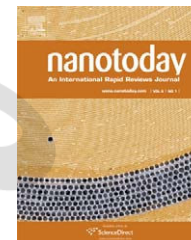


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REVIEW

Noble metal nanoparticles/carbon nanotubes nanohybrids: Synthesis and applications

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Summary We briefly review the recent advances in the synthesis of noble metal nanoparticles/carbon nanotubes nanohybrids and their applications in heterogeneous catalysis, fuel cells, and chemo/biosensors.
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Introduction

Carbon nanotubes (CNTs), including single-walled CNTs (SWCNTs) and multi-walled CNTs (MWCNTs), are important carbon-based materials [1,2]. Since the CNTs were discovered [3,4], they have been intensively studied and have received a great deal of attention for their applications in a wide variety of areas, due to their excellent properties which involving high specific surface area, high electronic conductivity, outstanding chemical and electrochemical stability, one dimensional tubular-structure and so on [5–8].

On the other hand, owing to their unique electric, magnetic, optical, and catalytic properties, metal nanoparticles (NPs) have emerged as a new class of compounds that are

interesting in several areas from chemistry to physics, to material sciences, to biology and medicine [9,10]. Importantly, these properties differ from those of the bulk materials and mainly depend on the particle size and morphology [11–13]. The hot research points in metal NPs focus on the synthesis of noble metal NPs such as Au, Ag, Pt, Pd, Ru and their alloys [14–18].

Noble metal NPs/CNTs nanohybrids are a new kind of composite materials which successfully integrate the unique properties of two class materials (CNTs and noble metal NPs) and exhibit some new functions caused by the cooperative effects between the CNTs and noble metal NPs. Therefore, noble metal NPs/CNTs nanohybrids have shown very attractive applications in many fields, especially in heterogeneous catalysis, fuel cells and chemo/biosensors (Fig. 1). Since the first report about the synthesis and application of noble metal NPs/CNTs nanohybrids in 1994 [19], the number of literatures escalates at an enormously increasing rate each year. This review focuses on the recent progress in the synthesis and applications of noble metal NPs/CNTs nanohybrids.

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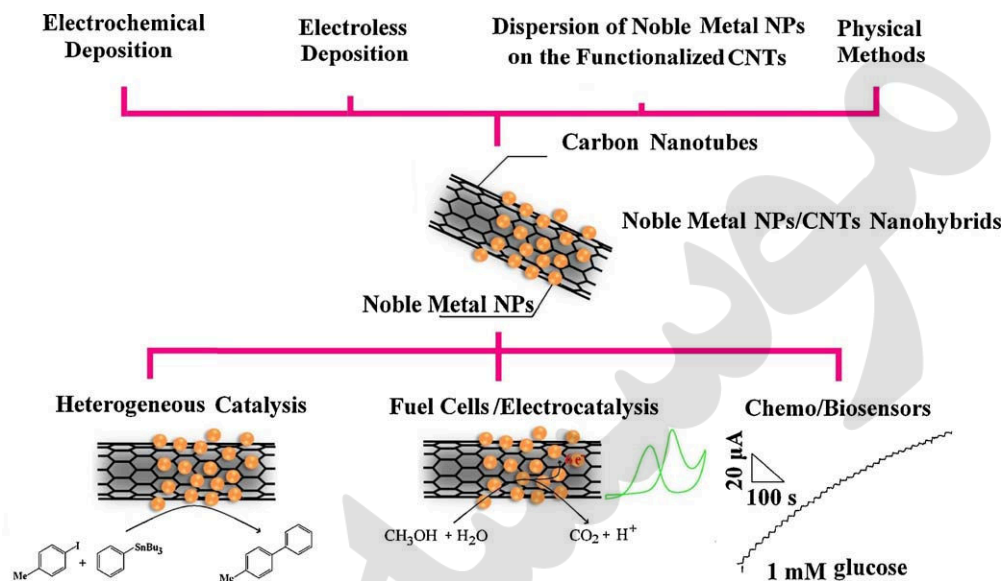


Figure 1 Brief summary of preparation and application of noble metal NPs/CNTs nano hybrids.

Synthesis of noble metal NPs/CNTs nano hybrids

Numerous synthetic methods have been developed for the preparation of noble metal NPs/CNTs nano hybrids in the literatures, each providing varying degrees of control of the size and distribution of metal NPs on the surface of CNTs. These strategies can be divided into four categories: electrochemical deposition, electroless deposition, dispersion of noble metal NPs on the functionalized CNTs, physical methods. The particle sizes of noble metal NPs in the representative noble metal NPs/CNTs nano hybrids are summarized in Table 1. In this section, a discussion about the recent progress in preparation of the noble metal NPs/CNTs nano hybrids are made according to the above four categories.

Electrochemical deposition method

Electrochemistry is a powerful technique for deposition of various NPs (especially metal NPs), as it enables effective control over nucleation and growth of metal NPs. Most research has been conducted on the deposition of noble metal NPs and their alloys, such as Au, Ag, Pt, Pd, and bimetallic PtRu [20–30], those were usually used in heterogeneous catalysis, fuel cells and chemo/biosensors. In this method, the noble metal NPs/CNTs nano hybrids are obtained via reduction of noble metal complexes, such as $\text{H}[\text{AuCl}_4]$, $\text{H}_2[\text{PtCl}_4]$, and $(\text{NH}_4)_2[\text{PdCl}_4]$, by electrons. CNTs typically do not react with the noble metal salts but act as molecular conducting wire and supports for the deposition of noble metal NPs. Importantly, the size of the noble metal NPs and their distribution on the sidewalls of CNTs can be controlled by the concentration of the noble metal salts and various electrochemical deposition parameters, including nucleation potential and deposition time. Besides, electrochemical deposition method also has the following advantages: noble metal NPs with very high

purity, forming rapidly and having good adhesion to the CNTs substrate.

He et al. took the advantages of substrate-grown-directly CNTs and the high purity of electrochemically deposited NPs to decorate CNTs with Pt or bimetallic Pt–Ru NPs with diameters of 60–80 nm (Fig. 2) [20,29]. After the MWCNTs were pre-treated by electrochemical oxidation, the deposition took place potentiostatically at -0.25 V from a solution containing chloroplatinic acid or ruthenium chloride and chloroplatinic acid in $0.5\text{ M H}_2\text{SO}_4$. Quinn et al. further demonstrated that noble metal (Au, Pt, Pd) NPs/SWCNTs nano hybrids could be synthesized by electrodeposition under direct potential control and the particle size of noble metals NPs and surface coverage could be tuned with potential, deposition time, and metal salt concentration [31].

Usually, high dispersion and small particle size of noble metal NPs on CNTs are desired not only from the extraordinary catalytic activity but also from the low cost. However, the noble metal NPs/CNTs nano hybrids prepared by electrodeposition method usually receive noble metal NPs with big particles size (ranging from tens to hundreds nanometers), as shown in He's work. It is an challenge to synthesize noble metal NPs with high dispersion and small particle size on CNTs by electrochemical deposition method due to the contradiction between a larger driving force (more negative deposition potential) for critical nuclei formation and an inhibitive mechanism for deterring crystal growth (less deposition charge or smaller current density). In order to solve this problem, Tsai et al. tried to synthesized Pt (PtRu) NPs/CNTs nano hybrids by electrochemical deposition in ethylene glycol (EG) containing H_2SO_4 aqueous solution. They successfully obtained Pt (PtRu) NPs with small size (4.5–9.5 nm for Pt and 4.8–5.2 nm for PtRu) and uniform dispersion on the surface of CNTs (Fig. 3). It was found that EG not only enhanced the dechlorination of Pt and Ru precursor salts and led to the formation of NPs but also acted as a stabilizing surfactant to prevent the particles from agglomeration during the electrodeposition processes, resulting in

Table 1 The particle sizes of noble metal NPs in the representative noble metal NPs/CNTs nanohybrids.

