22 Production of Metal Nanoparticles on Carbon Nanotubes by Gamma Irradiation

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CONTENTS

22.1 INTRODUCTION

Carbon nanotubes (CNTs) are being studied for a variety of applications due to their outstanding mechanical, chemical, electrical, and optical properties (Baughman et al. 2002; Popov 2004; Belin and Epron 2005). In addition, CNTs' structures are being modified to expand their use in new applications (Baughman et al. 2002; Hirsch 2002; Raghuveer et al. 2006; Hou et al. 2008). AQ1 Decorating CNTs with certain metal nanoparticles is a promising option for catalysis (Wildgoose et al. 2006), hydrogen storage (Cheng et al. 2001; Hou et al. 2003; Sarkar and Banerjee 2004; Zacharia et al. 2005; Strobel et al. 2006; Chen et al. 2008; Rakhi et al. 2008; Suttisawat et al. 2009; Yuruma et al. 2009), and sensing (Star et al. 2006; Vairavapandian et al. 2008).

The decoration of CNTs with nanoparticles has been carried out by many electrochemical, chemical, and physical methods (Xue et al. 2001; Qu and Dai 2005; Quinn et al. 2005; Ren and Xing 2006; Sun et al. 2006; Wildgoose et al. 2006; Georgakilas et al. 2007; Karousis et al. 2008). Ionizing radiation is currently being investigated both as a new alternative to create defects in the surface of the nanotubes and as a method for the production of metallic nanoparticles (Belloni et al. 1998; Joshi et al. 1998; Doudna et al. 2003; Skakalova et al. 2003, 2004; Guo et al. 2005; Hulman et al. 2005; Sarkany et al. 2005; Krasheninnikov and Nordlund 2010; Remita and Remita 2010). The gamma (γ) irradiation has shown significant advantages over other methods since radiation parameters such as energy, dose, and dose rate can be finely controlled. In addition, reducing agents are generated uniformly throughout the aqueous solution. The reduction potential of these agents

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makes them able to reduce free ions at each encounter. Successful attempts have been made to directly deposit metallic nanoparticles such as gold, platinum, and ruthenium on CNTs by gamma irradiation with a homogeneous distribution. Nonetheless, several factors must be considered to obtain the desired results (Liu et al. 2003; Oh et al. 2005; Lee et al. 2007; Zhang et al. 2010; Rojas and Castano 2012).

In this chapter, we present gamma irradiation as a promising technique to decorate CNTs with metal nanoparticles. The influence of parameters such as dose, dose rate, and stabilizer concentration on particle size will be discussed.

22.2 RADIATION EFFECTS ON CARBON NANOTUBES

A common misconception is that radiation (ions, electrons, gamma rays, etc.) have exclusively detrimental effects on the properties of materials. To the contrary, irradiation can also induce positive effects on materials, particularly for nanostructured systems under controlled irradiation conditions. For example, both ion and electron beams have been used to synthesize both nanoclusters and nanowires, modifying in a controllable manner their morphology, as well as altering their electronic, mechanical, and magnetic properties (Krasheninnikov and Nordlund 2004). In addition, irradiation of CNTs with energetic particles (electrons or ions) can successfully create molecular junctions between nanotubes (forming cross and Y-shaped structures) (Terrones et al. 2002). Ion irradiation has also been used for the production of CNT-amorphous diamond nanocomposites and as a technique to improve adherence of nanotubes to both metallic and graphite substrates (Krasheninnikov and Nordlund 2004).

Functionalization of CNTs is of special importance for diverse applications as it can lead not only to the improvement of their solubility but also to their ability to be coupled with other materials creating composites with fascinating characteristics (Hirsch 2002). Irradiation-induced defects normally increase the reactivity of nanotubes at the surface. Thus, functional groups can be attached to both graphene and nanotubes in specific areas (Guo et al. 2005; Salah et al. 2009; Fedoseeva et al. 2010). The induced defects in the sp^2-bonded carbon systems due to focused electron and ion beams are governed by the knock-on displacement of carbon atoms, creating vacancies and interstitials in the nanotubes (Krasheninnikov and Nordlund 2010).

Although the effects of highly energetic particles (both electrons and ions) on CNTs have been extensively studied (Krasheninnikov and Nordlund 2010), limited attention has been given to the effects of gamma irradiation on CNTs. Recent studies have been published on the improvement of both Young's modulus and the electrical conductivity of gamma irradiated paper made of single-walled carbon nanotubes (SWNT). It was found that these two properties reached a maximum value at a dose of 170 kGy.* It has been suggested that highly energetic photons create defects on the nanostructure leading to the formation of bonds between the nanotubes. Once a critical defect concentration is reached at a certain dose, some of the previously created bonds might be broken, thus affecting the final mechanical and electrical properties of the nanotubes. In addition, it was also observed that the effect of irradiation was much stronger for samples irradiated in the air in comparison to those in a vacuum (Skakalova 2003).

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Gamma irradiation of SWNTs has been used as a pretreatment for chemical functionalization with thionyl chloride ($SOCl_2$). This process was based on the premise that the concentration of defects is likely to influence the concentration of functional groups attached to the nanotubes (Skakalova 2004). This study showed that further functionalization with $SOCl_2$ after irradiation enhances even more both the Young's modulus and the electrical conductivity.

