] employed sidewall functionalization of SWNTs to prepare nanoscale hybrid material of SWNT–QD (CdSe–ZnS quantum dots) and SWNT–AuNPs conjugates and examined the photoluminescence (PL) properties of the hybrid material. The excessive sidewall functionalization of the SWNTs into nitro and amino derivatives provided a weak PL and water-solubility to the SWNT derivatives. The SWNT–QD and SWNT–AuNPs conjugates were also characterized by AFM imaging, which confirmed the formation of one-dimensional conjugates of QD and AuNPs. From absorption and PL spectral measurements, it was observed that the conjugation of QD and AuNPs to SWNTs induce a charge transfer and non-radiative energy transfer interactions between the components. These interactions perturbed their energy states, absorption, and PL characteristics. The schematic diagram for the preparation of SWNT–QD and SWNT–AuNPs conjugates is shown in Scheme 6.

The hierarchical nanoscale hybrid structures based on the SWNT and nanoparticle hybrid materials and an understanding of their optical properties would be promising building blocks of light harvesting system[82,83] and nanoscale optoelectronic devices.

Chemical vapor deposition: Chin and co-workers[84] deposited a polycrystalline gold coating (thickness: 5 nm) onto MWNTs and studied their optical limiting (OL) properties. The improvement of the OL performance of the MWNT–AuO_5 was mainly due to the surface plasma adsorption processes in the polycrystalline Au nanoparticles at 532 nm, resulting in an increase in the nonlinear scattering properties of the MWNTs, which was measured by nanosecond laser pulses. The enhancement of the nonlinear scattering was attributed to the surface plasmon absorption. Yamada et al.[85] reported the first preparation of MWNTs over a AuNPs catalyst using hydrocarbon gas (C_2H_2 and C_2H_4) for chemical vapor deposition (CVD) with the dependence of the carbon

Table 1. Survey of different approaches for the synthesis of CNT-AuNPs composites.

Technique	Type of CNTs	Gold source	Reducing agent/energy used	AuNPs diameter [nm]	Ref.
wet chemistry	MWNTs	$AuCl_3$	stirring/heated under Ar atmosphere	1–5	[34]
gas and heat treatment	MWNTs	$HAuCl_4$	citric acid/stirring	1–2[a]	[37]
solvent-free	MWNTs	$HAuCl_4$	citric acid/ultrasonication	1–5	[40]
self-assembly of AuNPs on functionalized CNTs	MWNTs	$HAuCl_4 \cdot 4H_2O$	$NaBH_4$/stirring in H_2O at room temperature	5	[41]
microwave radiation	MWNTs	$HAuCl_4$	ethylene glycol/microwave radiation	3–10	[45]
non-covalent functionalization method	MWNTs	$AuCl_3$ (gold nanoclusters)	ultrasonication in toluene	1–3	[55]
polymer-wrapping and layer-by-layer technique	MWNTs	silica-coated AuNPs	sonication	2–6	[57]
non-covalent self assembly	MWNTs	AuNPs	sonication	8	[60]
layer-by-layer approach[b]	MWNTs	gold nanorods	sonication	30	[62]
non-covalent supramolecular approach	MWNTs	$HAuCl_4 \cdot 3H_2O$	$NaBH_4$/stirring in H_2O	5	[65]
electrostatic adsorption	CN_xMWNTs[c]	gold colloids	sonication	10	[69]
selective attachment	MWNTs	$HAuCl_4$	citric acid/stirring	10	[37]
electro-chemical reduction	MWNTs	$HAuCl_4 \cdot 3H_2O$	$NaBH_4$/stirring in H_2O	polydisperse	[73]
high-density assembly	MWNTs	$HAuCl_4$	sodium citrate and $NaBH_4$/stirring in H_2O	2–4	[74]
solution-phase dispersion	SWNTs	$KAuCl_4$	none	3	[75]
sonication assisted technique	MWNTs	$HAuCl_4$	NaOH/sonication	–	[77]
sonication	SWNTs/MWNTs	AuNPs	stirred in CH_2Cl_2 and sonication	2–5	[80]
chemical vapor deposition	MWNTs	pure Au target	e-beam evaporator	5	[84]
	MWNTs	$HAuCl_4 \cdot 4H_2O$	$NaBH_4$/stirring in H_2O at room temperature	2–7	[85]
wet chemical self-assembling	SWNTs	Au wire	ultrasonication in absolute ethanol	20–60	[88]
one-dimensional self organized technique	carbon film	AuNPs	α-terpineol in toluene/annealed at 200–400 °C	5	[91]

[a] Inside the nanotubes. [b] Assembly of gold nanorods on MWNTs. [c] Nitrogen doped MWNTs.

source on the prepared CNT structure. The adopted AuNPs were stabilized by dodecanethiol (DT), used as a nanoparticle catalyst after being supported on SiO_2–Al_2O_3 (AuNPs–DT/SiO_2–Al_2O_3). They also controlled the diameter of the CVD-grown MWNTs dependence on the size of the dodecanethiol-stabilized AuNPs.

