Gold-carbon nanotube nanocomposites: synthesis and applications

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Abstract: Nanocomposites are combinations of nanomaterials with other molecules or nanoscaled materials, such as nanoparticles or nanotubes. In general, these novel nanocomposites have different physical and chemical properties from the constituent particles or wires, and will thus allow new kinds of applications. Among these nanocomposites, gold-carbon nanotube (Au-CNT) composites are of particular interests, due to their easy fabrication protocols and broad potential applications. Au-CNT nanocomposites commonly refer to gold nanoparticles deposited on carbon nanotubes. To obtain Au-CNT nanocomposites, different methods have been developed, including direct and linked deposition of gold nanoparticles on CNT. Au-CNT nanocomposites combine the excellent physical and chemical properties of both gold nanoparticles and carbon nanotubes. The easy modification surface of gold nanoparticle and the excellent conductivity of carbon nanotube as well the high surface area, point towards a broad range of applications, such as biosensing, gas sensing, and electrochemistry. This paper reviews the recent progress of different kinds of Au-CNT nanocomposites and their synthesis and applications.

Keywords: nanocomposites; gold nanoparticles; carbon nanotubes; synthesis; applications; sensors.

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1 Short introduction

Gold nanoparticles can be traced back to 19th century, when Faraday (1857) made the first gold colloids. Today, the synthesis of gold nanoparticles is commonly based on the Turkevich et al. (1951) and Frens (1973) methods. There are several reviews on the synthesis and applications of gold nanoparticles, both general (Daniel and Astruc, 2004), theoretical (Ghosh and Pal, 2007), and experimental ones (Ghosh and Pal, 2007; Huang et al., 2007; Guo and Wang, 2007; Hu et al., 2006a) are available. The group of Rosi and Mirkin (2005) is making notable contributions, mainly focusing on optical biosensing. Beside optical studies (Thomas and Kamat, 2003), electrochemical investigations based on gold nanoparticles are obtaining much attention (Welch and Compton, 2006; Wang, 2007; Shipway et al., 2000).

Many applications of gold nanoparticles have been developed and applied in real applications, while more demands are emerging in other areas. To further increase the application areas of nanoparticles, multifunctionalised materials have been developed (Breuer and Sundararaj, 2004). These nanocomposites combine the properties of their components, but may also provide novel properties (Datta et al., 2007; Zhang et al., 2010c). Recently, various gold-based nanocomposites have been developed, such as gold-carbon nanotube (Au-CNT) nanocomposites (Zhang and Wang, 2007; Kim and Sigmund, 2004; Zhang et al., 2009b; Kim et al., 2005; Choi et al., 2002; Hu et al., 2006b; Raghuveer et al., 2006), polymer-gold nanocomposites (Park et al., 2004; Pérez-Juste et al., 2005; Li et al., 2009a; Yagci et al., 2008; Corbierre et al., 2005; Mandal et al., 2002), biomolecule-gold nanocomposites (Park and Stroud, 2003; Qi et al., 2006; Zhang et al., 2007; Zhang et al., 2006b), and so on. These composites are used in a number of applications, e.g., sensors (Zhang et al., 2006a; Chen et al., 2008; de Oliveira Marques et al., 2009; Shimada et al., 2007), optics (Zijlstra et al., 2007; Qu et al., 2001; Ispasoiu et al., 2000), and in the medical area (Lee et al., 2008; Mishra et al., 2007; Bielinska et al., 2002; Ding et al., 2007).

Here, we give a brief review of Au-CNT nanocomposites, covering the categories of gold nanocomposites, the methods to fabricate gold nanocomposites, and their applications.

2 Types of gold nanocomposites

The easy modification of gold nanostructures makes them a suitable material for forming composites with other molecules or materials. Many kinds of gold nanocomposites have been developed for different purposes during the last ten years. These types of gold nanocomposites can be defined as:

1 inorganic-gold nanocomposites
  - Au-CNT nanocomposites (Zhang and Wang, 2007; Kim and Sigmund, 2004; Zhang et al., 2009b; Kim et al., 2005; Choi et al., 2002; Hu et al., 2006b; Raghuveer et al., 2006)
  - metal (metal oxide)-gold nanocomposites (Kinoshita et al., 2004; Song et al., 2009; Voevodin et al., 2001; Subramanian et al., 2004)

- non-metal-gold nanocomposites (Kulak et al., 2003; Kim et al., 2008; Tai et al., 2001; Nooney et al., 2002; Cheng et al., 2003)
- other inorganic-gold nanocomposites

2 organic-gold nanocomposites

- polymer-gold nanocomposites (Park et al., 2004; Pérez-Juste et al., 2005; Li et al., 2009a; Yagci et al., 2008; Corbierre et al., 2005; Mandal et al., 2002)
- biomolecule-gold nanocomposite (Park and Stroud, 2003; Qi et al., 2006; Zhang et al., 2007).

Here, in this review, we focus on the Au-CNT nanocomposites.

3 Synthesis of Au-CNT nanocomposites

Carbon nanotubes are one of the most intensively investigated nanomaterials, since their discovery in 1991 (Iijima, 1991). The intrinsic properties of carbon nanotubes, including high surface area, high electrical conductivity, and hollow geometry, are making them attractive in many scientific and industrial fields (Wildgoose et al., 2006; Dresselhaus et al., 2004; Terrones, 2004). However, there are some disadvantages. For example, their surface is highly inert, making them hard to modify or functionalise. To make the surface of carbon nanotubes more flexible, researchers are making efforts to decorate carbon nanotubes with different materials. Gold nanostructures, usually nanoparticles, are the most commonly investigated to form composites with carbon nanotubes, due to the excellent properties of gold.

Au-CNT nanocomposites can be classified according to their attachment modes:

1 direct attached Au-CNT nanocomposites, where gold nanostructures are attached to carbon nanotubes directly without any linking molecules

2 linked Au-CNT nanocomposites, where there are some linkages between the carbon nanotubes and the gold nanostructures.