Noble metal NPs	Particle size (nm)	Synthesis methods	Ref
Pt	2.0–3.0	Pulsed electrodeposition	[34]
	1.47–2.60	PDDA-functionalized CNTs	[16]
	1.9–2.1	Aniline-functionalized CNTs	[62]
	3.0	Ionic liquid-functionalized CNTs	[51]
	2.0–3.0	Hydrofluoric acid treated-CNTs	[47]
	1.8	PVP-functionalized CNTs	[68]
	1.9	PIL-functionalized CNTs	[66]
	2.8	PAH-functionalized CNTs	[74]
	2.63	Nitrogen-doped CNTs	[85]
	2.0–3.0	Sputtering deposition	[92]
	2.0	Sputtering deposition	[94]
	2.5–4.0	γ -Irradiation	[96]
PtRu	4.8–5.2	Electrodeposition	[32]
	2.0	1-Aminopyrene-functionalized CNTs	[61]
	1.3	PIL-functionalized CNTs	[66]
PtSn	4.0	Tetrahydrofuran-functionalized CNTs	[64]
Pd	3.8	4-Aminobenzenesulfonic acid-functionalized CNTs	[54]
	3.0	Electroless deposition	[41]
	6.0	Thiol group-functionalized CNTs	[53]
	2.0	HPW-PDDA-functionalized CNTs	[81]
	2.0	Electron beam irradiation	[82]
	2.5–4.5	SDS-functionalized CNTs	[83]
Au	3.3	Ionic liquid-functionalized CNTs	[14]
	5.0–7.0	Electroless deposition	[41]
	3.0–7.0	Dendrimers-modified CNTs	[52]
	4.3	Polythiophene-functionalized CNTs	[71]
Ru	2.0–5.0	Acid oxidation-CNTs	[18]
Ag	2.0	Nitrogen-doped CNTs	[88]

a better dispersion and smaller particles size of Pt or PtRu NPs [32,33].

Chen et al. further deposited Pt NPs on CNTs with high dispersion and smaller particles size (2–3 nm) by the pulsed electrodeposition technique in restricting viscous electrolytes [34]. They ingeniously used glycerol to adjust viscosity of the H_2PtCl_6 solution. After electrodeposition, the glycerol could be easily removed from the surface of

metal NPs by rinsing in hot water. The results showed that the particle size of Pt NPs could be easily controlled by adjusting the diffusion restriction of electrolyte and the number of the potential pulses.

Moreover, several new electrodeposition methods have been developed recently for synthesis of noble metal NPs/CNTs. Xiao et al. used ultrasonic-electrodeposition method to prepare AuPt NPs on the surface of MWCNT-

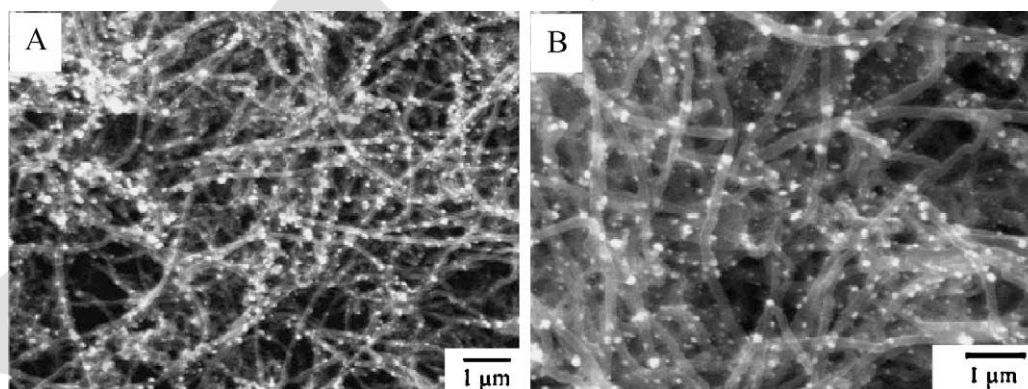


Figure 2 SEM images with low (A) and high (B) magnifications of PtRu/CNTs nanohybrids.

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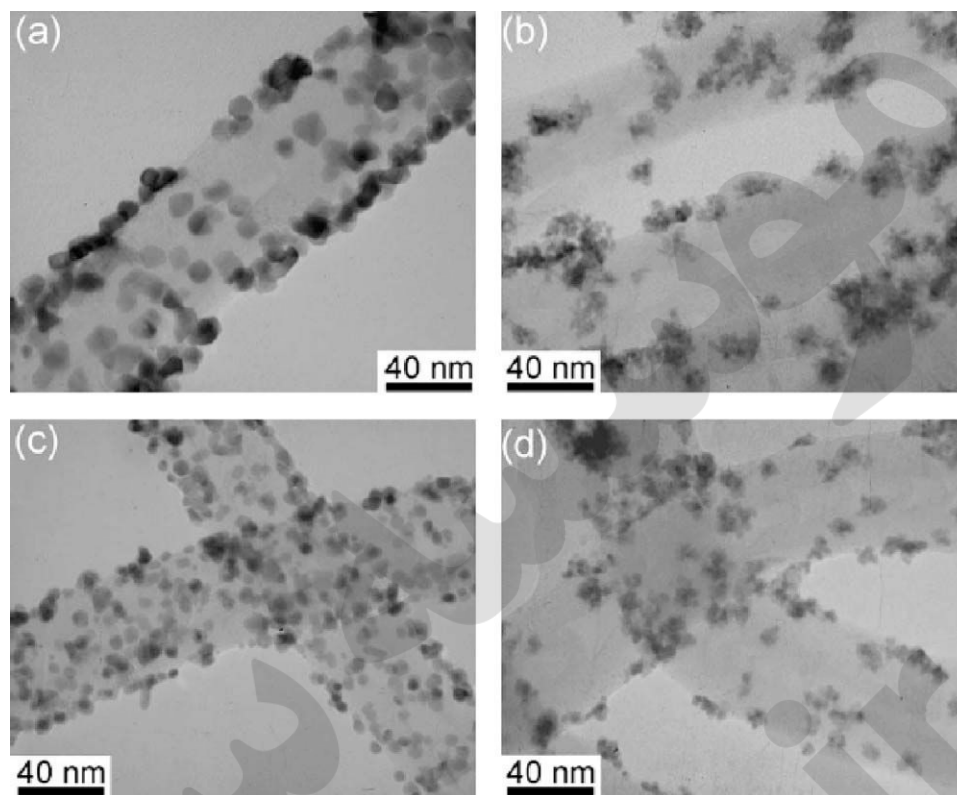


Figure 3 TEM micrographs of the working specimens with Pt, (a) A01 and (c) B01, and the working specimens with Pt–Ru, (b) A02 and (d) B02. A01, A02, B01, and B02 were respectively corresponding four potentiostatic deposition conditions: (1) $-0.30 V_{SCE}$, $0.25 M H_2SO_4 + 0.5 M EG + 0.2 mM H_2PtCl_6 \cdot 6H_2O$ (A01); (2) $-0.30 V_{SCE}$, $0.25 M H_2SO_4 + 0.5 M EG + 0.2 mM H_2PtCl_6 \cdot 6H_2O + 0.4 mM RuCl_3 \cdot xH_2O$ (A02); (3) $-0.45 V_{SCE}$, $0.25 M H_2SO_4 + 0.5 M EG + 0.2 mM H_2PtCl_6 \cdot 6H_2O$ (B01); and (4) $-0.45 V_{SCE}$, $0.25 M H_2SO_4 + 0.5 M EG + 0.2 mM H_2PtCl_6 \cdot 6H_2O + 0.4 mM RuCl_3 \cdot xH_2O$ (B02). Reprinted with permission from [32], ©2006 Elsevier..

ionic liquid (ILs) (i.e. trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide, $[P_{6,6,6,14}][NTf_2]$) composite [24]. Pt/MWCNTs nanohybrids could also be prepared by co-electrodeposition/stripping protocol developed by Huang et al. [35].

Electroless deposition

Electroless deposition method relies on a chemical, as opposed to electrochemical reduction process, whereby a chemical species whose redox potential is suitably lower than that of the metal species being reduced provides the driving force for the reaction. Lots of metal NPs/CNTs nanohybrids, especially noble metal NPs/CNTs nanohybrids, have been prepared by electroless deposition method [36–40]. A representative work was done by Dai's group [6]. They proposed that a direct redox reaction occurred between the metal ions and CNTs. Au and Pt NPs could be spontaneously deposited on SWCNTs with very high selectivity when SWCNTs were immersed into the corresponding metal salt solutions.

Comparing with electrodeposition, electroless deposition process is limited by the fact that metal ions can be transformed to metal NPs on the CNT support only when the redox potential of metal ions is higher than that of CNTs. Consequently, Cu^{2+} and Ag^+ cannot be reduced into metal

NPs on CNTs by electroless deposition due to their lower redox potentials. In order to overcome this limit of electroless deposition, Qu and Dai have further developed a novel process called substrate-enhanced electroless deposition (SEED). In this case, metal Au, Pt, Pd NPs and some metals with lower redox potential than that of CNTs (such as Cu and Ag) could spontaneously deposit onto the CNTs by supporting the CNTs on a metal substrate with a lower redox potential than that of the metal ion. CNTs are not the reducing agent in this method and they only act as cathodes and templates for metal deposition from the corresponding metal salts (Fig. 4) [5].

