

# Encapsulation of Palladium Nanoparticles by Multiwall Carbon Nanotubes-graft-Poly(citric acid) Hybrid Materials

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**ABSTRACT:** Citric acid was polymerized onto the surface of functionalized multiwall carbon nanotubes (MWCNT-COOH) and MWCNT-graft-poly(citric acid) (MWCNT-g-PCA) hybrid materials were obtained. Due to the grafted poly(citric acid) branches, MWCNT-g-PCA hybrid materials not only were soluble in water but also were able to trap water soluble metal ions. Reduction of trapped metal ions in the polymeric shell of MWCNT-g-PCA hybrid materials by reducing agents such as sodium borohydride led to encapsulated metal nanoparticles on the surface of MWCNT. Herein palladium nanoparticles were encapsulated and transported by MWCNT-g-PCA hybrid materials

(MWCNT-g-PCA-EPN) and their application as nanocatalyst toward Heck reaction in different conditions was investigated. The catalytic activity of palladium ions supported by MWCNT-g-PCA hybrid materials (MWCNT-g-PCA-PdCl<sub>2</sub>) toward Heck reactions is much more than for MWCNT-g-PCA-EPN. Structure, characteristics and catalytic activity of synthesized systems was investigated using spectroscopy and microscopy methods. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 2188–2196, 2010

**Key words:** Poly(citric acid); palladium nanoparticles; carbon nanotube; hybrid materials; nanocatalyst

## INTRODUCTION

Carbon nanotubes (CNTs) are arousing more and more interest from both scientists and engineers because of their unique electronic, mechanical, thermal, and chemical properties associated with their high aspect ratio and one-dimensional (1D) tubular structure (Refs. 1 and 2 and some reviews and books). Because of their unique structure and interesting properties such as large surface area, they are excellent carbonaceous materials for supporting metallic nanoparticles or promoters of catalysts for various chemical reactions.<sup>3</sup> However the surface of pristine CNTs has consisted of conjugated carbon-carbon bonds and is not expected to have a strong interaction with metal nanoparticles. Although functionalization of CNTs by acid is an effective way to increase their interaction with metal nanoparticles,<sup>4–6</sup> they are poor soluble materials with low processability. The most common way to increase the solubility and processability of CNTs is to attach large organic molecules such as polymers on their surface. Several strategies, based on “covalent attachment” and “noncovalent attachment” have been used to attach polymers onto the surface of CNTs.<sup>7–9</sup> Covalent

attachment of polymer chains to the surface of CNTs can be accomplished by either “grafting to” or “grafting from” approaches.

In “grafting to” approach, polymers are connected to functionalized CNTs through chemical reaction between their functional groups. The “grafting to” attachment is characterized by low grafting density because of the hindrance of the polymer chains which have reacted with CNTs.<sup>10</sup>

The “grafting from” approach involves the growth of polymers from the surface of CNTs by first covalently attaching of polymerization initiators and then exposing the nanotube-based macroinitiators to monomers. This approach results in the higher grafting density and control over the polymer growth with the possibility of designable structure.<sup>11–13</sup>

Conjugating of polymers which are able to support metal nanoparticles to CNTs not only improves their solubility and dispersability but lead to new hybrid nanostructures suitable for chemical catalysis. High surface area of CNT and several significant advantages of polymer-supported organotransition metal catalysts in synthetic and industrial chemistry such as the ease of separation of catalyst from the desired reaction products and the ease of recover and reuse of the catalyst, cause CNT grafted polymers (CNT-g-polymers) hybrid materials to be good candidates to support metal nanoparticles and use as catalytic systems toward chemical reactions such

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as Heck reaction.<sup>14,15</sup> Since the discovery of Heck reaction by Heck and Misoroki in the early 1970s, it has been widely used in organic synthesis.<sup>16</sup> This methodology has been found to be very versatile and applicable to a wide range of aryl species and a diverse range of olefine.<sup>17</sup> In this reaction usually aryl halides react with alkenes in the presence of palladium and a suitable base in a single step under mild conditions.<sup>18</sup> In fact, the choice of a suitable supporting material is an important factor that may affect performance Heck reaction.<sup>19</sup> Various polymer and dendrimer-supported and organic solid-supported (e.g. carbon, metal oxides, sol-gel, clays, and zeolites) metal catalysts for Heck cross-coupling reaction have been reported.<sup>20-23</sup> Surfactant-solubilized multiwall CNTs decorated with palladium nanoparticles and palladiums supported on single wall CNTs have showed very good catalytic activity toward carbon-carbon bond formation in Heck reactions.<sup>24</sup>

In this work, MWCNTs were opened and functionalized by acid (MWCNT-COOH) and citric acid was polymerized on their surface to produce MWCNT-g-PCA hybrid materials. Trapping and reducing of palladium ions by MWCNT-COOH and MWCNT-g-PCA hybrid materials was led to decorate MWCNT by palladium nanoparticles (MWCNT-DPN) and encapsulated palladium nanoparticles onto the surface of MWCNT-g-PCA hybrid materials (MWCNT-g-PCA-EPN) respectively. Catalytic activity of these systems toward Heck reaction was also investigated.