Surface-linked Au-CNT nanocomposites may further be classified as covalently linked and non-covalently linked. Here, we define those Au-CNT nanocomposites as covalently linked, with only one molecule or group between a carbon nanotube and a gold nanoparticle, and where the molecule is covalently bonded with carbon nanotube and has an Au-S bond to the gold nanoparticle. Other types are called non-covalently linked Au-CNT nanocomposites.

Among non-covalently linked Au-CNT composites, there are several different bonds, forces, or interactions between the carbon nanotubes, gold, and the linking molecules. For the interaction between the carbon nanotubes and the linking molecules (a detailed description is below) these include:

- п-п stacking
- hydrophobic forces
- electrostatic interactions.

For the interaction between gold nanostructures and link molecules (see details below), there are:

- Au-S bonds
- interaction of amino group and gold
- electrostatic interactions.

In some cases, there is just one molecule that links the gold nanoparticle and the carbon nanotube, while others may have two or more molecules that form the link.

3.1 Direct deposition of gold nanoparticles on carbon nanotube

In direct deposition methods, gold nanoparticles are deposited on an unmodified or functionalised carbon nanotube but without any modification of external link molecules. The functionalising process here is commonly used to generate some functional groups on carbon nanotube surface by breaking some C-C bonds and make new functional groups. For example, acid treatment of carbon nanotubes generates –COOH groups on the surface of the nanotubes. The direct gold deposition methods can be generally divided into physical and wet chemical methods.

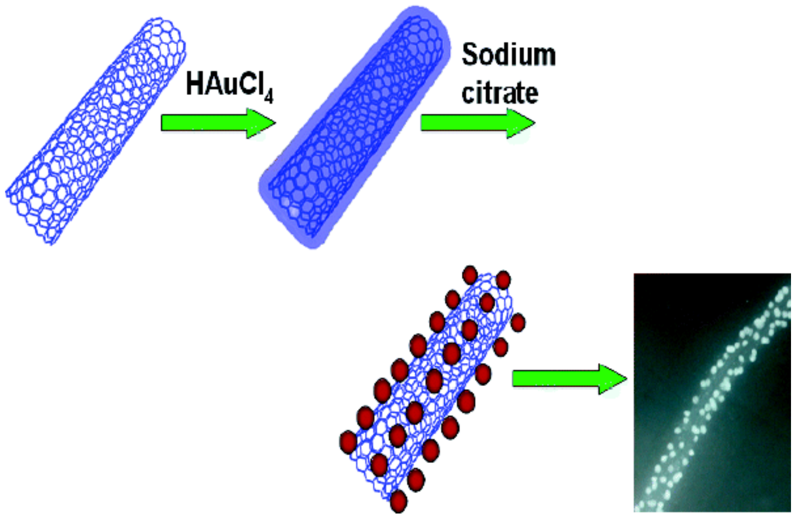
3.1.1 Physical deposition

Thermal deposition of gold nanoparticles is one of the most commonly used physical methods. Gingery and Buhlmann (2008) reported on a thermal evaporation method to deposit gold nanostructures on unmodified carbon nanotubes in an enclosed evaporation chamber at 2×10^{-4} Pa, where the shapes of the deposited gold could be small spherical particles or long wire-like structures. Bittencourt et al. (2006) and Felten et al. (2006) developed a similar thermal method in an ultra high vacuum environment at 1×10^{-10} mbar using a Knudsen evaporator, where the carbon nanotubes were subjected to oxygen plasma to induce oxygen species to the carbon nanotube before the deposition. Electron-beam deposition was also used to coat carbon nanotube with gold and other metal nanoparticles (Zhang et al., 2000), showing the different deposition behaviour of different metal inside a CM20 TEM with accelerates voltage of 200 kV. Another physical method to deposit gold nanoparticles on carbon nanotubes called solvated metal atom dispersion method (SMAD) has been developed recently; first gold is evaporated in an acetone solvent atmosphere to make highly reactive gold clusters, that then are deposited onto carbon nanotubes (Tello et al., 2008). The procedure included condensation at liquid nitrogen temperature.

3.1.2 Wet chemical deposition

Compared with physical deposition, wet chemical methods are usually simpler, without the requirement of vacuum equipments. There are two different wet chemical methods: *in situ* and *ex situ*. The *in situ* procedure deposits gold nanoparticles on carbon nanotube during the synthesis of gold nanoparticles, while the gold nanoparticles are synthesised before the deposition process in the *ex situ* procedure. Zhang and Wang (2007), and Zhang et al. (2009b) developed one step *in situ* methods (Figure 1) to deposit gold nanoparticles on acid purified carbon nanotubes. The carbon nanotubes are first mixed with gold salt to form a precursor coat on the carbon nanotubes, and the mixture is then heated to boiling, followed by adding sodium citrate to form gold nanoparticles on the nanotubes. The size of the gold nanoparticles may be adjusted by simply changing the ratio of sodium citrate and $HAuCl_4$. These gold nanoparticles enhanced the electrochemical response of biomolecules on electrodes, pointing towards biosensor applications (Gu et al., 2007; Lin et al., 2009). Raghuveer et al. (2006) reported a microwave-assisted *in situ* derivatisation of carbon nanotubes with gold nanoparticles, where the microwave treatment functionalised the carbon nanotubes with –COOH moieties (Voggu et al., 2008; Xu et al., 2008). The –COOH moieties contribute to the deposition of gold nanoparticles. Another *in situ* electrochemical deposition method was recently reported by Gao and Zheng (2009), using a method developed for electrochemical deposition of gold nanoparticle on indium tinoxide (ITO) (Tsai and Chen, 2008), and where the carbon nanotubes are modified by amino-terminated ionic liquid. In addition, UV irradiation can also cause the growth of gold nanoparticles on carbon nanotube, using acetone as photosensitive agent (Zhang et al., 2008).