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* The absorbeddosc is a measure of the energy deposited in a medium by ionizing radition per unit mass. It is usually given as Joules per kilogram (J/kg) and represented by the SI unit, the gray (1 GY $\equiv$ 1 J/kg), or the rad. 1 Gy = 100 rad = 6.254×1018 eV/kg.

The functionalization of multiwalled carbon nanotubes (MWCNTs) with both thionyl chloride and decylamine has also been studied after gamma irradiation. The concentration of functional groups attached to the nanotubes was found to increase monotonically, with increasing irradiation doses in the range of 50–250 kGy. This happens due to a significant increase in defects on the side-walls of the nanotubes created by the gamma photons. Finally, more stable dispersions of MWCNTs in organic solvents, such as both acetone and tetrahydrofuran (TFT), were observed, indicating a better solubility of the nanostructure after gamma irradiation (Guo et al. 2005). Irradiated MWCNTs have also shown a modification of their original structural characteristics, such as inter-wall distance, which seem to be dependent on the surrounding medium (Xu et al. 2011). These results have indicated that gamma irradiation might be an effective pretreatment for further functionalization on the structural modification of CNTs (Guo et al. 2005).

22.3 SYNTHESIS OF METALLIC NANOPARTICLES SUPPORTED ON CARBON NANOTUBES

The decoration of CNTs with nanoparticles has been carried out by diverse methodologies: electroless deposition (Qu and Dai 2005), thermal decomposition (Xue et al. 2001), chemical reduction in supercritical CO_2 solutions (Sun et al. 2006), impregnation using an aqueous solution (Tessonnier et al. 2005), and electrodeposition (Quinn et al. 2005). These techniques commonly use noble metal salts as precursors for the preparation of the nanoparticles, which are obtained by a reduction process.

Applications of the electroless deposition methodology are limited by the fact that only metal ions with redox potential higher than that of the nanotubes can be reduced. For example, Au ($AuCl^{-4}$/Au, +1.002 V vs. SHE) and Pt ($PtCl_4^{2-}$/Pt, +0.775 vs. SHE) nanoparticles have been successfully synthesized by a spontaneous reduction of the metal ions by SWCNTs. On the contrary, neither Cu^{2+} (Cu $(NO_3)_2$/Cu, +0.340 V vs. SHE) nor Ag^+ ($Ag(NH_3)^{2+}$/Ag, +0.373 V vs. SHE) can be reduced without the presence of a reducing agent (Choi et al. 2002). This problem was solved by placing the nanotubes on a metal substrate with a redox potential lower than that for the metal ions. With this method, ions can be reduced into nanoparticles onto the CNT surface even if their redox potential is lower than that of the CNTs. This method is referred to as substrate enhanced electroless deposition (Qu and Dai 2005).

Thermal decomposition has been used for the synthesis of nanoparticles of Pd, Pt, Au, and Ag on CNTs. In the process, CNTs are dispersed in either water or acetone by the addition of a metal salt. A subsequent evaporation of the solvent is carried out at a temperature of approximately 100°C. As a final step, both decomposition and a reduction of the mixture are conducted at temperatures between 300°C and 700°C under an H_2 atmosphere. Using this method, nanoparticles with sizes between 8 and 20 nm were obtained on the surface of the nanotubes (Xue et al. 2001).

Nanoparticles such as Pd-Rh have been successfully attached to MWCNTs by a chemical reduction in supercritical CO_2 solutions (SC CO_2). Supercritical fluids (SCFs) have a combination of properties such as low viscosity, high diffusivity, near zero surface tension, and strong solvent power for some small molecules that make them applicable in different areas in material science. Although inorganic salts are not generally soluble in SC CO_2, some polar solvents, such as ethanol, methanol, and acetone, can act as cosolvents to enhance the solubilization of inorganic precursors in supercritical solutions. After reactions, dry and high-purity products are easily obtained by in situ extraction using SC CO_2 as a solvent (Sun et al. 2006).

Electrodeposition is another method used to produce metal nanoparticles on CNTs. This process was performed in a two electrode arrangement in a solution containing the CNTs with $HAuCl_4$, K_2PtCl_4, or $(NH_4)_2PdCl_4$. As a result of this study, Au, Pt, and Pd nanoparticles were deposited on the CNTs by controlling the deposition potential, duration of the pulse, and the concentration of the metal salt in the electrochemical system (Quinn et al. 2005).

Radiochemical methods have also been recently explored as a promising technique to both produce and deposit metallic nanoparticles on CNTs. In addition to the ability to create defect sites on the sidewall of CNTs, gamma irradiation is proven to provide other advantages in the synthesis of nanoparticles such as fine control of energy of radiation, dose, and dose rate. Also, reducing agents are generated uniformly within the solution. These reducing agents' strong reduction potential makes them able to reduce free ions at each encounter. Finally, the controlled reduction of metal ions can be made with no need of any excess of additional reducing agents. Thus, no undesired oxidation products from the reactants are produced (Belloni et al. 1998; Liu et al. 2003; Lia et al. 2007).