## EXPERIMENTAL SECTION

### Materials

The used MWCNT were prepared by chemical vapor deposition procedure in the presence of Co/Mo/MgO as catalyst at 900°C. The outer diameter of MWCNT was between 20 and 40 nm. MWCNT were washed by acid several times to improve their purity. Monohydrate citric acid, palladium chloride (PdCl<sub>2</sub>), ethyl acrylate, iodobenzene, bromobenzene, and triethyl amine were purchased from Merck.

### Characterization

Nuclear magnetic resonance (<sup>1</sup>H-NMR) spectra were recorded in CDCl<sub>3</sub> solution on a Bruker DRX 400 (400 MHz) apparatus with the solvent proton signal for reference. <sup>13</sup>C-NMR spectra were recorded on the same instrument using the solvent carbon signal as a reference. All polymer NMR spectra were recorded on 25 mg/mL of sample. Infrared spectroscopy (IR) measurements were performed using a Nicolet 320 FTIR. Transmission electron microscopy (TEM) analyzes were performed by a LEO 912AB electron microscope. Ultraviolet (UV) spectra were recorded

on a shimadzu (1650 PC) scanning spectrophotometer using H<sub>2</sub>O as solvent. Gas chromatography-mass spectroscopy (GC-MS) (Shimadzu+17A, Ver 3) (column: DB-5ms, control mode: split, injection: 260°C) was used to determine the yield of Heck reactions. Ultrasonic bath (Model: 5RS, 22 KHZ, Italy) was used to dispersed materials in solvents.

### Opening of MWCNTs

MWCNTs were opened according to reported procedures in literature.<sup>12</sup> Briefly, MWCNTs (2 g) were added to 40 mL of sulfuric and nitric acid mixture (3/1) in a reaction flask and refluxed for 24 h at 120°C. The mixture was cooled and diluted by distilled water and then it was filtrated. The product (MWCNT-COOH) was washed by distilled water and dried at 60°C for 3 h by vacuum oven.

### Preparation of MWCNT-g-PCA hybrid materials

MWCNT-COOH (0.05 g) was added to a polymerization ampule equipped with magnetic stirrer and vacuum inlet. Monohydrate citric acid (2.5 g) was also added to ampule and it was sealed under vacuum. The mixture was heated up to 120°C and stirred in this temperature for 30 min. Produced water was removed by opening the vacuum inlet and temperature of reaction was raised to 140°C. The vacuum inlet was closed and mixture was stirred at this temperature for 1 h. Then produced water was removed by opening the vacuum inlet and temperature of reaction was raised to 160°C. Polymerization was continued in this temperature under dynamic vacuum (open vacuum inlet) for 1.5 h. The mixture was cooled and dissolved in tetrahydrofuran (THF) and product was precipitated in cyclohexane. Purified product was obtained as a viscous brown compound in 85% yield.

### Preparation of MWCNT-DPN

MWCNT-COOH was obtained according to reported procedures in literature.<sup>12</sup> Complexation and reduction of palladium ions by MWCNT-COOH was led to MWCNT-DPN.

Typically, MWNT-COOH (0.8 mg) and palladium chloride (1 mg) were added to distilled water (20 mL) and mixture was stirred at room temperature for 24 h. Then 5 mL of aqueous solution of NaBH<sub>4</sub> (0.01M) was added to 15 mL of the mixture dropwise at room temperature over 20 min and it was stirred in ultrasonic bath (22 KHZ) at room temperature for 15 min. Mixture was filtered and washed by distilled water and product was dried by vacuum oven at 70°C for 3 h. Purified product was obtained as a solid black compound in 45% yield.