Figure 1 *In situ* procedure of the deposition of gold nanoparticles on carbon nanotubes (see online version for colours)



Source: Reprint from Zhang and Wang (2007); Copyright 2007 American Chemical Society

Ex situ wet chemical methods for direct deposition of gold nanoparticles on carbon nanotubes have not been used as much as the *in situ* wet chemical methods, which may due to the low reactivity of carbon nanotubes. Shi et al. (2009) introduced deposition of pre-made gold nanoparticles on carbon nanotubes through ethanol assistance, which reduce the interfacial tension between carbon nanotubes and aqueous solution and impart solubility of carbon nanotubes. In another one step sonication method by Cui et al. (2005), 2 nm sized gold nanoparticles were deposited on carbon nanotubes directly after one to three-hours of sonication, resulting in reduced tangling of the nanotubes and permitting the assembly of preferentially oriented monolayer films.

For direct deposition, physical methods yield nanocomposites with high purity, since no or less extra decoration is performed. The wet chemical methods have simple procedures, without the need for vacuum equipment as in the physical deposition methods, and allow for high decoration efficiency. The chemical methods require more steps than the physical methods and those treatments may involve damaging steps of the carbon nanotubes surface structure.

3.2 Linked deposition of gold nanoparticles on carbon nanotube

Direct deposition of gold nanoparticles does not require any linking molecules between gold and carbon nanotubes, and they have many advantages like simple procedure and purification. However, the direct deposition methods also have some disadvantages, e.g., the forces between gold nanoparticles and carbon nanotubes are weak, thus, gold nanoparticles may be detached under extreme condition such as strong ultrasonication. Moreover, the direct deposition methods are mainly *in situ* methods, causing the gold nanoparticles to be less uniform due to different local variations on the carbon nanotubes. In contrast, by first synthesising highly uniform gold nanoparticles and then immobilise these nanoparticles on carbon nanotubes by suitable links, relatively ordered Au-CNT nanocomposites could be formed. Of course, these methods also contain some disadvantages, such as a more complicated process, longer processing time, etc.

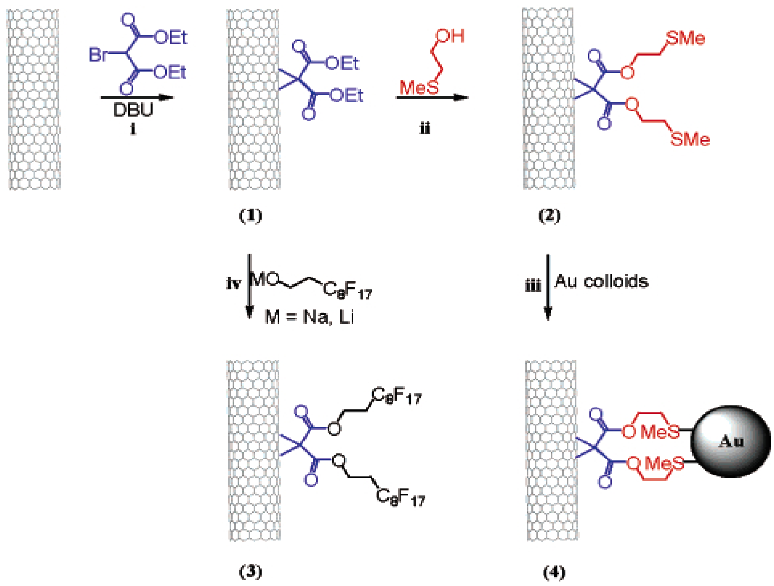
As mentioned above, the links between carbon nanotubes and gold nanoparticles can be classified as covalent or non-covalent. The covalent links just have one molecule or group between carbon nanotube and gold nanoparticles. This molecule or group must have one covalent bond with the carbon nanotube and an Au-S bond with the gold nanoparticle. Alternatively, there may be two or more molecules between, but these molecules are also covalently bonded. Non-covalent link may have one or more molecules or groups between gold and nanotube. There may exist some covalent or Au-S bonds in these non-covalent linked Au-CNT nanocomposites, but these bonds may just be used to modify or functionalise the carbon nanotubes or gold nanoparticles, and the real bonding forces or interaction for the formation of Au-CNT nanocomposites are not covalent bonds. For example, if gold nanoparticles and carbon nanotubes are both modified with long chain hydrophobic molecules, they can form nanocomposite by hydrophobic forces between the modified molecules, while the covalent bond on the carbon nanotubes and the Au-S bond on the gold nanoparticles do not directly contribute to the formation of nanocomposites.

3.2.1 Covalently linked Au-CNT nanocomposites

Chen et al. (1998) and Georgakilas et al. (2007) gave the first description of covalently functionalised single walled carbon nanotubes in 1998. After that, many kinds of ways to functionalise the carbon nanotube with covalent bonds have been developed. Wong's group reviewed the most commonly used way to modify carbon nanotube, based on oxidised carbon nanotubes or pristine carbon nanotubes (Banerjee et al., 2005). Oxidised carbon nanotubes with carboxylate groups can be used to bond with –OH, $-NH_2$, et al., while pristine carbon nanotubes can be directly functionalised by R-(CO)-O-O-(CO)-R, Li/NH_3, (Banerjee et al., 2005). These covalent bonding methods have been demonstrated for nanoparticles deposition on carbon nanotubes (Banerjee and Wong, 2002). Marsh et al. (2008) modified multi-walled carbon nanotubes with 2-aminoethanethiol (in the presence of dicyclohexylcarbodiimide, and assembled gold nanoparticles on these carbon nanotubes, by bonding the gold nanoparticles to the nanotube by the thiolate groups.

Coleman et al. (2003) covalently deposited gold nanoparticles on single walled carbon nanotubes using the Bingel reaction (Figure 2). The deposition is based on the reaction of carboxylate groups on carbon nanotubes with amino groups in 2-aminoethanethiol (Azamian et al., 2002), and the reaction of the thiol group in 2-aminoethanethiol with gold nanoparticles. Zanella et al. (2005) investigated the deposition of gold nanoparticles on different aliphatic bifunctional thiol modified carbon nanotubes. Also, based on the carboxylate group on the carbon nanotubes, $HSCH_2CH_2OH$ can be modified on carbon nanotubes through the reaction of –OH and –COOH groups, for immobilising gold nanoparticles (Hu et al., 2005). Recently, a layer-by-layer (LBL) method for covalently attaching gold nanoparticles on multi-walled carbon nanotubes was reported using cysteamine (CYS) and N-Hydroxysuccinimide (NHS) (Ma et al., 2008), resulting in –(CYS-NHS-CNT-NHS-CYS-GNP)n- structures (*n* is the layers of the composites). Moreover, using the reaction of aryl group with carbon nanotube (Kariuki and McDermott, 1999), one can covalently deposit gold nanoparticles on carbon nanotubes (Shi et al., 2006).