22.4 RADIATION CHEMISTRY FOR THE PRODUCTION OF METALLIC NANOPARTICLES

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During water radiolysis, radicals such as $H^{\bullet}$, $OH^{\bullet}$, $H+$, H_2O_2, H_2, and electrons in aqueous solution (e^-_{aq}) are produced. The concentration of species created in this process is given by the G factor. This factor represents the number of molecules, or radicals, produced per 100 eV of radiation energy absorbed. The normally accepted values of product yields in a Co-60 gamma irradiated aqueous solution, with both neutral pH and ambient temperature, are presented in Table 22.1 (Appleby and Schwarz 1969).

The species $H^{\bullet}$, e^-_{aq}, and $OH^{\bullet}$ are very reactive. Both $H^{\bullet}$ and e^-_{aq} are strong reducing agents with redox potentials of E° ($H+/H^{\bullet}$) = −2.3 V_{NHE} and E° (H_2O/e-aq) = −2.87 V_{NHE}, respectively. Therefore, both can reduce metal ions present in the solution to a state of zero valence. This process takes place through the direct reaction of the metal ion with either $H^{\bullet}$ or e^-_{aq} in the case of monovalent ions. In contrast, the reduction of multivalent metal ions in aqueous solutions is a multistep process where atoms in unusual valence states are initially formed. This initial reduction is followed by further reduction and agglomeration until a stable nanoparticle is obtained (Belloni et al. 1998).

TABLE 22.1

Radical and Molecular Product Yield in Gamma Irradiated Aqueous Solutions

Product	$H^{\bullet}$	$OH^{\bullet}$	H^+	H_2O_2	H_2	e^-_{aq}
G factor (#species/100 eV)	0.61	2.86	2.70	0.61	0.43	2.70

Source: Data from Appleby, A. and Schwarz, H.A., *J. Phys. Chem.*, 73, 1937, 1969.

TABLE 22.2

Reactions of Scavenger with Radicals and the Respective Redox Potentials of the Radical Products

Scavenger	Radical	Products	Redox Potential
$(CH_3)_2CHOH$	$OH^{\bullet}$	$(CH_3)_2C^{\bullet}OH + H_2O$	$E^{\circ}((CH_3)_2CO/(CH_3)2C^{\bullet}OH) = -1.8\ V_{NHE}$
	$H^{\bullet}$	$(CH_3)_2C^{\bullet}OH + H_2$	
$HCOO-$	$OH^{\bullet}$	$COO- + H_2O$	$E^{\circ}(CO_2/COO-) = -1.9\ V_{NHE}$
	$H^{\bullet}$	$COO- + H_2$	

OH$^\bullet$ radicals, however, are strong oxidizing agents, with E° (OH$^\bullet$/H$_2$O)$=+2.8$ V$_{NHE}$. Thus, metal atoms are brought to a higher oxidation state. A scavenger of OH$^\bullet$ radicals, such as primary alcohols, secondary alcohols, or formate ions, are required in the solution prior to irradiation for the reduction of metal ions to proceed. The secondary radicals, produced by the reaction between the scavenger and radiolysis species H$^\bullet$ and OH$^\bullet$, are also strong reducing agents. The corresponding reactions are summarized in Table 22.2 (Belloni et al. 1998).

22.5 EFFECTS OF THE STABILIZER, GAMMA DOSE, AND DOSE RATE ON THE SYNTHESIS OF NANOPARTICLES

During the reduction process of the metal ions that takes place with gamma irradiation, the atoms tend to dimerize when they either encounter or combine with ions. This occurs because the binding energy between either atoms or clusters with unreduced ions is stronger than either the atom–solvent or the atom–ligand energy. In order to limit the coalescence process of the aggregates, polymeric molecules, or cluster stabilizers, are added to the solution to be irradiated. Functional groups, such as carboxyl groups, that have a high affinity for the metal ions, ensure the anchoring of the molecule at the cluster surface. At the same time, the polymeric chain of the molecule protects the cluster from coalescing with another at the early stage by means of electrostatic repulsion or steric hindrance (Belloni et al. 1998).

When nanoparticles are to be prepared by irradiation, the stabilizer must be selected in such a way that it does not reduce the ions before irradiation. Polymers, such as poly vinyl alcohol (PVA) (Eisa et al. 2011), polyvinyl pyrolidone (PVP) (Gasaymeh et al. 2011), sodium polyvinyl sulfate (PVS), polyacrylamide (PAM) (Zhu 1998), poly *N*-methylacrylamide (PNMAM), poly ethyleneimine, and surfactants such as sodium dodecylsulfate (SDS) (Joshi et al. 1998), do not affect the electronic state of the ions but fulfill the conditions for stabilization.

Figure 22.1a shows a scanning electron microscope image (SEM) of MWCNT-Pd produced in a solution containing water and isopropanol in a ratio of 2:1 and 0.015 M of SDS as stabilizer. The sample was irradiated at 40 kGy. At a very low SDS concentration, less than the critical micelle concentration (CMC) of the SDS in water (approximately 18 mM), either few or no nanoparticles were obtained after irradiation. Instead, large agglomerates were formed due to the lack of dispersion stability. By increasing the amount of surfactant, even at low doses, some nanoparticles were observed in the sample, as shown in Figure 22.1b. The right amount of SDS allows palladium nanoparticles to form a homogeneous dispersion, leading to the formation of nanoparticles, with different sizes at different doses (Rojas and Castano 2011).