On the other hand, Lorençon et al. reported a one-pot method to synthesis noble metal NPs/CNTs nanohybrids by a redox reaction between metal ions and reduced CNTs [41]. This process involved two steps. First, CNTs were reduced by metallic Na in an aprotic organic solvent, which could obtain a solution of exfoliated negatively charged CNTs. In the second step, metal cations were added to the solution and immediately reduced upon contact with the CNTs, because of excess of electrons, forming metal NPs along the CNTs surface. This method is very straightforward and also does not require metal ion with a redox potential higher than that of CNTs. They successfully anchored Au and Pd NPs to the surface of MWCNTs and SWCNTs by this method without any surfactants or previous CNT surface functionalization.

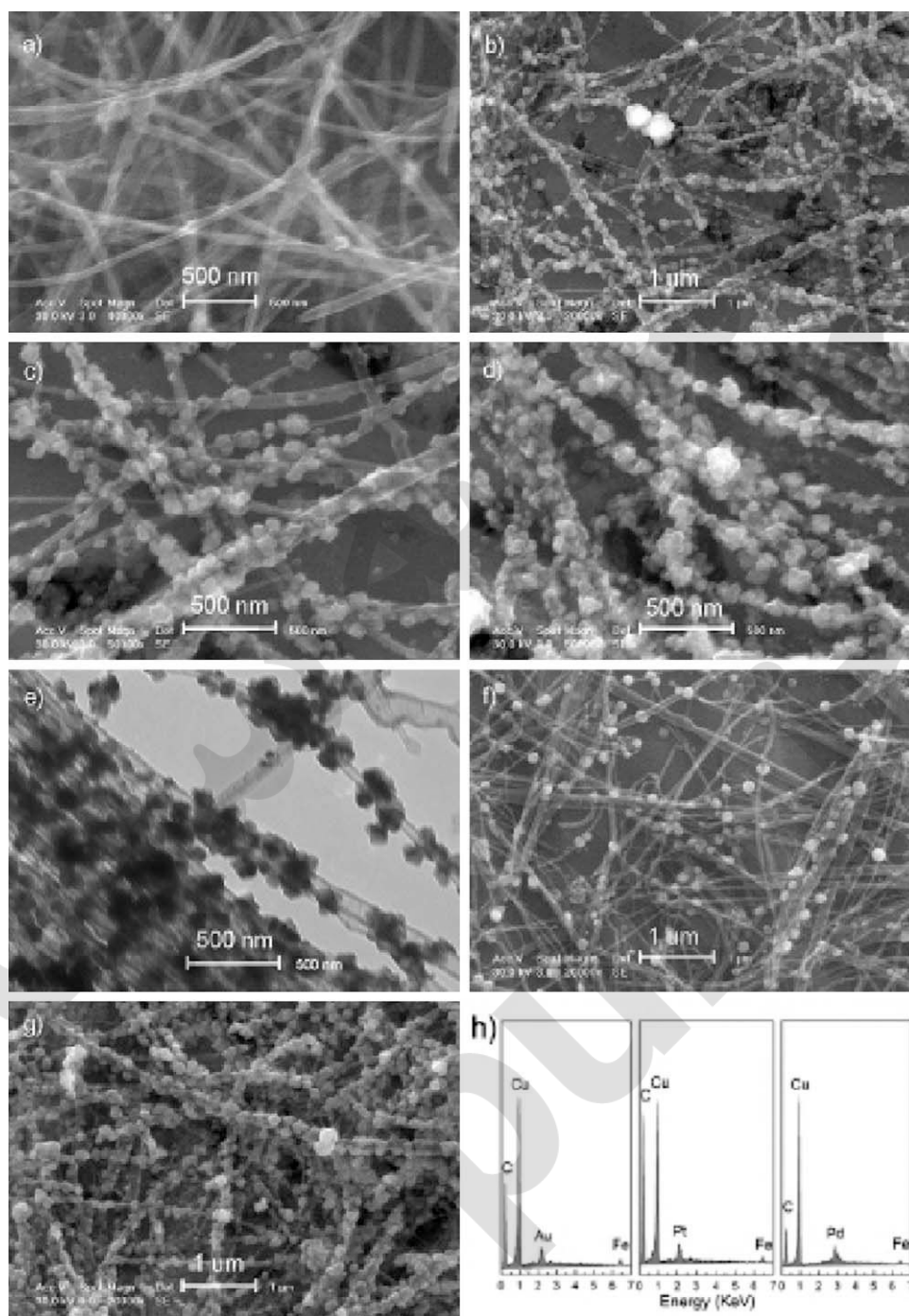


Figure 4 SEM images of MWCNTs supported by a copper foil after being immersed into an aqueous solution of HAuCl_4 (3.8 mM) for different periods of time: (a) 0 s, (b) 10 s, (c) same as for (b) under a higher magnification, (d) 30 s. (e) A transmission electron microscopic (TEM) image of Au NPs-coated MWCNTs, (f) the Cu-supported MWCNTs after being immersed into an aqueous solution of K_2PtCl_4 (4.8 mM) for 10 s, and (g) the Cu-supported MWCNTs after being immersed into an aqueous solution of $(\text{NH}_4)_2\text{PdCl}_4$ (7.0 mM) for 10 s. (h) EDX spectra for the Au, Pt, and Pd NPs-coated MWCNTs on Cu foils. Reprinted with permission from [5], ©2005 American Chemical Society.

Dispersion of noble metal NPs on the functionalized CNTs

It is well known that for CNTs without surface modification, there are insufficient binding sites for anchoring the precursors of metal ions or metal nanoparticles, which usually

leads to poor dispersion and large metal nanoparticles, especially under high loading conditions [42,43]. To introduce more binding sites and surface anchoring groups, surface functionalization of CNTs is generally carried out. In general, CNTs could be functionalized by (a) covalent attachment of functional groups through forming covalent bonds to

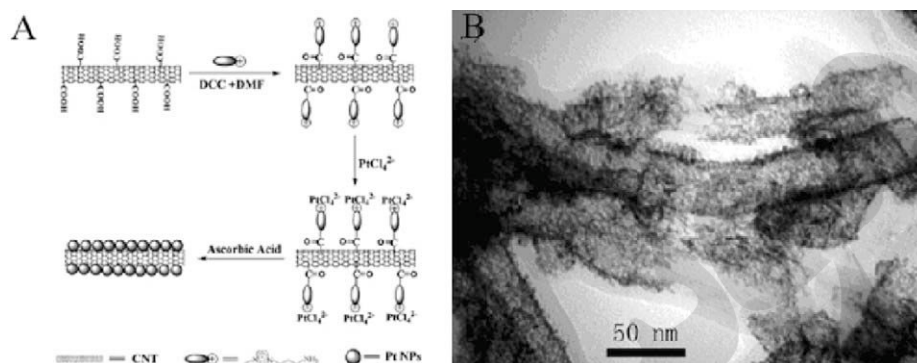


Figure 5 (A) Illustration of the procedure for preparing CNTs/IS-ILs/Pt nanohybrids. DMF represents N, N-dimethylformamide; (B) TEM images of CNTs/IS-ILs/Pt hybrid nanostructure. Adapted from Ref. [51].

the π -conjugated skeleton of the CNTs or (b) non-covalent absorption such as π - π stacking, hydrophobic interaction, electrostatic attraction or wrapping of various functional molecules or polymers.

In recent years, a large number of literatures reported chemical modification of CNTs via covalent grafting of a wide range of functional groups and molecules onto the surface of CNTs. The most common covalent functionalization involves the addition of carbonyl and carboxyl groups onto the CNT surface via an aggressive oxidation treatment with a HNO_3 or $\text{HNO}_3/\text{H}_2\text{SO}_4$ mixture [44–46]. The carbonyl and carboxyl groups on the surface of CNTs are the nucleation sites for the deposition of noble metal NPs on the surface of CNTs and dispersion of noble metal NPs (Pt, Pd, PtRu, Au, Ag NPs and so on) on the surface of carbonyl and carboxyl functionalized CNTs is successfully achieved. This functionalization process can also be carried out by pretreatment of CNTs in HCl, HF, O_3 , KMnO_4 , H_2O_2 [47–50].