### Preparation of MWCNT-g-PCA-EPN

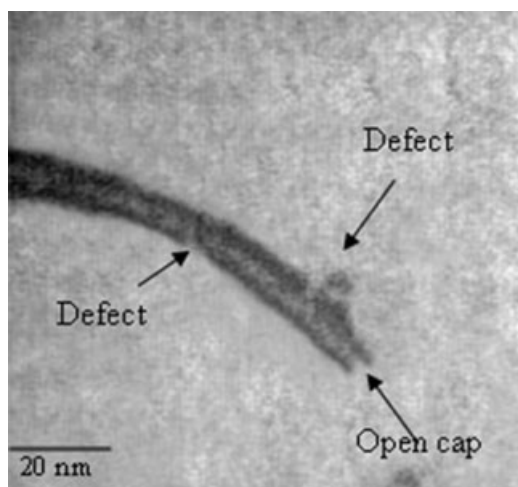
Water solutions of PdCl<sub>2</sub> (0.26 g in 3 mL) and MWCNT-g-PCA (0.2 g in 10 mL) were mixed and placed in an ultrasonic bath (22 KHz) for 20 min to well disperse metal ions in the polymeric shell of hybrid material. Mixture was stirred at room temperature for 8 h and reduction was accomplished by addition 0.08 mL of aqueous solution of NaBH<sub>4</sub> (0.01M) to it and stirring at room temperature for 1 h. Water was evaporated by vacuum oven and residue was dissolved in THF and precipitated in cyclohexane. Product as an amorphous black compound, in 53% yield, was dried by vacuum oven at 60°C for 2 h.

### General procedure for the catalytic tests

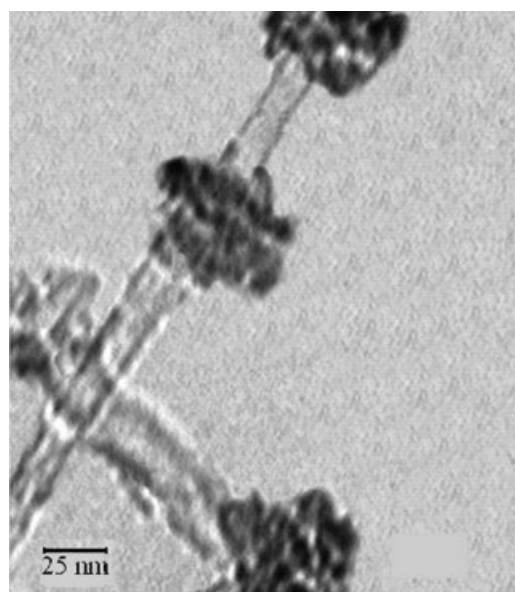
The cross-coupling of ethyl acrylate with iodobenzene or bromobenzene catalyzed by supported palladium ions and nanoparticles was accomplished in different conditions. Typically, a solution of catalyst (0.3 mL), triethylamine (1 mL), ethyl acrylate (0.6 mL) and iodobenzene or bromobenzene (0.6 mL) were added to 20 mL of *N,N*-dimethyl formamide (DMF) and mixture was refluxed at 106°C for 24 h. Samples in interval times were withdrawn, filtrated and injected in the GC-Mass column to evaluate the products and reaction yield.

## RESULTS AND DISCUSSION

The novel functionalized MWCNT structures were found to have remarkable catalytic effects when used as support. Since the surface of MWCNTs itself is rather inert and there is not any functional group, it is difficult to deposit metal nanoparticles and control the homogeneity of metal deposition on their surface by conventional methods. Functionalization



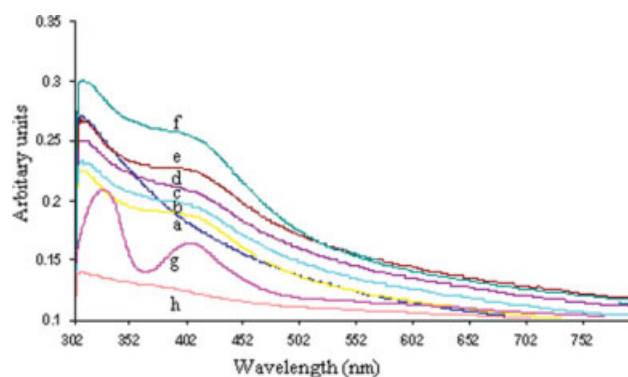
**Figure 1** TEM image of opened MWCNT by acid treatment.