(a)   (b)
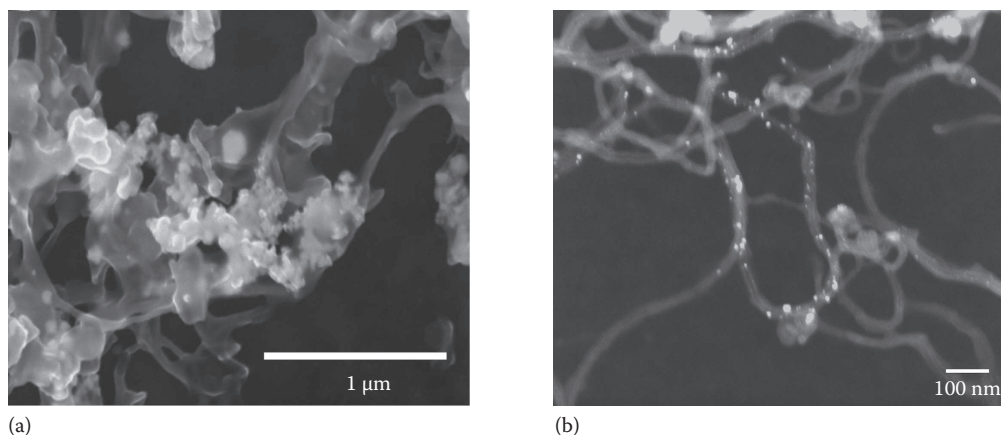
FIGURE 22.1 Images of MWCNTS-Pd after gamma irradiation: (a) SEM of sample irradiated at 30 kGy containing SDS at 15 mM and (b) STEM of sample irradiated at 40 kGy containing SDS at 0.05 M.   AQ5
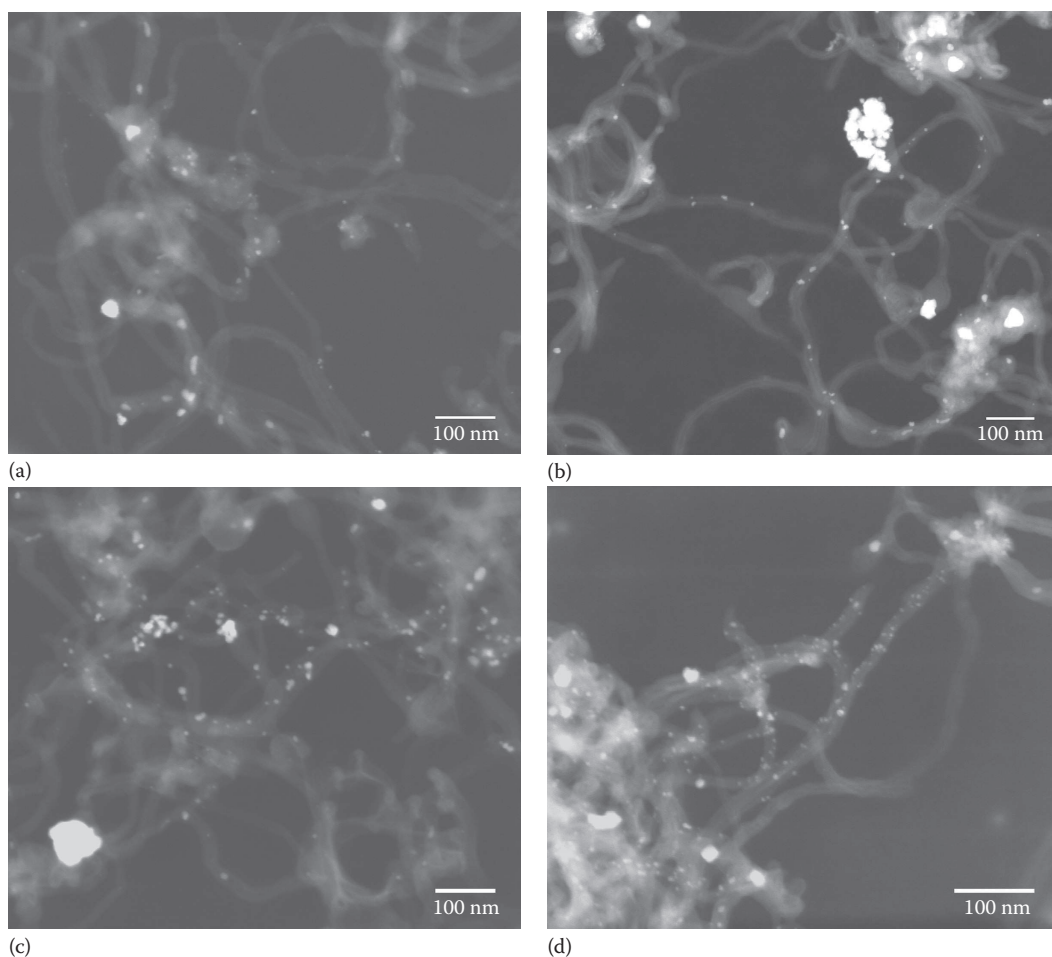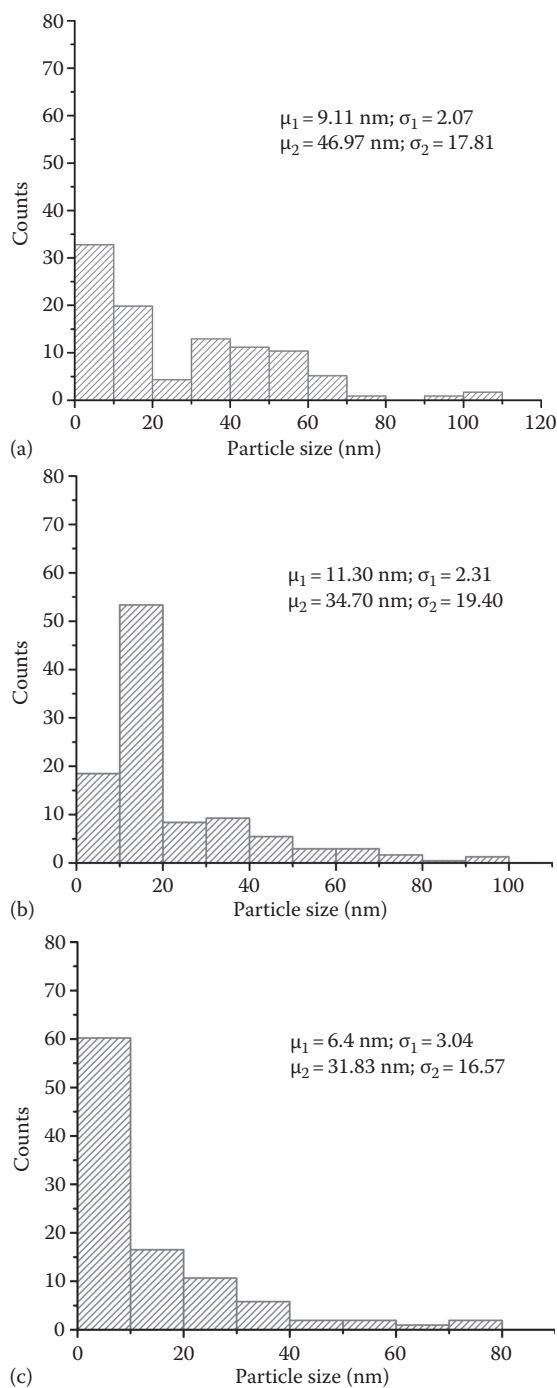
FIGURE 22.2   STEM images of MWCNTs decorated with Pd nanoparticles with 0.07 M SDS irradiated at a dose rate of 10 kGy/h and different doses at (a) 10 kGy, (b) 20 kGy, (c) 30 kGy, and (d) 40 kGy. (Reprinted from *Radiat. Phys. Chem*., 81 (1), Rojas, J.V. and Castano, C.H., Production of palladium nanoparticles supported on multiwalled carbon nanotubes by gamma irradiation, 16–21, Copyright 2012, with permission from Elsevier.)