Figure 2 Schematic representation of the chemistry used to cyclopropanate SWNTs (see online version for colours)



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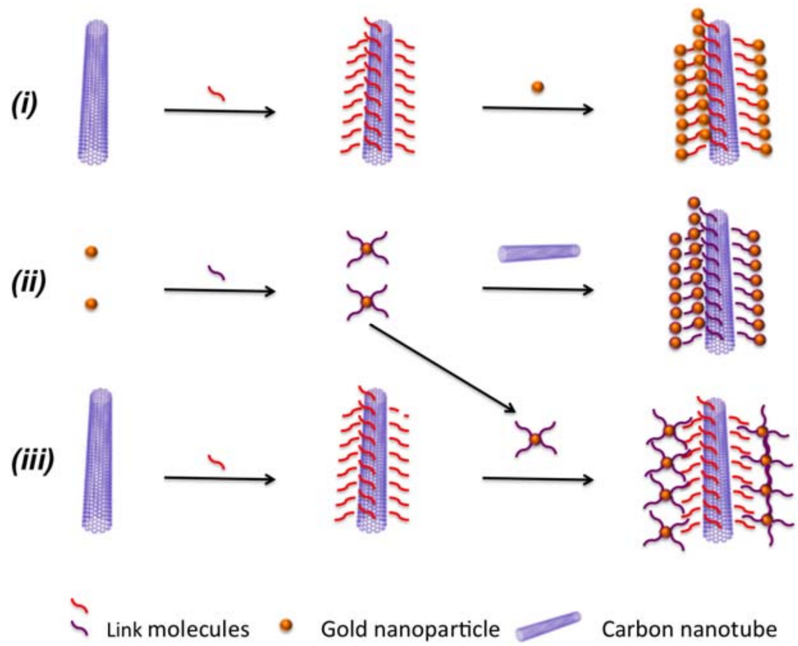
3.2.2 Non-covalent linked Au-CNT nanocomposites

Covalent decoration of carbon nanotubes with gold nanoparticles means to immobilise gold nanoparticles strongly on carbon nanotubes, but the procedures to functionalise carbon nanotubes and the grafting of thiol group are not very easy. Moreover, in many cases, the covalent link is not necessary for further application of gold nanocomposites. Therefore, many non-covalent linked Au-CNT nanocomposites are produced.

As described above, there are different forces or interactions between the linking molecules and the carbon nanotubes or gold nanoparticles. There could be one or a few linking molecules between carbon nanotubes and gold nanoparticles. In these cases, three types of procedures can be adopted (Figure 3).

- *Type 1*: The linking molecules are first attached to the carbon nanotubes and then the gold nanoparticles are deposited.
- *Type 2*: The linking molecules are first attached to the gold nanoparticles, and then these modified gold nanoparticles are bonded to the carbon nanotubes.
- *Type 3*: Both carbon nanotubes and gold nanoparticles are modified with linking molecules, and the nanocomposites are fabricated through the interaction of these two types of linking molecules.

Figure 3 Schematic drawing of the routes to fabricate linkage bridged Au-CNT nanocomposites (see online version for colours)



Type 1 procedure

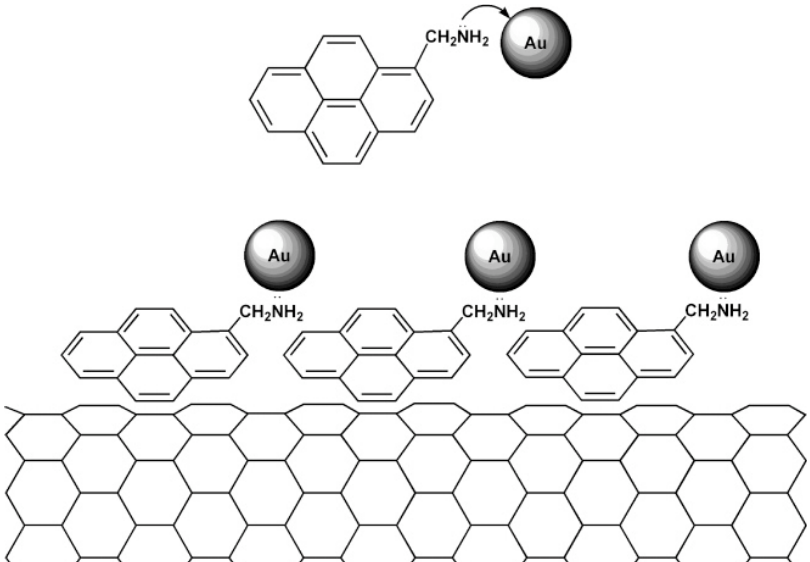
The modification of carbon nanotubes can be with covalent bonds or non-covalent interactions. To generate covalent bonds between carbon nanotubes and linking molecules, one can use some of the methods described in Section 4.2.1. There are also some other methods to from covalent bonds. Jeong et al. (2009) functionalised carbon nanotubes with 3-(aminopropyl) triethoxysilane (APTES) and then deposited gold nanoparticles on carbon nanotubes by the interaction between gold and the amino group of APTES.

For non-covalent bonding, there are several ways to attach linking molecules to carbon nanotubes, including π stacking, hydrophobic forces, and electrostatic interactions.