Although carboxyl-functionalized CNTs can anchor and disperse noble metal NPs on the surface of CNTs, it is hard to achieve noble metal NPs with small particle size and high dispersion. In order to realize this object, the carboxyl-functionalized CNTs could be further grafted with functional molecules which can effectively control the particles size and dispersion of noble metal NPs on the surface of CNTs. An ingenious approach was developed by Niu's group [14]. They firstly grafted amine-terminated ionic liquids (NH_2 -IL) to the carboxyl-functionalized MWCNTs (MWCNTs-COOH) by formation of the amide linkage between MWCNTs-COOH and NH_2 -IL. Then the gold salt $[\text{AuCl}_4]^-$ was absorbed on the ionic liquid-functionalized CNTs via electrostatic interaction and ionic exchange and Au NPs with uniform dispersion and narrow size distribution were easily produced by in situ reduction on CNTs. Using imidazolium-salt-based ionic liquids (IS-ILs) as linkers, Guo et al. further prepared CNTs/IS-ILs/Pt NPs nanohybrids (Fig. 5) [51]. The authors found that IS-ILs on the surface of CNTs could effectively enrich the PtCl_6^{2-} by coupling effect and promote the nucleation of Pt NPs due to their low interface energy. The as-prepared three-component CNTs/IS-ILs/Pt NPs nanohybrids exhibited higher electrocatalytic activity towards methanol oxidation reaction than the commercial E-TEK Pt/C catalyst due to small

Pt NPs with uniform particle size (about 3 nm) on CNTs/IS-ILs.

Another representative work was reported by Lu and Imae [52]. MWCNTs were covalently modified with fourth-generation NH_2 -terminated poly (amido amine) (G4-PAMAM) dendrimers (CNT/DEN) and then used as support for Au NPs. The particle size of Au NPs could be concisely controlled by simply tuning the ratio of HAuCl_4 to the covalently bonded dendrimers on CNTs (Fig. 6). The results indicated that there were two types of interactions between dendrimers and Au NPs: the encapsulation of NPs in dendrimers, and the coordination of NPs outside dendrimers. Furthermore, Ag, Cu, Pt and Ag@Au NPs were successfully synthesized in situ on the surface of CNT/DEN with controllable particle size. By the covalent linkage fashion, Pd NPs were also deposited on thiol group- [53], benzenesulfonic- [54], and ionic liquid-functionalized MWCNTs [55] and Au NPs were dispersed on the amine-functionalized MWCNTs [56].

In general, surface covalent functionalization of CNTs could increase the surface binding sites, avoid the aggregation of noble metal NPs, improve the dispersion and reduce the average size of noble metal NPs, but is also inevitably accompanied with a few problems, such as uneven distribution of the surface functional groups, structural damage, and thus partial loss in conductivity of CNTs. To minimize the above disadvantages, it is highly desirable to develop a mild surface functionalization process to introduce surface functional groups on the CNT surface with high density and uniform distribution. Besides, the structural damage to the CNTs should be avoided, which would be benefit to retain the good physicochemical properties of CNTs.

It was reported that the noble metal NPs could be attached to the pristine CNTs via π - π stacking which was the moderately strong interaction between delocalized π -electrons of CNTs and those in aromatic organic compounds, such as derivatives of pyrene, thionine, or triphenylphosphine [57–60]. These molecules are often modified with thiol, amine, or carboxyl groups, which can be used as the linkers to anchor noble metal NPs onto CNT surface. One of the major advantages of this method is that the molecules containing conjugated π aromatic structure can strongly absorb on the CNT surface after work-step (e.g., washing, filtration) and thus effectively anchor noble metal

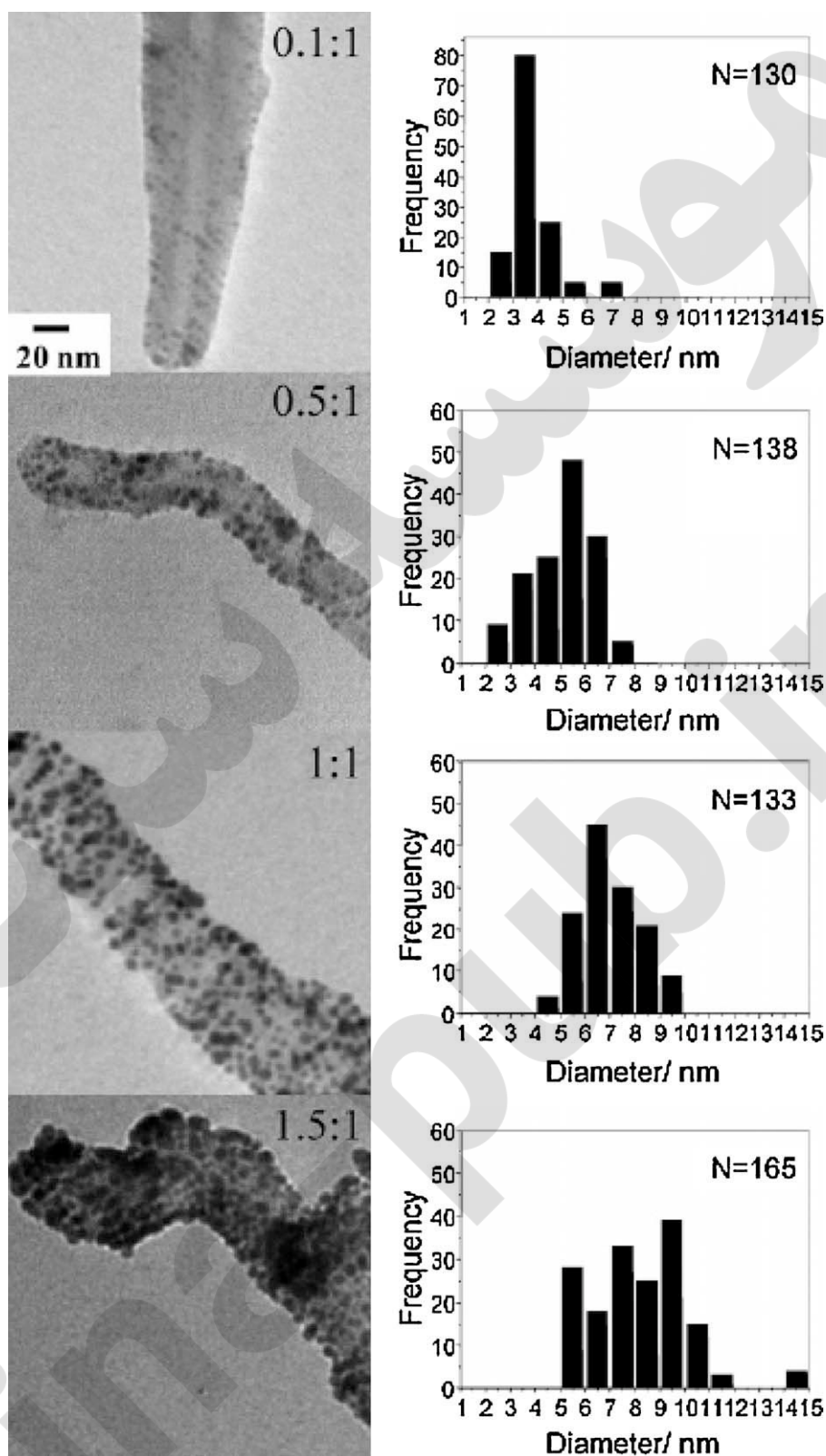


Figure 6 TEM images of CNT/DEN/Au at different $M:D$ ratios and histograms of the Au particle size distribution in the CNT/DEN/Au structure. N in each histogram denotes the counted number of Au NPs. The magnification is the same for all TEM images, and $M:D$ values are indicated in each TEM image.