Previous studies on the deposition of palladium nanoparticles on MWCNTs using $PdCl_2$ as the metal precursor at different doses between 10 and 40 kGy have demonstrated a noticeable variation of the nanoparticle yield. Also, a decrease in the nanoparticle size with the increase in dose has been observed (see Figure 22.2). The proposed mechanism with this study implies that the increase in dose leads to a larger amount of reducing agent produced in the solution. This causes a rapid Pd^{+2} reduction thus forming numerous Pd seeds, which then generate separate smaller particles, rather than a few big ones (Rojas and Castano 2012). In addition to the nanoparticles obtained on the surface of the CNTs, bigger particles were also obtained from the process. Histograms with size distribution of the palladium nanoparticles at different doses and the curve of average size versus dose are shown in Figure 22.3. Two remarkable features are observed with increasing dose: (1) the frequency of big particles gradually decreases and (2) the peaks position gradually shifts to a smaller diameter. Both the average size (μ) and the standard deviation (σ) of the Pd nanoparticles are shown, where μ_1, σ_1 and μ_2, σ_2 correspond to the first and second peak in the histogram, respectively (Rojas and Castano 2012).

Dose rate is also a factor that must be considered as it controls the rate at which the ions are being reduced. As previously mentioned, the radiation-induced radicals are generated

FIGURE 22.3 Particle size distribution (diameter in nm) of Pd nanoparticles on MWCNTs with 0.07 M SDS irradiated at a dose rate of 10 kGy/h and different doses at (a) 10 kGy, (b) 20 kGy, (c) 30 kGy, and (Reprinted from *Radiat. Phys. Chem.*, 81 (1), Rojas, J.V. and Castano, C.H, Production of palladium nanoparticles supported on multiwalled carbon nanotubes by gamma irradiation, 16–21, Copyright 2012, with permission from Elsevier.)