π stacking

The six-membered ring structure of carbon nanotube offers opportunities for some molecules to π stack onto its surface (Figure 4), e.g., using highly aromatic molecules like 1-pyrenebutanoic (Chen et al., 2001). Liu et al. (2003) and Wang et al. (2002) immobilised gold nanoparticles on carbon nanotubes through the π stacking of pyrene molecules with carbon nanotubes. The gold nanoparticles were bonded to the thiol group through the Au-S bonds. Similar procedure were used by Ou and Huang (2006), where they used 1-pyrenemethylamine as linkage that can π stack onto carbon nanotubes, and interact with gold nanoparticles through lone pair of electrons on the nitrogen atom. Thionine and N,N-bi(2-mercaptoethyl)-perylene-3,4,9,10-tetracarboxylic diimide (MEPTCDI) are also used to link carbon nanotubes and gold nanoparticles through π stacking (Wang et al., 2008b, 2007; Zhou et al., 2007).

Figure 4 A schematic illustration of gold nanoparticle assembly on carbon nanotubes through 1-pyrenemethylamine interlinker



Source: Reprint from Ou and Huang (2006); Copyright 2006 American Chemical Society

Hydrophobic interactions

The hydrophobic surface allows the interaction of carbon nanotube with other molecules through hydrophobic-hydrophobic interaction (Chen et al., 2003). For example, molecules with long carbon chains can bind to carbon nanotube through hydrophobic interaction, e.g., sodium dodecyl sulphate (SDS) (Richard et al., 2003). Zhang et al. (2006a) fabricated Au-CNT nanohybrids by using SDS, which hydrophobically adsorbed on carbon nanotube and mediated the attachment of gold nanoparticles. Similar methods can be found in other papers, where the nanocomposites were used for high sensitive chemical and biological sensing (Xiao et al., 2008; Cao et al., 2008; Alexeyeva et al., 2006), as well as in an application to measure the total length of carbon nanotubes using an 'electrochemical ruler' (Streeter et al., 2008).

Electrostatic interaction

Beside π stacking and hydrophobic interactions, electrostatic interaction of carbon nanotubes with linking molecules is another common method. Chemically oxidised carbon nanotubes have many carboxyl groups, which lead to negatively charged surfaces of carbon nanotubes. Electrostatic interactions will result between these carboxyl groups and positively charged molecules. Jiang et al. (2003) electrostatically modified acid treated carbon nanotubes with cationic polyelectrolyte, charging the carbon nanotubes positively and were then used for the assembly involving negative charged gold nanoparticles, electostatically. Similarly, poly(diallyldimethylammonium chloride) (PDDA) was used to link carbon nanotube and gold nanoparticles, using electrostatic interaction (Yao and Shiu, 2008).

Type 2 and Type 3 procedure

Though the modification of carbon nanotube, as a first step for fabricating Au-CNT nanocomposites is the most common one, there are also some other methods that can be used to form Au-CNT nanocomposites, like Types 2 and 3 procedures. Gold nanoparticles can bond and interact with other molecules through different modes. For example, thiolate group containing molecules are commonly used to modify gold nanoparticles for different purposes. Han et al. (2004) assembled gold nanoparticles on carbon nanotube by first functionalised gold nanoparticles with decanethiolate (DT) followed by the immobilisation of the gold nanoparticles on CNT utilising the links of 11-mercaptoundecanoic aced (MUA) and 1,9-nonanedithiol (NDT). Beside the thiol group, the interaction of amino group with gold also offers possible way to functionalise gold nanoparticles. Rabbani et al. (2009) modified gold nanoparticles with 4-(dimethylamino)pyridine (DMAP) through the donor-acceptor interaction between gold atoms and endocyclic nitrogen in DMAP, and then attached the gold nanoparticles to CNT by electrostatic interactions.

There are few reports that use the Type 3 procedure, since the Types 1 and 2 procedures can produce Au-CNT nanocomposites for most purposes. But the Type 3 procedure could be of importance for some special applications. Ellis et al. (2003) studied the assembly of octanethiolate (OT) modified gold nanoparticles on acetone modified carbon nanotubes through hydrophobic interactions, which may be used for device applications. Fitzmaurice's group reported the self-assembly of crown-modified gold nanoparticles on cation modified multiwalled carbon nanotube, through the formation of the surface-confined pseudorotaxane (Sainsbury and Fitzmaurice, 2004). Sainsbury et al. (2005) also self-assembled TOAB-stabilised gold nanoparticles on covalently modified carbon nanotubes through different interactions, indicating the different binding modes.

4 Application of Au-CNT nanocomposites

Au-CNT nanocomposites have been developed during a relatively short time and many applications have been demonstrated based on these materials. So far, most of the applications are focusing on sensors, e.g., biosensors, gas sensors, and trace element sensors.