In another method, CNTs with AuNPs were prepared by repeated CVD polymerization of poly(*p*-phenylenevinylene) (PPV) nanotubes onto the inner surface of the nanoporous alumina membranes, which is followed by carbonization, during which AuNPs were embedded.[86] The PPV nanotubes and their carbonization were described by Kim and Jin.[87] The AuNPs were well dispersed all over the carbonized PPV nanotube (CPNTs) walls without any aggregation. During the carbonization process, the particle size of the AuNPs increased only slightly compared to the original AuNPs (5.3 ± 1.0 nm). Probably electron transfer occurred from the AuNPs to the π-conjugated PPV and carbonized product, which stabilized the AuNPs. As a result, the AuNPs were immobilized by the surrounding PPV, preserving their size, and were dispersed uniformly on the walls of the CPNTs, even after evaporation of the protective dodecylamine and carbonization at high temperature. The field-emission properties of the AuNPs–CPNTs revealed a fairly low threshold voltage and a high amplification factor. The AuNPs also appear to reduce the work function of CNTs, probably by electron transfer from the metal.

Assembly of CNTs on gold surface: In this section an overview is presented on the self-assembly of CNTs on gold surface and their spontaneous self-organization into well-ordered superlattices. It remains a great challenge to find effective ways to organize nanotubes into well-ordered arrays. Two main (wet chemical self-assembled) techniques can be discerned for the self-assembly of CNTs on gold surface.

Thiol-functionalized CNTs on the gold surface: Liu and coworkers[38] cut long SWNT ropes into open-ended short-length pieces and functionalized them by oxidation in concentrated sulfuric and nitric acids. The first report of SWNT by the wet chemical self-assembled technique was based on the formation of thiol-functionalized SWNT monolayers on the gold surface.[88] The assembled monolayers on the gold surface via Au–S bonding, the carboxy-terminated nanotubes were further thiol-derivatized by reaction with NH_2-$(CH_2)_2$-SH in ethanol with the aid of the condensation agent dicyclohexylcarbodiimide (DCC) for 24 h at room temperature (Scheme 7a). The chemical bonding of the carboxylic group of the SWNT and the amine group of the thiol was confirmed by FT-IR spectroscopy through the amide I band at $1600\ cm^{-1}$. The self-assembled monolayer (SAM) of the thiol-functionalized nanotubes was prepared by dipping an Au(111) wire into the ethanol suspension followed by ultrasonication in absolute ethanol and drying in a high purity nitrogen steam.