(continued)

$\mu_1 = 4.25$ nm; $\sigma_1 = 1.09$
$\mu_2 = 36.08$ nm; $\sigma_2 = 14.19$

(d)

(e)
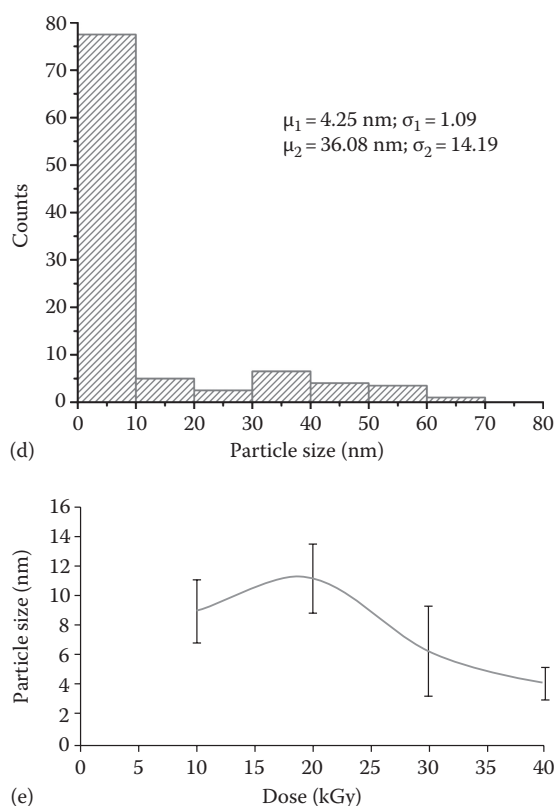
FIGURE 22.3 (continued)   Particle size distribution (diameter in nm) of Pd nanoparticles on MWCNTs with 0.07 M SDS irradiated at a dose rate of 10 kGy/h and different doses at (d) 40 kGy, (e) Plot of particle size vs. dose. (Reprinted from *Radiat. Phys. Chem*., 81 (1), Rojas, J.V. and Castano, C.H, Production of palladium nanoparticles supported on multiwalled carbon nanotubes by gamma irradiation, 16–21, Copyright 2012, with permission from Elsevier.)

homogeneously within the bulk sample. When the samples are irradiated with a high dose rate (pulse regime), all of the reducing species are produced and scavenged within a few seconds. This is followed by the clustering of the atoms created separately. The pulse regime can be achieved with electron accelerators where mean dose rates of 2.2 kGy/s or higher are reached. If, however, samples are irradiated with a low dose rate, continuous radiation regime, the production of reducing radicals is slower than the clustering of atoms. The isotopes ^{60}Co and ^{137}Cs are frequently used for the continuous radiation regime, as the dose rate can be controlled to stay within the range of 0.25–35 kGy/h (Belloni et al. 1998; Wishart 2008). In the latter situation, the reduction process occurs primarily on the surface of already formed aggregates. In this case, the reduction of atoms does not contribute to the formation of new clusters but instead to the growth of the ones initially formed (Remita and Remita 2010).

22.6   INTERACTION MECHANISMS BETWEEN CNTS AND NANOPARTICLES

There are two primary methods used to both synthesize and deposit nanoparticles on CNTs. The first method consists of growing growth of nanoparticles in the presence of CNTs directly onto the CNTs' surface. In this instance, a metal precursor, such as salts, is used and, together, with the nanotubes, are dissolved in a specific amount in a solution containing water, an OH• scavenger, and a stabilizer. This mixture is then irradiated with gamma rays so that the metal ions can be reduced by radicals

produced by the irradiation. During irradiation, not only are the ions reduced but the generation of new defects on the surface of the CNTs is also promoted. These defects are beneficial as they serve as preferred nucleation sites for the reduced metal ions. With this process, nanoparticles can be deposited onto the CNT walls primarily through van der Waals interactions. These appear to be strong enough to assure significant adhesion of the nanoparticles to the nanotubes (Georgakilas et al. 2007). Suitable examples of the results obtained by this method are presented in Figure 22.4a through c, where a and b are TEM images of palladium nanoparticles on MWCNTs by gamma irradiation using palladium chloride ($PdCl_2$) (Rojas and Castano 2012). Figure 22.4c corresponds to a SEM image of

(a)

(b)