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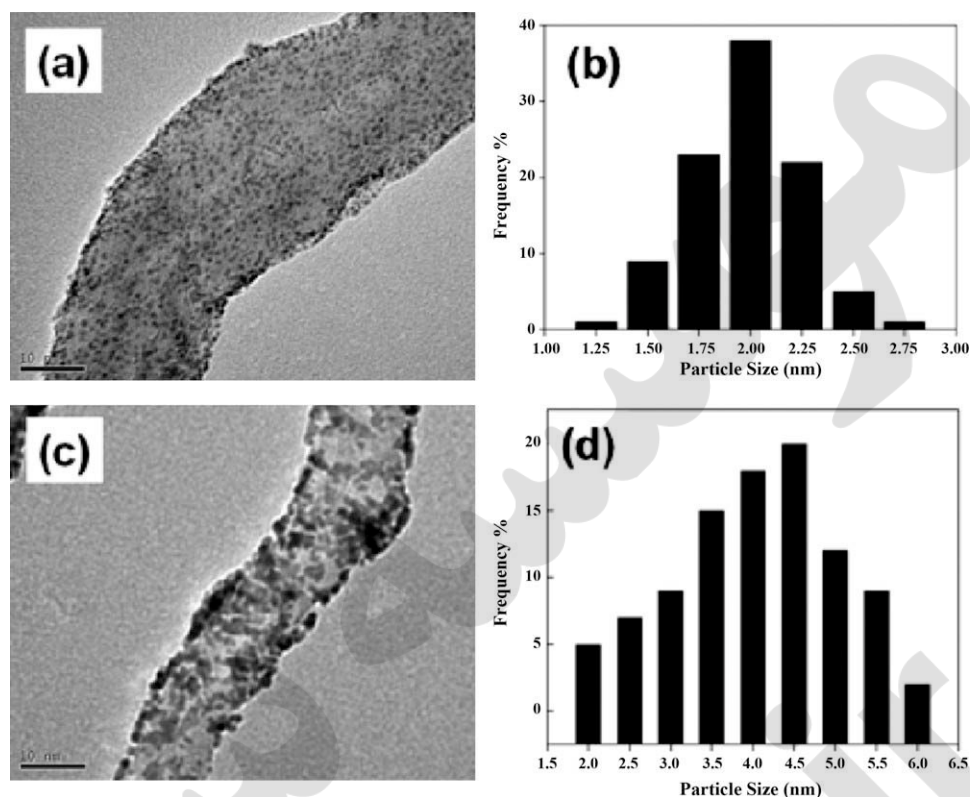


Figure 7 TEM images and distribution histograms of PtRu nanoparticles on 1-AP-MWCNTs (a and b) and AO-MWCNTs (c) and (d). The PtRu loading was 40 wt.%. Reprinted with permission from [61], ©2008 American Chemical Society.

NPs on the sidewall of CNTs. It was reported that Au NPs could be bound by thiol-terminated [57] or amino-terminated pyrene [58] through either the thiol or amine linkage. The pyrene molecules itself could be noncovalently attached to the sidewall of a CNTs via π - π stacking interaction and Au NPs with diameters of 2–4 nm were densely deposited on the surface of the MWCNTs [58]. Another representative work reported the synthesis of PtRu/MWCNTs nanohybrids by using 1-aminopyrene (1-AP) as the linker (Fig. 7) [61]. The noncovalent functionalization of MWCNTs by 1-AP was simple and could be carried out at room temperature without the use of expensive chemicals or corrosive acids, thus preserving the integrity and the electronic structure of MWCNTs. In this method, the amino groups of 1-AP immobilized on MWCNT surface possess weak positive charge. This leads to the self-assembly of PtCl_6^{2-} , followed by subsequent self-assembly of Ru^{3+} , resulting in uniform distribution of PtRu precursors on the surface of MWCNTs. The bimetallic PtRu NPs with the average particle size of 2.0 ± 0.2 nm were uniformly deposited on the surface of MWCNTs with no aggregation. The resulting nanohybrids have shown higher electrocatalytic activity and better stability for the methanol electrochemical oxidation than the PtRu NPs supported on the acid-oxidized MWCNTs and XC-72 carbon black. Based on the similar principle, noble metal NPs could be adsorbed onto CNTs with the assistance of triphenylphosphine (PPh_3) [60], aniline [62], 2-aminophenoxazin-3-one (APZ) [63], tetrahydrofuran [64] and benzyl mercaptan (BM) [65].

The attractiveness of the π - π stacking approach is fundamentally related to its inherent experimental facility and simplicity. Moreover, this functionalization process for CNTs is structurally non-destructive, which allows for the preservation of the intrinsically electronic conductivity of CNTs. In addition, unlike with covalent functionalization, it is easy to uniformly assemble noble metal NPs with a small particles size onto the surface of CNTs by π - π stacking.

The polymers have also been used to anchor noble metal NPs to the surface of CNTs [66–68]. In this strategy, CNTs are wrapped with polymer to introduce surface functional groups on the CNTs with high density and uniform distribution for the anchoring of noble metal NPs. Pt and PtPd NPs could be immobilized onto the surface of polypyrrole (PPY)-modified CNTs (CNTs-PPY) [69] and Au NPs were uniformly dispersed on the surface of CNTs modified with polyaniline (PANI) [70] or polythiophene [71]. Another exciting work was done by Hwang's group. The PVP-modified CNTs were used as the support for the noble metal NPs, Pt and PtRu NPs [68]. Compared with traditional acid-oxidized method, the PVP modification process not only cause much less structural damage but also generate a higher density of surface functional groups, resulting in a better dispersion of noble metal NPs with smaller average sizes on the surface of CNTs.

The Chen's group has developed an effective method to modify CNTs with ionic liquid polymer (PIL) [66]. The PIL film on the CNTs introduces a large number of surface functional groups on the CNTs with uniform distribution to anchor and grow noble metal NPs, creates a distribution of ionic

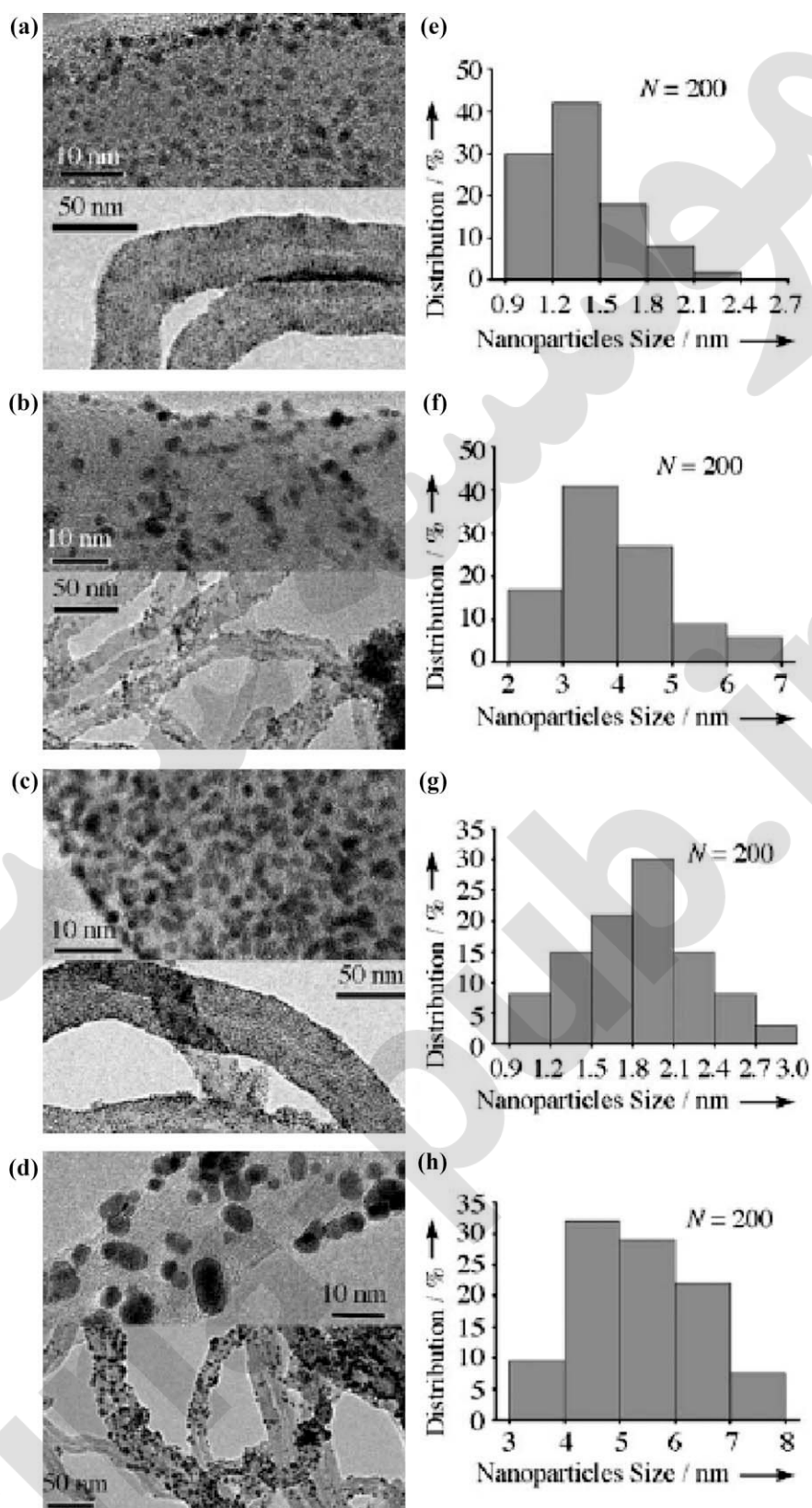


Figure 8 TEM images (left) and size distributions (right) of nanoparticles of nanohybrids. (a and e) PtRu/CNTs-PIL; (b and f) PtRu/CNTs; (c and g) Pt/CNTs-PIL; (d and h) Pt/CNTs. Adapted from Ref. [66].