4.1 Biosensors

4.1.1 Glucose biosensors

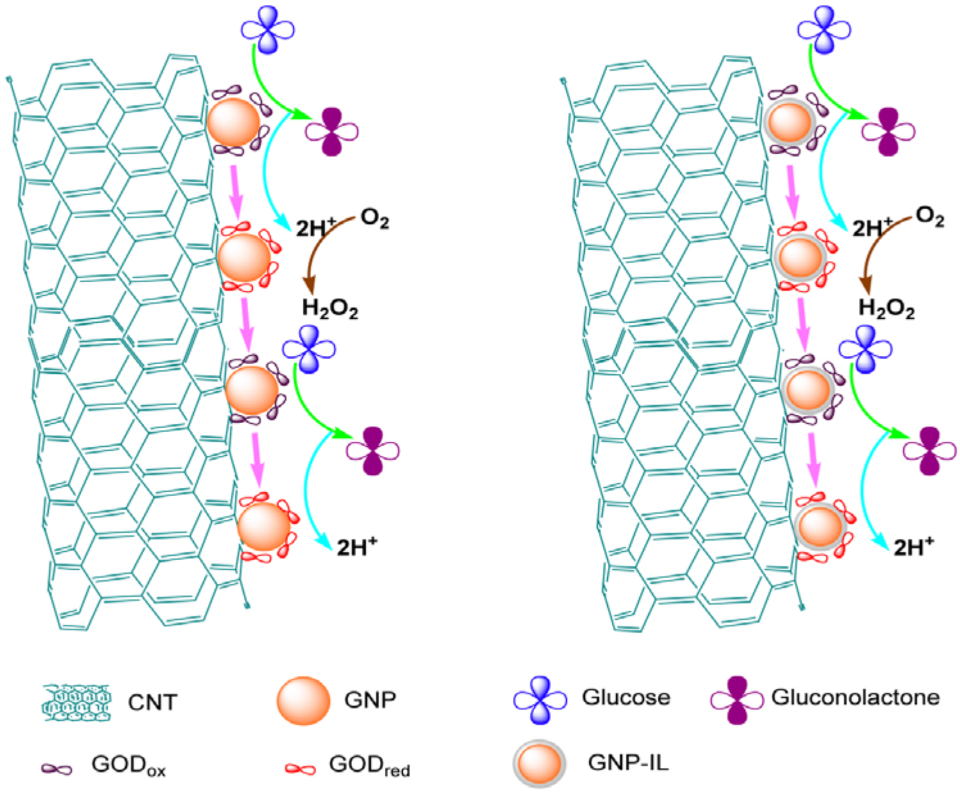
Glucose, as one of the most important molecules in the biology, attracts much attention in many fields, including the biosensing investigations. For Au-CNT nanocomposites, the application of these materials in glucose biosensing is one of the most investigated areas. Commonly, glucose sensors are based on the detection of the oxidation signal of H_2O_2 or the reduction signal of dissolved O_2. Both these two methods give good experimental results and have theoretical support, but there are also disadvantages, e.g., the oxidation of H_2O_2 requests a polymer membrane to avoid the interference of other molecules, while the reduction of O_2 has a low upper limit of the linear range (Liu et al., 2007). A scheme of the Au-CNT nanocomposites supported glucose sensor is shown in Figure 5, indicating the reaction processes (Jia et al., 2008):

$$\mathrm{GOD_{ox}} + \mathrm{Glucose} \rightarrow \mathrm{GOD_{red}} + \mathrm{Gluconolactone} + 2\mathrm{H}+ \quad (1)$$

$$\mathrm{GOD_{red}} + 2\mathrm{H}+ + \mathrm{O_2} \rightarrow \mathrm{GOD_{ox}} + \mathrm{H_2O_2} \quad (2)$$

Liu et al. (2007) showed that the use of Au-CNT nanocomposites can not only increase electrocatalysis of oxygen reduction, but also prompts the permeability of oxygen, which increased the limit of linear range, as well as the sensitivity of glucose sensing. A linear range of 9.0 mM and a detection limit of 128 µM was reached using a sensor based on gold nanoparticle/poly(diallydimethylammonium chloride)/multi-walled carbon nanotubes/glucose oxidase (GNP/PDDA/MWNTs/GOD) modified electrodes were obtained. Lately, the linear range of glucose response has been increased to 12 mM on a glucose oxidase immobilised carbon nanotube/gold nanoparticle/polyethylenimine-functionalised ionic liquid (CNT/AuNPs/PFIL/GOD) thin film composites electrode, owing to the ionic conductivity increase, which is contributed by the ionic liquid (Jia et al., 2008). Recently, the linear range was increased to 20 mM and the detection limit was decreased to 25 µM, due to the positive charge, and $–NH_2$ group of ionic liquid-NH_2 (IL-NH_2) (Li et al., 2009b). Without glucose oxidase, glucose sensors can also be based on gold nanoparticles/carbon nanotubes/ionic nanocomposite modified electrode, named naoenzymatic glucose voltammetric sensor, showing a linear range of 5.0–120 µM (Zhu et al., 2009). Similarly, based on the enhancement of ionic liquid, the detection limit of glucose is decreased to 0.8 µM/L on an IL-GNP-IL-SWNT modified electrode. In another report, based on the oxidation of hydrogen peroxide, a slope of 2.6 mA/M and a linear range of 0.05–1 mM based on a glucose oxidase-gold colloid-carbon nanotube-Teflon (GOx-Aucoll-CNT-Teflon) electrode, where the linear range was much less than GOx-CNT-Teflon electrode, while the slope was about two times higher (Manso et al., 2007). Table 1 lists the data mentioned.

Figure 5 Schematic drawing of Au-CNT nanocomposites supported glucose sensors, showing two kinds of nanocomposite, (a) gold nanoparticles are directly deposited on carbon nanotube (b) ionic liquid linked nanocomposites (see online version for colours)



(a) (b)

Table 1 Glucose sensors

Composite	*Linear range*	*Detection limit*	*Reference*
GNPs/PDDA/MWCNT/GOD	–9.0 mM	128 µM	Liu et al. 2007
MWCNT/GNPs/PFIL/GOD	2–12 mM	--------	Jia et al. 2008
MWCNT/PSS/Au-IL/GO	0–20 mM	25 µM	Li et al. 2009b
MWCNT/IL/Au	5–120 mM	2.0 µM	Zhu et al. 2009
GOx/Au_{coll}/MWCNT/Teflon	0.05–1.0 mM	17 µM	Manso et al. 2007

4.1.2 Protein/enzyme-based biosensors

Beside glucose biosensors, which are the most investigated Au-CNT supported biosensors, there are also protein/enzyme-based biosensors that are also based on Au-CNT nanocomposites. Table 2 lists the biosensors for protein/enzyme detection.

Protein-based hydrogen peroxide sensors are considered biosensors, since hydrogen peroxide is an essential compound in food and pharmaceutical analysis. There are two types of hydrogen peroxide biosensors classified by mediators: mediated biosensors and mediate-free biosensors (Chen et al., 2007). Chen et al. (2007) made a third-generation hydrogen peroxide biosensor, based on hemoglobin/gold nanoparticles/hemoglobin/multi-walled carbon nanotube/glassy carbon (Hb/GNPs/Hb/MWNT/GC) electrode. The detection limit of hydrogen peroxide was decreased to 8.0×10^{-8} M, and the linear range was increased from 2.1×10^{-7} M to 3.0×10^{-3} M, compared with a Hb/MWNT/GC electrode that has a detection limit of 6.0×10^{-7} M and a linear range from 1.4×10^{-6} M to 2.6×10^{-3} M (Chen et al., 2007). These data are also better than MP-11 (microperoxidase)/GNPs/MWNTs/GC electrodes, where the detection limit is 3.0×10^{-6} M and the linear range is from 1.0×10^{-5} M to 2.0×10^{-4} M (Liu et al., 2005). Besides the above two proteins, horseradish peroxidase detection was approached by using hydrogen peroxide biosensor based on gold-thionine-carbon nanotube modified electrode, showing a detection limit of $–10^{-7}$ M and linear range of –7 mM (Wang et al., 2008b). Similar in approach to these enzyme-based sensors, Zhu et al. (2005) developed a reagentless electrochemical biosensor for hydrogen peroxide sensing, showing a detection limit of 1 μM and a linear range of 2.0 μM to 3.5 mM.