(c)
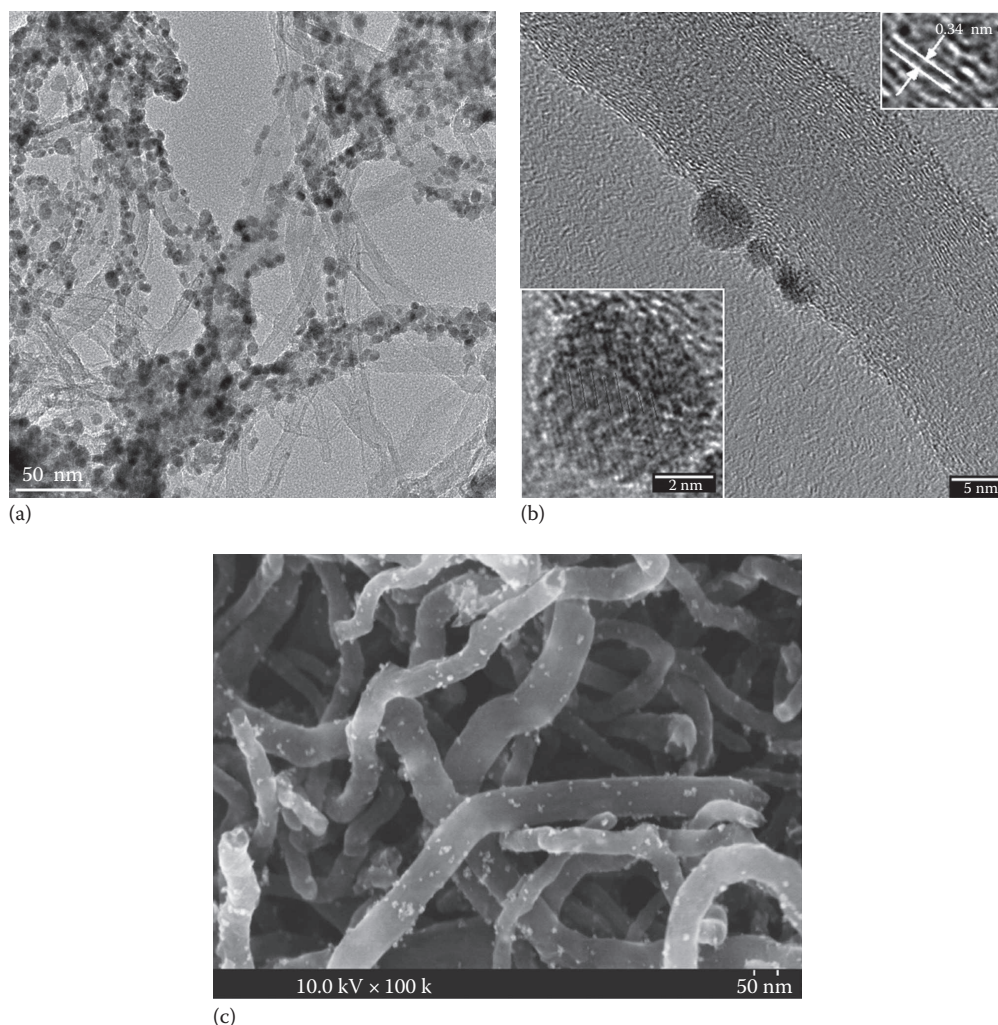
FIGURE 22.4 (a) TEM images of MWCNT decorated with Pd nanoparticles at 40 kGy and 0.07 M SDS. (Reprinted from *Radiat. Phys. Chem.*, 81 (1), Rojas, J.V. and Castano, C.H, Production of palladium nanoparticles supported on multiwalled carbon nanotubes by gamma irradiation, 16–21, Copyright 2012, with permission from Elsevier.) (b) High resolution TEM image of MWCNT decorated with Pd nanoparticles showing the d-spacing of Pd ((d_{111}) of 0.2246 nm) and interwall space of an MWCNT. (c) SEM image of the Pt/Ru nanoparticles on MWCNTs prepared in aqueous solution with a water/isopropanol ratio of 60:40 (v/v) irradiated to 40 kGy. (Reprinted from *Radiat. Phys. Chem.*, 79, Zhang, X., Ye, Y., Wang, H., Yao, S., Deposition of platinum–ruthenium nano-particles on multi-walled carbon nano-tubes studied by gamma-irradiation, 1058–1062, Copyright 2010, with permission from Elsevier.)
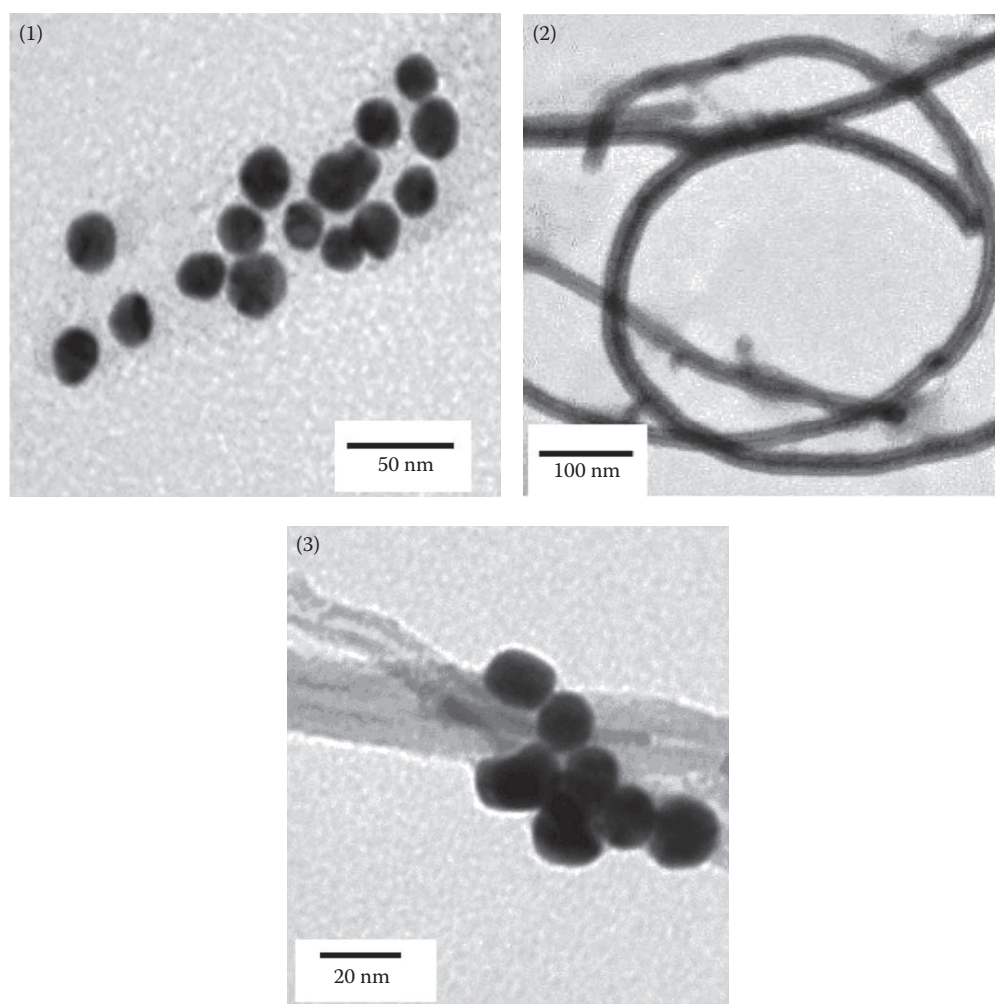
FIGURE 22.4 (continued)   (d) TEM images of (1) gold nanoparticles reduced from 0.17 mMH AuCl$_4$ using 1% solution of Na$_3$C$_6$H$_5$O$_7$ 2H$_2$O, (2) CNTs (2 mg/mL), and (3) attached gold nanoparticles on the surface sites of CNTs in aerated solutions due to gamma ray irradiation in air. (Reprinted from *Radiat. Phys. Chem.*, 78, Salah, N., Habib, S.S., Khan, Z.H., Al-Hamedi, S., Djouider, F., Functionalization of gold and carbon nano-structured materials using gamma-ray irradiation, 910–913, Copyright 2009, with permission from Elsevier.)