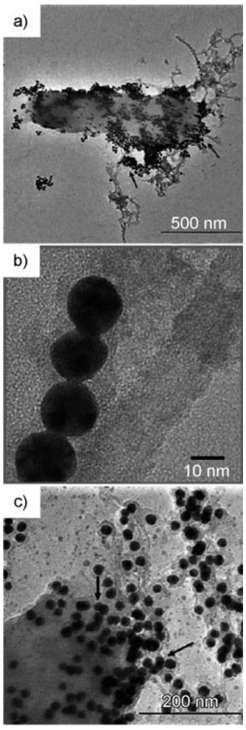
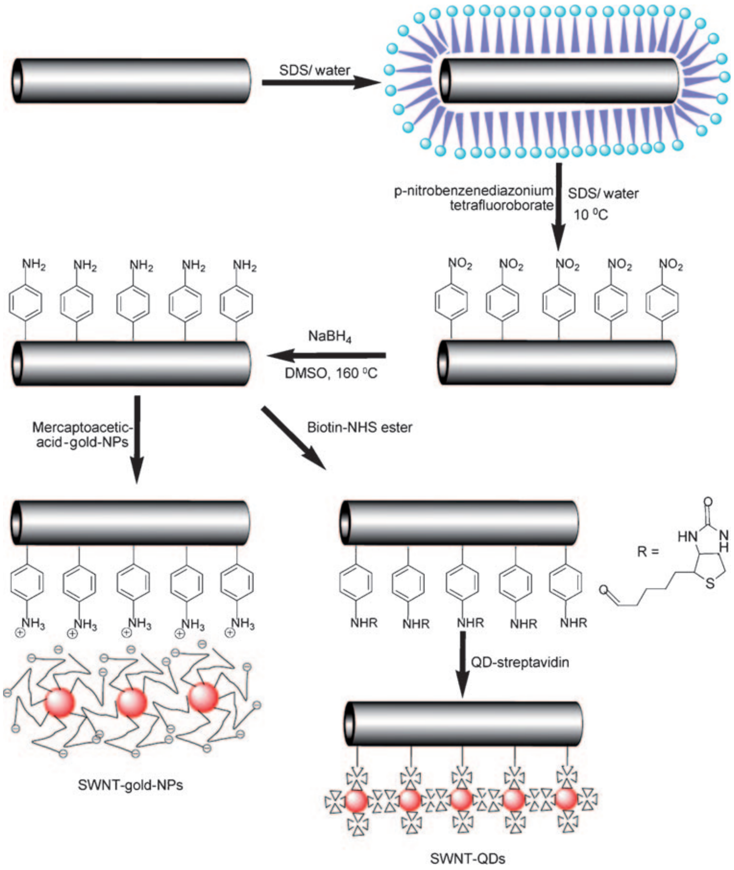
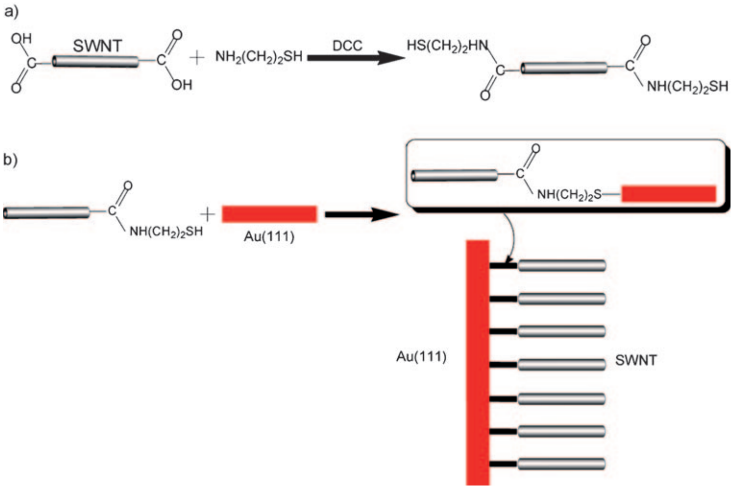


Figure 7. a) TEM picture of the *Acidothiobacillus ferrooxidans* cell after the exposure to microwave (5 s). Accumulation of CNTs on the cell wall is clearly visible. AuNPs also accumulate on the cell wall, but mostly at the CNT-cell contact points (see arrows). b) High-resolution TEM image of a CNT and 4 AuNPs aligning themselves at the CNT surface. c) TEM picture of the area of contact of the cell with CNTs, and of massive AuNPs transfer into the cell. Again, it is clear that AuNPs enter the cell by first aligning themselves along a CNT, and then entering the cell in the vicinity of the CNT tip (see arrows). Reproduced with permission *Nano Lett.* **2004**, *4*, 985–988.



Scheme 6. Steps involved in the functionalization of SWNT and successive conjugation to AuNPs and streptavidin conjugated quantum dots.

The resulting structures have been also confirmed by AFM in Figure 8, where the substrate showed a series of atomically flat triangle terraces, characteristic of Au(111) facets before the adsorption of nanotubes, where needle-like protrusions are clearly seen on the gold surface after adsorption. It is concluded from these observations, that the thiol-derivatized SWNTs have been successfully immobilized on gold via the Au–S chemical bonding, where the nanotubes are perpendicularly placed on the substrate surface (Scheme 7b). The length of the SWNTs self-assembled on gold, as measured from AFM images, falls into the range of 5–25 nm, while the diameters fall in the 20–60 nm range. The short nanotubes are relatively randomly adsorbed on the gold surface because of the strong hydrophobic interactions between them. In contrast, the pre-adsorbed nanotubes function as nucleation centers and with increasing adsorption time, the bundling proceeds.



Scheme 7. a) Thiolization reaction of carboxyl-terminated CNTs with cysteamine (H_2N-CH_2CH_2-SH) and b) assembled structure of SWNTs on gold.