species with positive charge that prevents aggregation of the CNTs and induces stable nanotube suspensions in water. The PIL film on the CNTs also produces a uniform distribution of imidazole groups that serve as functional groups for the immobilization of Pt and Ru precursors on the surface of CNTs through electrostatic interaction and coordination. The results showed that PtRu and Pt NPs with small particle size ((1.3 ± 0.4) nm for PtRu NPs and (1.9 ± 0.5) nm for Pt) were dispersed uniformly on the PIL-functionalized CNTs (CNTs-PIL) (Fig. 8) and the obtained PtRu/CNTs-PIL and Pt/CNTs-PIL nanohybrids showed superb performance for direct electrooxidation of methanol.

The polymer functionalization technique also includes the formation of polyelectrolyte shells on the CNT surface, which has become one of the effective routes used to functionalize CNTs for assembly of noble metal NPs. Polyelectrolytes are especially rich in different terminal functionalities. Hence, the choice of polyelectrolyte determines whether the surfaces of CNTs are positively or negatively charged [72–79]. Consequently, either noble metal NPs or precursor ions with opposite charge can be anchored via electrostatic interaction. For example, Wang et al. used positively charged poly(diallyldimethylammonium chloride) (PDDA) to functionalize CNTs and to attach Pt NPs. The obtained Pt NPs/PDDA/CNTs nanohybrids demonstrated high electrocatalytic activity towards methanol oxidation [80]. Yin et al. also deposited Pt NPs to the poly(allylamine hydrochloride) (PAH) functionalized CNTs, which showed high catalytic activity towards oxygen reduction reaction (ORR) [74].

Another method for the synthesis noble metal NPs/CNTs nanohybrids is based on the electrostatic layer-by-layer (LBL) self-assembly technique [73,75,81]. It was reported by Liz-Marzán's group that CNTs absorbed poly(sodium 4-styrenesulfonate) (PSS), followed by self-assembly of a layer of the positive charged PDDA which was used to anchor Au NPs [75]. Jiang et al. also functionalized MWCNTs with PDDA to obtain positively charged PDDA-MWCNTs. Tungstophosphoric acid ($H_3PW_{12}O_{40}$ HPW) was then self-assembled on MWCNTs via the electrostatic force between the negatively charged HPW and positively charged PDDA-functionalized MWCNTs, followed by Pd deposition and reduction onto the HPW assembled PDDA-MWCNTs (the obtained nanohybrids were denoted as Pd/HPW-PDDA-MWCNTs) (Fig. 9). The Pd NPs (average particle size about 2 nm) in the HPW assembled PDDA-MWCNTs showed a homogeneous dispersion with narrow particle size, and no agglomerations were observed. The assembly and incorporation of HPW significantly reduced the size and enhanced the distribution of Pd NPs on MWCNTs [81].

Furthermore, based on the hydrophobic interaction, CNTs were also functionalized with a hemimicelle self-assembly of amphiphilic molecules [82] or supermolecular self-assembly of sodium dodecyl sulfate (SDS) [83,84] and used as the supports for Pd NPs and Pt NPs.

Besides, as another kind of the functionalized CNTs, nitrogen-doped CNTs were also used as the supports for noble metal NPs. The nitrogenated chemically active sites (substitutional and pyridinic nitrogen) in nitrogen-doped CNTs (NCNT) could effectively anchor and disperse noble metal NPs on the surface of NCNTs [85–91]. One of the representative works was reported by Terrones' group. Pt NPs

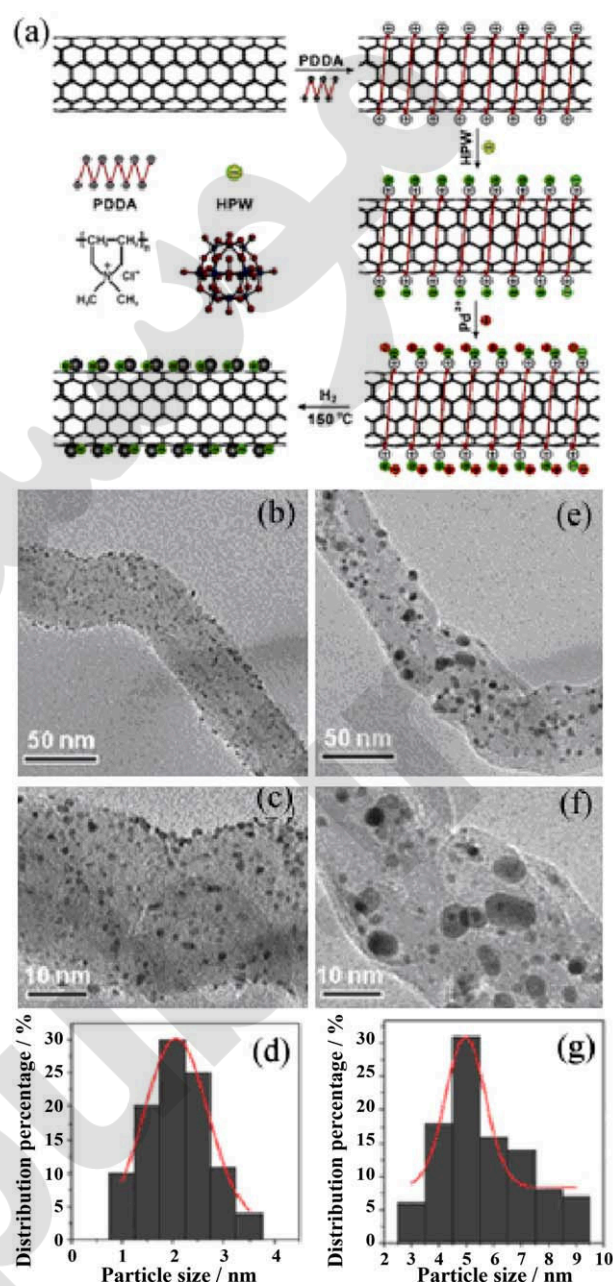


Figure 9 Scheme of self-assembly of HPW onto PDDA-functionalized MWCNTs and synthesis of Pd NPs on HPW assembled PDDA-MWCNTs (a); TEM images and histograms of Pd/HPW-PDDA-MWCNTs at different magnification (b–d) and Pd/acid treated-MWCNTs (e–g). Pd loading was 20 wt.%. Reprinted with permission from [81], ©2010 The Royal Society of Chemistry.

with the average diameter of 6 nm were highly dispersed on the surfaces of NCNTs. The obtained Pt/NCNTs nanohybrids showed high catalytic activity towards hydrogenation of cinamaldehyde to cinammyl alcohol and hydrocinnamaldehyde [86].

Physical methods

Physical methods, including sputtering deposition, ion and electron beam irradiation deposition and evaporation depo-

sition, are also used widely to prepare noble metal NPs/CNTs nano hybrids, as they provide excellent control over the size, shape, and uniformity of the noble metal NPs.

Sputtering deposition is an efficient method for the synthesis of noble metal NPs/CNTs nano hybrids [92–95]. Using this method, uniform-size noble metal NPs can be conveniently deposited on the external wall surface of CNTs, by selecting appropriate metal cathodes, and by controlling the current and sample exposure time. One of representative works was reported by Roy's group [92]. Pt NPs with the particle size of 3–5 nm were deposited uniformly onto the surface of the vertically aligned carbon nanotubes (VACNT) by DC sputtering system.