platinum–ruthenium nanoparticles using hexachloroplatinic acid hexahydrate (H$_2$PtCl$_6$) with ruthenium (III) chloride hydrate (RuCl$_3$) as metal precursor (Zhang et al. 2010). In these two experiments, the solutions containing both a salt and the nanotubes with water/isopropanol and a suitable stabilizer were irradiated at a dose of 40 kGy.

The second method consists of generating nanoparticles separately from the nanotubes and, subsequently, modifying them with the appropriate functional groups for linkage to the CNTs' surface. These links can be such that either the functional groups create covalent bonds with the functional groups present on the CNT surface or they can simply get attached to the CNT surface through weak intermolecular interactions such as π–π stacking, hydrophobic attraction, or electrostatic attraction (Georgakilas et al. 2007). Using this method, gold nanoparticles, synthesized by the citrate method, have been attached to SWCNTs (Salah et al. 2009). In this second method, the nanoparticles, as well as the nanotubes, were irradiated separately in order to create active sites. Only later were they mixed together, producing the results shown in Figure 22.4d.

22.7 SUMMARY

CNTs decorated with metallic nanoparticles are currently being studied for a wide variety of applications. This arises from the fact that the properties of raw nanotubes are substantially modified with the addition of the nanoparticles. Different methods have been developed to synthesize metallic nanoparticles on CNTs, each one with their own advantages and disadvantages. Gamma irradiation has several advantages over others such as a fine control over the dose and dose rate. Additionally, the radicals that are created during the process are distributed homogeneously in the solution, they have a strong reducing potential, and there are no unwanted residues after the reaction. The overall control of the irradiation parameters, in combination with the right amount of both metal precursor and stabilizer, leads to a fine control of the nanoparticles' size. Gamma irradiation has also shown to have beneficial effects over both the electrical and mechanical properties of CNTs. It is also a potential technique that can be use as pretreatment for their further functionalization.

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[AQ1]   Please note that reference citations Makala et al. 2006, Sarkar et al. 2004, Strobel 2006, Zhu 1998, and Karousis et al. 2009 have been changed to Raghuveer et al. 2006, Sarkar and Banerjee 2004, Strobel et al. 2006, Zhu et al. 1998, and Karousis et al. 2008 as per reference list. Please check.

[AQ2]   Please note that Skakalova (2003) and (2004) are cited in the text but not provided in the reference list. Please check.

[AQ3]   Please check if "e-$_{aq}$, e-aq, and e-$_{aq}$" can be changed to "e_{aq}^{-}."

[AQ4]   Please note that both "gamma" and "γ" have been used in this chapter. Please check and make the reprsentation consistent.

[AQ5]   Please expand STEM.

[AQ6]   Please provide in-text citation for Rashidi et al. (2010) and Wang et al. (2006).

[AQ7]   Please provide publisher location for Remita and Remita (2010) and Wishart 2008.