Surface condensation: The wet-chemical technique is also called "surface condensation method", wherein the carboxylic SWNTs are immobilized on the amino-terminated gold surface via a condensation reaction between the carboxyl and amino groups with the aid of DCC as a condensation agent.[89] The carbon nanotubes were carboxylated at both open ends and both termini had the same probability of participating in the condensation reaction.[88] The post-oxidation treatment was followed as described in the literature.[88]

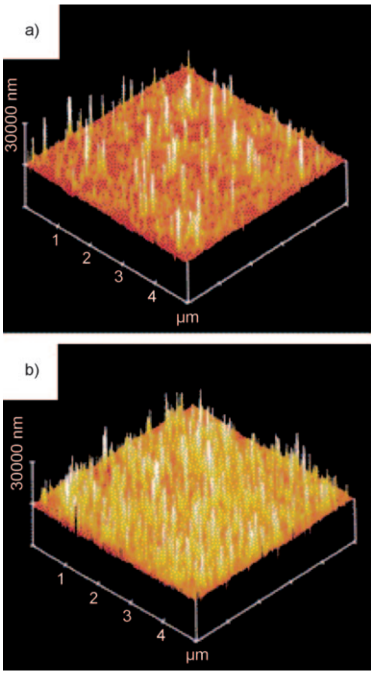
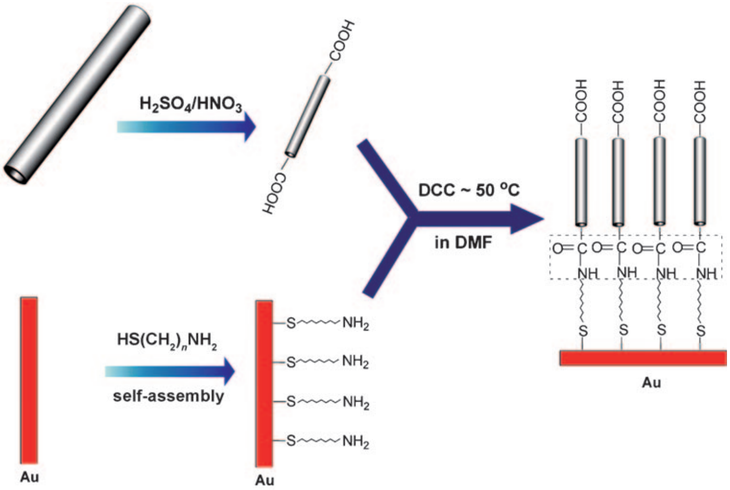


Figure 8. AFM images of SWNTs self-assembled on Au(111) surface via a wet chemistry approach at a) 0.5 h and b) 3 h assembling times. Reproduced with permission *Langmuir* **2000**, *16*, 3569–3573.

The shortened nanotubes were immersed in dimethylformamide (DMF) and then DCC was added in to the suspension, and the mixture was ultrasonicated. Scheme 8 illustrates the basic methodology to immobilize the SWNTs onto the gold using the surface condensation reaction.[89] Firstly, the gold substrate was modified with $NH_2(CH_2)_{11}SH$ SAM-terminated by amino groups. The carboxy-terminated SWNTs were then reacted with the SAM with the aid of DCC in DMF.

Figure 9 shows the typical Raman spectra of the $NH_2(CH_2)_{11}SH$ monolayer on gold before and after reaction with the SWNT. No Raman bands were observed with the pure $H_2N\text{-}(CH_2)_{11}\text{-}SH$ monolayer, while characteristic bands appeared at 172 cm^{-1} and 1588 cm^{-1} after the condensation. This indicates that the CNTs have been deposited on the substrate in the condensation process. The $H_2N\text{-}(CH_2)_{11}\text{-}SH$-covered gold, after dipping into the DCC-free nanotube suspension showed small peaks around 1335 and 1595 cm^{-1}, but no diagnostic Raman peaks of SWNTs around 172 cm^{-1}. Figure 9c and e show the Raman spectra of immobilized carboxylic nanotubes on gold after ultrasonication in ethanol for 15 s and 7 min, respectively, where no discernible change in the Raman spectra was observed for the ultrasonication treatment, indicative of the strong chemical bonding of the nanotubes to the substrate. Only the short tubes can be immobilized on gold surfaces via condensation reaction and it has been proved by Liu et al.[88] that the thiolated nanotubes were deposited on the gold via Au–S bonds.



Scheme 8. Schematic diagram of the surface condensation reaction method for fabricating highly aligned SWNTs on gold.