Other enzyme-based biosensors include an alcohol dehydrogenase (ADH) amperometric biosensor using an Au-CNT modified electrode developed by Manso et al. (2008). This ADH-Au-MWCNTs-Teflon biosensor can determine ethanol with a detection limit of 4.7 μM/L, which is better than CNTs-based ADH biosensors. Du et al. (2010) reported an amperometric acetylcholinesterase biosensor, based on an Au-CNT-Chitosan modified electrode, with a detection limit of 0.6 ng/ml, close to high performance liquid chromatography (HPLC) determination.

Table 2 Protein/enzyme-based biosensors

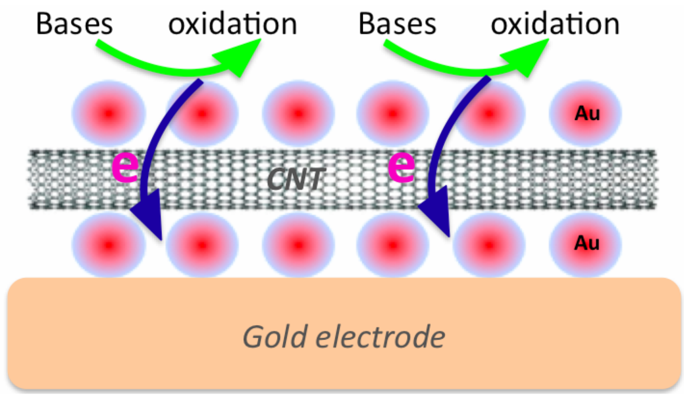
Composite	*Sensing molecule*	*Linear range*	*Detection limit*	*Reference*
Hb/GNPs/Hb/MWCNT	H_2O_2	0.21 μM–3 mM	80 nM	Chen et al. (2007)
MP-11/GNPs/MWCNT	H_2O_2	10 μM–200 μM	3 μM	Liu et al. (2005)
GNPs/Thionine/MWCNT	H_2O_2	–7 mM	0.1 μM	Wang et al. (2008b)
GNPs/MWCNT	H_2O_2	2 μM–3.5 mM	1 μM	Zhu et al. (2005)
ADH/GNPs/MWCNT/Teflon	Ethanol	0.01–1.0 mM	4.7 μM	Manso et al. (2008)
AChE/GNPS/MWCNT/Chitosan	ATCl	1–1,000 ng/ml 2–15 μg/ml	0.6 ng/ml	Du et al. (2010)
AFP/GNPs/CNT/Chitosan	1-NP	1-55 ng/ml	0.6 ng/ml	Lin et al. (2009)

Antigen and antibody reactions can also be detected using sensors based on gold-carbon nanocomposites. Lin et al. (2009) developed a sensitive amperometric immunosensor based on carbon nanotube/gold nanoparticle doped chitosan film and applied the sensor for studies of real serum samples. Their results showed acceptable agreement with classical immunoradiometric assay (IRMA), with a detection limit of 0.6 ng/ml for 1-naphthyl phosphate (1-NP) using an AFP/GNPs/CNT/Chitosan modified electrode.

4.1.3 DNA biosensors

Recently, Zhang and Wang (2010) investigated the selective enhancement of electrochemical signal of DNA bases on Au-MWCNT modified gold electrodes (Figure 6), showing different behaviours of DNA bases where the enhancement of pyridine bases were much higher than purine bases due to different electrode surface mechanisms. Yogeswaran et al. (2007) performed similar work based on Au-CNT modified electrodes, and the gold nanoparticles in their study were covered with hydroxypropyl-ß-cyclodextrin. Tyrosine, guanine, adenine, and thymine bases were determined on the electrodes, with detection limit of 0.66, 0.09, 7.78, and 3.50 mM individually and 0.39, 3.33, 0.36 and 0.07 mM simultaneously using cyclic voltammetric method. The detection limits were not as low as using the differential pulse voltammetric method by Zhang and Wang (2010), where the detection limit of guanine, adenine, cytosine and thymine were 0.004, 0.006, 0.03 and 0.01 mM.

Figure 6 Electrochemical detection of DNA bases based on Au-CNT nanocomposites modified gold electrode (see online version for colours)



Source: Zhang and Wang (2010); Copyright Wiley-VCH Verlag GmbH and Co. KGaA. Reproduced with Permission

Au-CNT nanocomposites are also used to determine DNA hybridisation. Gu et al. (2007) reported on the detection of short sequence hybridisation based on Au-CNT nanocomposites. Methlyene blue was used as indicator for the hybridisation due to the different interaction of this molecule to single and double stranded DNA. The detection limit was found to be 1.0 pM. In another work, doxorubicin was used to study DNA hybridisation with longer sequences than in the Gu's study, and they reached a detection limit of 7.5 pM (Ma et al., 2008).

4.1.4 Other biomolecular biosensors

There are many small biomolecules that are of interest, e.g., uric acid, ascorbic acid, for detection using Au-CNT nanocomposites-based sensors. Guo et al. (2010) investigated tryptophan sensor, using Au-CNT hybrids as enhancing material. Based on the enhancement of the Au-CNT composites, the detection limit of tryptophan is one order lower than using pure carbon nanotube. Umasankar et al. (2007) measured ascorbic acid, epinephrine, and uric acid using PtAu-Nafin-MWCNT modified glassy carbon electrodes, with Pt and Au nanoparticles. Wang et al. (2008b) studied the electrocatalytic oxidation of bilirubin at ferrocenecarboxamide modified MWCNT-gold nanocomposite electrodes, showing long-term stability, reproducibility and short response time.