The ion and electron beam irradiation deposition were also introduced to deposit noble metal nanoparticles on the surface of CNTs [82,96,97]. Comparing with the chemical methods, this method has the advantages of homogeneous reduction and nucleation which lead to small and mono-dispersed noble metal NPs. It was reported by Wang et al. that Pt NPs with the diameter of 2.5–4.0 nm were decorated on the CNT surface successfully by γ -irradiation method and the obtained Pt NPs/CNTs nano hybrids showed good electrocatalytic properties as the cathodic material in proton exchange membrane fuel cells (PEMFCs) [96]. On the other hand, Pd NPs were also dispersed uniformly on the CNT surface by electron beam irradiation method and the particle size of Pd NPs was in the range of 1–3 nm (the average diameter was 2 nm) [82]. The obtained Pd NPs/CNTs nano hybrids showed excellent electrocatalytic properties towards ethanol oxidation in 1 M KOH aqueous solution.

Evaporation deposition methods, including thermal evaporation deposition and electron beam evaporation deposition, were also used to synthesize noble metal NPs/CNTs nano hybrids [98,99]. This method has the advantages of easily controlling the size and covering density of noble metal NPs on the CNT surface by varying the evaporation temperature and deposition time. One of the representative works in thermal evaporation deposition method was reported by Gingery and Bühlmann [98]. The authors fabricated Au NPs/MWCNTs nano hybrids and the particle size of Au NPs could be adjusted easily in the range from 4 to 150 nm. In addition, electron beam evaporation was used to deposit several noble metal NPs on the surface of SWCNTs, such as Rh, Pt, Au, and Pd NPs, and the obtained noble metal NPs/CNTs nano hybrids were used successfully to construct gas sensors for detection of H₂, CH₄, CO, and H₂S [99].

Although a large variety of noble metal NPs/CNTs nano hybrids have been successfully synthesized by physical methods, there are some disadvantages, such as the need of special and expensive equipments and difficulty for bulk preparation.

Applications of noble metal NPs/CNTs nano hybrids

The first report for the application of noble metal NPs/CNTs nano hybrids appeared in 1994. Ajayan et al. used Ru NPs/CNTs nano hybrids in heterogeneous catalysis involving hydrogenation of cinnamaldehyde [19]. Since then, the applications of CNTs-supported noble metal NPs have been

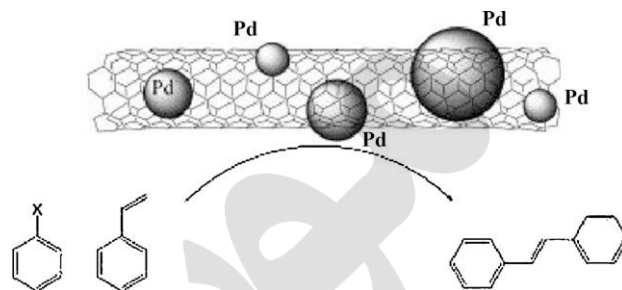


Figure 10 Scheme of Pd/SWCNTs nano hybrids for Heck coupling reaction.

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extensively studied. In this review, we briefly discuss the applications of noble metal NPs/CNTs nano hybrids in the heterogeneous catalysis, fuel cells and chemo/biosensors.

Heterogeneous catalysis

Recently, CNTs have received considerable attention as the supports of noble metal catalysts in heterogeneous catalysis due to their good mechanical strength, large surface area and good durability under harsh conditions. The interaction between noble metal NPs and CNTs in nano hybrids induces a peculiar microstructure or modification of the electron density of the noble metal clusters, and enhances the catalytic activity. The absorption of organic species is also favored by van der Waals interactions between the CNTs and organic molecules, leading to favorable reactant–product mass transportation. A large number of literatures have been reported that CNT-supported noble metal catalysts (e.g., Pt, Pd, Au, Rh, Ru and Ag) exhibited good catalytic behavior under various chemical reactions, involving Suzuki coupling [100,101], selective hydrogenation [102], CO oxidation [103], NH₃ synthesis [18] and hydrodehalogenation [104].

One of the most important issues in current organic synthesis is the development of new efficient carbon–carbon and carbon-heteroatom bond forming reactions. Corma et al. reported that Pd/SWCNTs nano hybrids exhibited higher catalytic activity than Pd/C for Heck reaction of styrene and iodobenzene and for Suzuki coupling of phenylboronic and iodobenzene (Fig. 10). The authors found indeed that the catalytic activity of Pd on SWCNT exhibited a characteristic pattern that was clearly different from Pd/C, the former system being special interesting from C–C cross-coupling reactions, for which Pd particle size seemed to play a crucial role compared to hydrogenations and oxidations [101].

In petrochemical and chemical industries, selective hydrogenation catalysts are crucial for the synthesis of a wide variety of chemicals. Tessonnier et al. developed Pd/MWCNTs nano hybrids that exhibited higher selectivity towards the C=C bond hydrogenation compared with Pd/C, which could be ascribed to the faster desorption of the C=C hydrogenated products from the active sites. Whereas on the Pd/C, the cinnamaldehyde absorbed in a different way, leading to the almost simultaneous hydrogenation of C=O and C=C bonds [102]. Also, Liu et al. observed that Pt/CNTs nano hybrids showed excellent catalytic activity for

hydrogenation of nitrobenzene to aniline under solvent-free conditions [105].

Moreover, heterogeneous catalysts not only require stable and active, but also are easy to be separated and reused for practical applications. Chun et al. developed a new method that the Pd NPs were deposited onto imidazolium bromide-functionalized ionic MWCNTs (Pd/IL-f-MWCNTs) [55]. The Pd/IL-f-MWCNTs exhibited higher catalytic activity for the hydrogenation of *trans*-stilbene in ionic liquid and allowed up to 50 times recycling.

Fuel cells and electrocatalysis

Due to their high power density, rapid start-up, and low operating temperatures, PEMFCs and direct methanol fuel cells (DMFCs) are promising power sources for vehicles and portable electronic devices. As the electrocatalysts in PEMFCs, Pt-based NPs supported on high-surface-area carbon, especially CNTs, have been extensively investigated. Numerous studies reported that Pt-based NPs/CNTs nanohybrids showed higher electrocatalytic activity for the methanol oxidation and oxygen reduction reaction (ORR) than the commercial Pt-based NPs/C catalysts due to one-dimensional structure, excellent electronic conductivity and good electrochemical properties of CNTs [60,68,80,81].

Wei et al. prepared 1-Pt/FMCNTs and 2-Pt/FMCNTs nanohybrids by spontaneous reduction deposition of Pt NPs on the FMCNTs after or before FMCNTs coated on the Teflon-boned carbon electrodes (TBCE) [106]. The two kind of nanohybrids exhibited higher electrochemical activity for the ORR than commercial Pt/C catalyst. The authors found that the utilization of Pt in electrodes of 1-Pt/FMCNTs, 2-Pt/FMCNTs, and Pt/C were 75.6%, 44.6%, and 39.2% respectively. Electrodes of 2-Pt/FMCNTs and Pt/C were fabricated by almost the same procedure, but the former has a 5.4% Pt utilization higher than the later, which can be ascribed to a much better-connected electron path contributed by FMCNTs in 2-Pt/FMCNTs than that in Pt/C electrode. It is well known that oxygen reduction in cathode of PEMFCs must be able to easily access the surface of the catalyst particles, a pathway for proton diffusion must exist in the proximity of the active sites on catalysts, and an electronic conducting pathway from the catalyst to the electrode is required for electron transport. When Pt catalyst is supported on the carbon black, many carbon black particles are isolated by the dielectric organic polymer and thus the Pt catalysts loaded on the carbon black particles are not going to participate in electrode reaction because of no electron pathway (Fig. 11). However, this may occasionally happen when using the CNTs since their tubular structure makes them easy to connect together. With the increase in the electron pathway, the utilization of Pt catalyst will also increase.