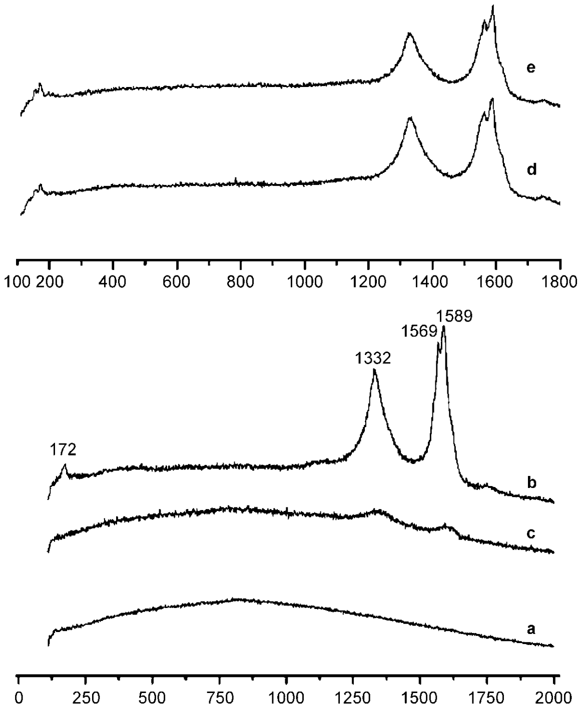


Figure 9. Raman spectra of a) $H_2N\text{-}(CH_2)_{11}\text{-}SH$ monolayer on gold; b) SWNTs immobilized on $H_2N\text{-}(CH_2)_{11}\text{-}SH$-covered gold; c) $H_2N\text{-}(CH_2)_{11}\text{-}SH$-covered gold after dipping into dicyclohexylcarbodiimide-free nanotube suspension for 12 h; the immobilized nanotubes on gold after ultrasonicated in ethanol for d) 15 s, and e) 7 min, respectively. Reproduced with permission from *J. Colloid Interface Sci.* **2002**, *245*, 311–318.

Interaction between AuNPs and Carbon

One-dimensional self-organized technique: AuNPs with a size below 10 nm to form one-dimensional carbon nanocages using self-organization were selected because of the easy control of the cluster size.[90] The surface of these nanoparticles was stabilized by α-terpineol in toluene solution. The magnified image of the prepared AuNPs on an amorphous carbon film is shown in Figure 10. One-dimensional ordering of the AuNPs with a size of 5 nm is observed for a length of

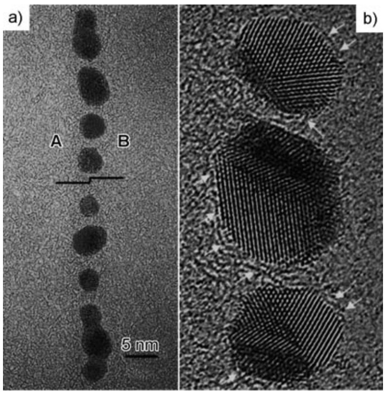


Figure 10. a) Low magnification image of one-dimensional self-organized AuNPs on amorphous carbon film. Atomic step edge of carbon thin film is indicated by solid line. b) Enlarged high-resolution electron microscopy (HREM) image of one-dimensionally self-organized AuNPs. Reproduced with permission from *Microelectron. Eng.* **2000**, *52*, 51–60.

70 nm and width of 15 nm. The atomic surface of the AuNPs is covered with α-terpineol as indicated with arrows. The contrast of the amorphous carbon in the upper region is brighter than that of the lower one and indicates the atomic step edge of the carbon film. The AuNPs grew to 15 nm by coalescence at elevated temperature and the amorphous carbon graphitized by the catalytic effect[91] of the active Au surface at low temperature, when compared to that of ordinary chemical formation of carbon nanocapsules.[92] All the AuNPs are surrounded and isolated by double or triple graphite sheets, which prevent the nanoparticle from growing and act as cluster protection. At high annealing temperatures (400 °C), the electron becomes a part of the amorphous carbon matrix and gets graphitized. In Figure 11, carbon nanocapsules with alternate arrangement (3 nm and 10 nm in size) were observed and may be due to the Au diffusion between the nanoparticles. The Au nanocrystal is almost a single crystal and the Au(111) is parallel to the carbon (002). The Au nanoparticle encapsulated in a carbon nanocapsule was also observed at the tip of nanotube.