4.2 Gas sensors

Three-dimensional electrocatalytic structures can be fabricated based on Au-CNT nanocomposites. The carbon nanotubes are used as a kind of scaffold for this porous structure. This three-dimensional electrocatalytic thin film can be used for gas sensing, e.g., for detection of oxygen. Alexeyeva et al. (2006), and Alexeyeva and Tammeveski (2008) indicated the remarkable electrocatalytic activity of the nanocomposites for oxygen reduction in acid media, regardless whether the gold nanoparticles were directly or indirectly deposited on carbon nanotubes. Shi et al. (2009) also showed the catalytic effect of Au-CNT nanocomposites for oxygen processes. Air humidity sensors have also been developed based on these nanocomposites. Qi et al. (2007) fabricated a sensitive humidity sensor at room temperature based on CNT-myoglobin-gold nanocomposites, and the sensor showed response to 0.3% humidity change.

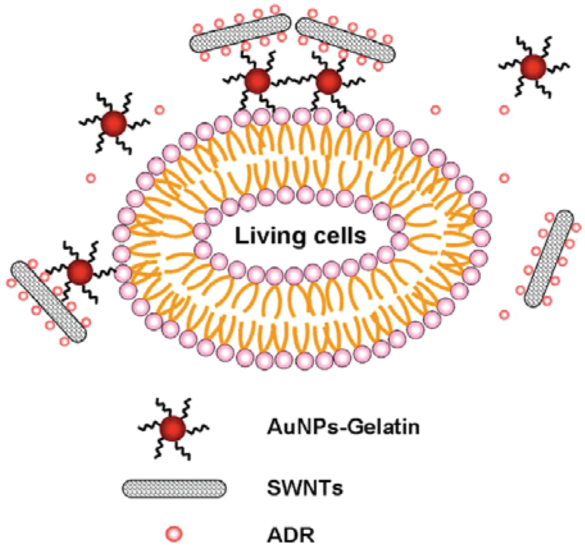
4.3 Toxicant sensors

Highly sensitive determination of toxicants is of great importance for health and environment. Compton’s group made an electrochemical sensor to detect arsenic (III), based on Au-CNT composites (Xiao et al., 2008). A low detection limit of 0.1 μg/L was achieved, but more importantly, a sensitivity of 1,895 μA/μM was obtained, using anodic stripping voltammetry. Xu et al. (2008) applied the composite for trace mercury determination, with a detection limit much lower than the World Health Organization’s guideline value, which is 0.06 μg/L. Besides single elements, organic toxicants like organophosphate pesticides are also harmful. Zhang et al. (2009a) detected parathion using linear scan voltammetry based on the Au-CNT composites, with a detection limit down to 100 nM.

4.4 Drug delivery

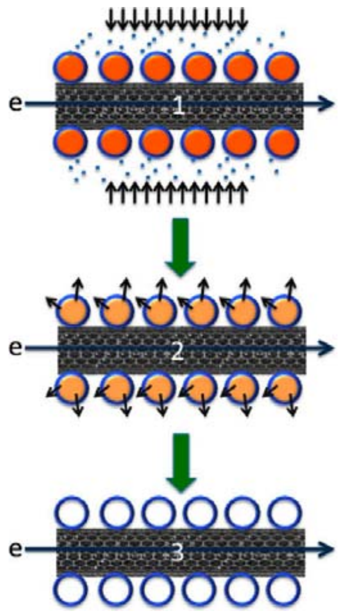
The application of gold nanoparticles and carbon nanotubes in drug delivery has already been reported, while there are only few works have been focused on the application of Au-CNT nanocomposites in drug delivery. Zhu et al. (2005) has reported recently the application of gelatin stabilised gold nanoparticles on carbon nanotube for cytosensing and drug delivery. *In vitro* experiments on HL-60 cell showed that the nanocomposites can both increase the sensitivity of cytosesing and enhance the interaction of adriamycin with HL-60 cell and the accumulation of adriamycin (Figure 7) in the cancer cell lines (Zhang et al., 2010a). Their works point out the new application of the Au-CNT nanocomposites in the biomedical area.

Figure 7 Schematic illustration of the enhanced effect on the drug uptake of Adriamycin (see online version for colours)



Source: Reprint from Zhang et al. (2009a); Copyright 2009 American Chemical Society

Figure 8 Schematic drawing of the procedure of synthesis carbon nanocages using Joule heating (see online version for colours)



Source: Reprint from Zhang et al. (2010b); Copyright 2010 Elsevier

4.5 Other applications

In addition to the signal enhancement of Au-CNT nanocomposites for sensors, other applications can be addressed using this composite. Zhang et al. (2010d) have synthesised carbon nanocages-based Au-CNT nanocomposites using Joule heating (Figure 8), by driving a heating current through the carbon nanotube that was connected to gold electrode on both terminals. Inspired by this work, one may fabricate three dimensional carbon structures, suitable for fuel cell applications due to the high conductivity, or for gas storage making use of the hollow structure.

5 Conclusions

The combination of gold nanoparticles with carbon nanotubes into a composite material makes use of both nanomaterials. Several different methods have recently been developed to fabricate Au-CNT nanocomposites towards different applications, but there is still room for new methods in other directions, e.g., gas condensation. There is a need for future work on synthesis to focus on controllable deposition of gold nanoparticles on carbon nanotubes, control over the size distributions, the distribution of gold on the carbon nanotubes, and the efficiency of the deposition, since not the entire surface of carbon nanotubes coated evenly with high density and not all of the carbon nanotubes are covered with gold nanoparticles. The applications of these nanocomposites can also be expected to be extended. The applications of Au-CNT nanocomposites are now more focusing on sensor mechanisms, as shown in this review. But more applications need to be developed based on the properties of these two nanostructures and the structures of the nanocomposites themselves.

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