On the other hand, methanol crossover from the anode to cathode is major hurdle that DMFCs must surmount in order to reach their commercialization. To cope with this problem, one of the solutions is to develop a novel and less methanol permeable membranes, and the other method is to employ a methanol-tolerant cathode catalyst. Yin et al. synthesized two kinds of Pt-Au/CNTs nanohybrids with different structures, one contained the separated Pt and Au NPs

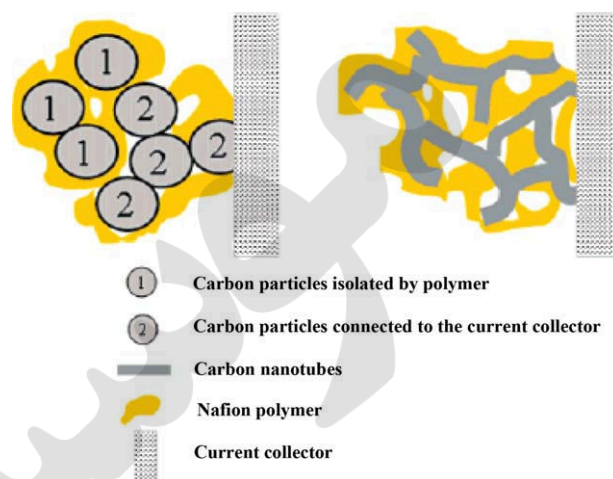


Figure 11 Scheme of the internal structure of the catalyst layer.

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(Pt/Au/CNTs), and another composed with alloy-like Pt-Au NPs (PtAu/CNTs). Compared with the Pt/CNTs nanohybrids, the two Pt-Au/CNTs nanohybrids showed a lower overpotential for ORR in the presence of methanol. Particularly, the Pt/Au/CNTs catalyst with separated Au and Pt NPs exhibited the significantly higher methanol tolerance than the alloy-like PtAu/CNTs nanohybrids, which should be ascribed to the less methanol adsorption on Pt surface due to the effect of Au NPs [107].

In recent years, the durability of PEMFCs has also been recognized as one of the most important issues to be addressed before the commercialization of the PEMFCs. Li et al. developed a route to stabilize Pt NPs supported on CNTs by anchoring Pt NPs on hydrofluoric acid treated CNTs [47] and Matsumori et al. used silica protection layer to improve the stability of Pt NPs supported on CNTs [108]. However, the former method involved the use of a non-environmentally friendly chemical (hydrofluoric acid), and some structural damage to the CNTs would occur, leading to the loss of their electrical conductivity [68,109]; the latter one would reduce the active surface area of the catalysts, resulting in the decrease of the catalytic activity of the catalysts. In order to solve the above problems, Chen et al. developed a novel method to stabilize the CNTs-supported Pt NPs by ionic liquid polymer thin film (Fig. 12) and the long-term operation stability of the obtained nanohybrids (PIL/PtNPs/AP-CNTs) for methanol electrooxidation has been improved obviously due to the mechanical isolation of PIL thin layer between PtNPs, electrostatic and coordinative action between PtNPs and N-heterocyclic cations of ILs to inhibit the migration and agglomeration of PtNPs [110].

Except for applications in ORR and methanol electrooxidation in fuel cells, the noble metal NPs/carbon nanotubes nanohybrids were also used in electrocatalytic oxidation of ethanol [64,111–114], ethylene glycol [115,116], glycerol [117], formaldehyde [69], hydrazine [118,119], etc.

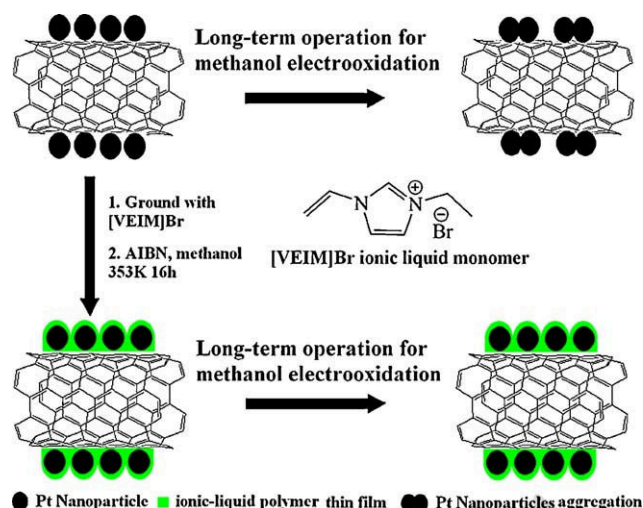


Figure 12 Schematic diagram for stabilization of Pt nanoparticles supported on CNTs by ionic liquid polymer. Reprinted with permission from [110], ©2010 The Royal Society of Chemistry.

Chemo/biosensors

Chemo/biosensors have important applications in environmental monitoring, chemical process controlling, as well as in agricultural and biomedical fields. In recent decades, noble metal NPs/CNTs nanohybrids have wide applications in chemo/biosensors [120–123]. Gas sensors constructed by noble metal NPs/CNTs nanohybrids is one of the representative applications. Those nanohybrids have shown high sensitivity towards many toxic/combustible gases, such as H_2 , CH_4 , H_2S , and CO [123,124,99]. Mubeen et al. synthesized Au NPs/SWCNTs nanohybrids which were able to detect H_2S at a low detection limit of 3 ppb in air at room temperature [123]. The sensors were reversible, and could increase the bias voltage which reduced the sensor recovery time probably by local Joule heating. The sensing mechanism is believed to be based on the modulation of the conduction path across the nanotubes emanating from the modulation of electron exchange between the gold and carbon nanotube defect sites when exposed to H_2S . Another representative application of the noble metal NPs/CNTs nanohybrids is in electrochemical biosensors [120,125–128]. The electrochemical biosensors modified with noble metal NPs/CNTs nanohybrids have demonstrated an excellent electrochemical detection behavior for some life-related molecules, such as glucose, hydrogen peroxide, NADH, dopamine, epinephrine, ascorbic acid, cytochrome c, and so on [120,121,125–137]. Meng et al. reported an amperometric nonenzymatic glucose sensor constructed with Pd NPs/SWCNTs nanohybrids and the obtained sensor showed high sensitivity ($\sim 160 \mu A mM^{-1} cm^{-2}$), low detection limit ($0.2 \pm 0.05 \mu M$), good stability and fast response ability (within 3 s) [121]. Unlike other nonenzymatic sensors operated under high pH conditions, the Pd NPs/SWCNTs/glassy carbon electrode showed good performance without surface contamination in neutral phosphate buffer solution (PBS pH 7.4) even in presence of high concentration of chloride ions, which made it a great potential for practical use. In addition,

Pt NPs were electrodeposited on the CNTs which were directly grown on the graphite electrode, and the resulting Pt NPs/CNT/graphite electrode was used as a matrix for immobilization of glucose oxidase. The excellent electrocatalytic activity and special three-dimensional structure of the enzyme electrode resulted in good characteristics such as large determination range (0.1–13.5 mM), short response time (within 5 s), large current density ($1.176 mA cm^{-2}$), high sensitivity ($91 mA M^{-1} cm^{-2}$) and stability [131].

A H_2O_2 biosensor based on Pd NPs/MWCNTs nanohybrids was also developed by Jeon's group [132]. The proposed H_2O_2 biosensor (Nafion/MWCNTs-Pd/GCE) exhibited a wide linear range from $1.0 \mu M$ to 10 mM, a low detection limit of $0.3 \mu M$ ($S/N=3$) and a fast response time within 10 s.

An electrochemical method for the measurement of guanine and adenine in calf thymus DNA was developed with the polythionine/Au NPs/MWCNTs [133]. This modified electrode exhibited enhanced electrocatalytic behavior and good stability for the direct electrochemical detection of guanine and adenine and could be developed to determine trace level of DNA.

Conclusions

As a new and very promising class of functional materials, noble metal NPs/CNTs nanohybrids become one of the family of composite materials with extraordinary properties by combining the advantages of noble metal NPs and CNTs. This review highlights the recent advances in the synthesis of noble metal NPs/CNTs nanohybrids and their applications in heterogeneous catalysis, fuel cells, and chemo/biosensors. The noble metal NPs/CNTs nanohybrids can be synthesized by electrochemical deposition, electroless deposition, dispersion of noble metal NPs on the functionalized CNTs and physical methods. Each of these methods in principle has a common goal, which is to obtain high dispersion and small particle size of noble metal NPs on the surface of CNTs. Nonetheless, there are still some challenges: the balance of conflicts between maintaining the original structure and properties of CNTs and introducing the anchor groups into CNTs by functionalization; the size, the shape, the structure, the dispersibility of noble metal NPs on CNTs; and the stabilization of noble metal NPs on CNTs. Despite being at an early stage of research, noble metal NPs/CNTs nanohybrids have demonstrated considerably enhanced activity and selectivity in heterogeneous catalysis; markedly improved activity, stability and lifetime in fuel cells; as well as increased sensitivities in chemo/biosensors. It is easy to foresee that this intriguing material will play very important roles in solving the energetic, environmental and biomedical problems in the future.

Acknowledgments

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