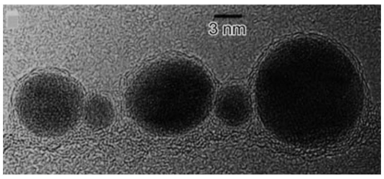


Figure 11. HREM image of alternate arrangement of different size of carbon nanocapsules with AuNPs. Reproduced with permission from *Microelectron. Eng.* **2000**, *51-52*, 51–60.

Applications

A number of applications of metal nanoparticles have advanced close to the stage of commercial implementation. A color change of AuNPs aggregate from ruby-red to blue has been exploited to develop extremely sensitive calorimetric method of DNA analysis to detect the trace amounts of oligonucleotide sequence. It also distinguished between perfectly complementary DNA sequences and those that exhibited different degree of base pair mismatches.[93] Films of AuNPs exhibit strong anisotropy if the particles are aligned into parallel rows and this effect can be exploited for polarizing filters and for displays. Applications of thiol-stabilized AuNPs in catalysis include the asymmetric dihydroxylation reactions,[94] carboxylic ester cleavage,[95] electrocatalytic reductions by anthraquinone functionalized AuNPs,[96] and particle-bound ring opening metathesis polymerization.[97] These catalytic applications have in common the exploitation of the carefully designed chemical functionality of the ligand shell, rather than the potential catalytic activity of a nanostructured clean metal surface. One of the most prominent potential long-term applications for AuNPs and clusters is the development of new, ultimately small electronic devices.[98,99] The single electron transistor action has been demonstrated for systems that contain ideally only one particle in the gap between two contacts separated by only few nanometers.

The attachment of metal nanoparticles to CNTs is a way to obtain new hybrid materials with useful properties for gas sensors and catalytic applications.[100] Gold supported on MWNTs was proposed as a basic element of the glucose biosensor.[101] The attaching of SWNTs to gold tips allows atomic force and scanning tunneling microscopy observations,[102,103] and the potential of MWNTs as a solid phase for adsorption and concentration of true metal ions.[104] A key element for the exploration of nanoparticle–CNT composite as sensor or catalytic materials is the possibility of an effective and controllable assembly of AuNPs on the surface of CNTs. The attachment of AuNPs onto CNTs could also serve to detect the presence of certain functional groups on their surface and thus to prove that the derivatization was successful.

The SWNTs and MWNTs have also been investigated in numerous promising areas such as field emitters,[13] memory elements,[105] sensors,[106] and nanotube equators.[19] The noble metal nanoclusters, particularly AuNPs, became the focus for many researchers because of their special optical properties,[107] unusual electronic properties including conductivity by activated electron hopping,[108] and remarkably a high catalytic activity.[109] The hybrid nanostructures combining the two kinds of materials might improve the performances and will further extend the applications.

The CNTs are great of interest due to their unique electronic, chemical and mechanical properties for creating new generation electronic devices and networks.[110–113] Despite the insolubility of CNTs in most common solvents, some progress towards their chemical processing for dispersion in solvents and rapping with polymer has recently been achieved.[114–119] To optimize the potential applications of CNTs, it is essential to modify the inner side-walls by chemical functionalization and attach suitable nanoclusters to the nanotubes.[120,121] Thus, functionalized nanoparticles could be used as versatile building blocks for the construction of nanodevices, for example, the attachment of AuNPs to CNT sidewalls shows particularly great promise towards novel, highly, efficient photo-electrochemical cells, fuel cells, or even sensor devices.

Summary and Outlook

The current and potential future applications of nanoparticles are discussed for future developments in this section. Research in self-assembled metal nanostructures has clearly succeeded promisingly in many different directions. While significant advances have been made in the controlled bottom-up assembly of such structures, the challenges to design and prepare three-dimensional objects of precisely controlled geometry remains an important goal for future research efforts. Along with the developments of a larger repertoire of construction strategies, a more profound understanding of the process involved and a host of new applications will emerge in the easily predictable areas such as electronics and sensors. The monolayers protected clusters promise new applications in molecular recognition and imprinting. Artificial receptors and enzymes could be developed using a combinatorial approach with a complex variety of functional ligands that can organize into highly specific supramolecular sites on the particle surface. Another clear mission for future research will be the exploration of multicomponent systems which do not only contain one type of nano-sized building block, but rather several different types of structurally cooperating components, for example, the combination of metal semi-conductor nanoparticles.[122,123] This may lead to the development of new materials and structures with functional properties superior to those of the current conventional materials.[124]

Acknowledgements

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