**Figure 2** TEM image of a MWCNT-EPN.

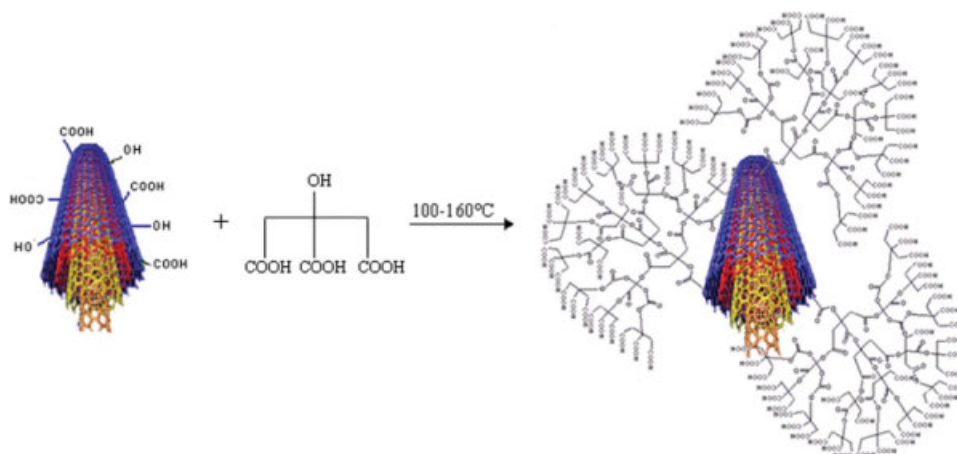
of the surface of MWCNTs can be realized by chemical oxidation treatment using different reagents such as HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> mixture. It is found that the oxygen-containing functional groups play an important role in anchoring metal nanoparticles on the walls of MWCNTs.

In this work MWCNTs were treatment with HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> mixture to produce hydroxyl and carboxyl functional groups on their surface (MWCNT-COOH). Figure 1 shows the TEM image of MWCNT-COOH. The tip of MWCNT is opened and defects can be seen on its surface where the —COOH and —OH functional groups are generated. These surface functional groups provide active sites to interact with metal ions. Due to the presence of hydroxyl functional groups on the surface of MWCNT-COOH, it was used to anchor palladium



**Figure 3** Representative adsorption profile for PdCl<sub>2</sub> on opened MWCNT-COOH, (a) fresh solution of MWCNT-COOH, (b) 5 min, (c) 15 min, (d) 1 h, (e) 5 h, (f) 24 h, (g) PdCl<sub>2</sub> solution, (h) Reduced solution. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]





**Scheme 1** Synthesis route of MWCNT-DPN. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

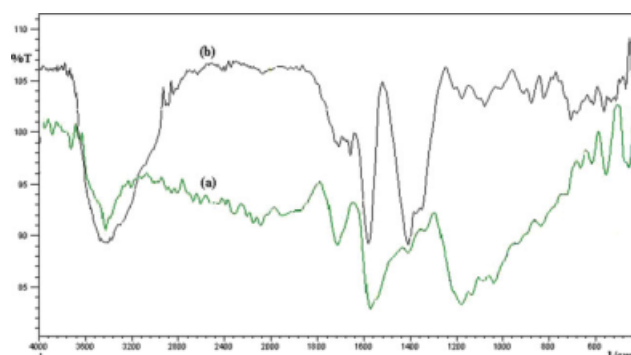
ions (MWCNT-COOH-PdCl<sub>2</sub>) and support palladium nanoparticles (MWCNT-DPN).

Figure 2 shows the TEM image of a MWCNT-DPN in which palladium nanoparticles are deposited on the surface of MWCNT-COOH in some special places where functional groups are generated (tips and defects). This result confirms the role of functional groups in anchoring and deposition of metal nanoparticles. The size of deposited nanoparticles was estimated to be below 10 nm. Deposition of palladium nanoparticles on the surface of MWCNT-COOH was evaluated by UV-vis experiments. Figure 3 shows a representative absorption profile for PdCl<sub>2</sub> on MWCNT-COOH. A ligand to metal charge transfer peak between 360–450 nm on addition of PdCl<sub>2</sub> to MWCNT-COOH was appeared. The intensity of the peak is seen to be increased consistently as a function of time indicating an increase in the concentration of anchored palladium ions on the surface MWCNT-COOH. According to UV experiments the total concentration of absorbed palladium ions on the surface of MWCNT-COOH was 25 wt %.

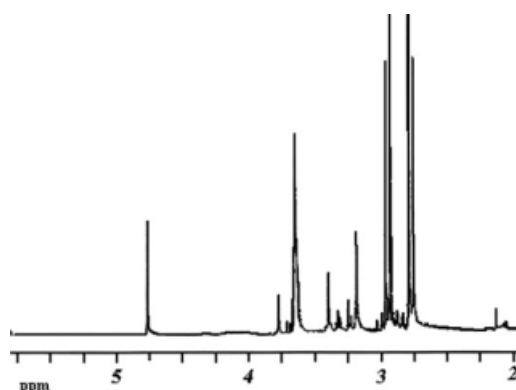
Citric acid is a cheap and available compound which has been used to produce, disperse and stabilize metal nanoparticles abundantly. Conjugation of citric acid to the surface of MWCNTs not only improve their solubility in aqueous and organic solvents but also develop their interactions with metal ions.

Scheme 1 shows the polycondensation of citric acid on the surface of functionalized MWCNT. In this reaction the stepwise raising of temperature is important, because citric acid decomposes in its melting point and the mixture should be heated step by step to avoid decomposition of citric acid.

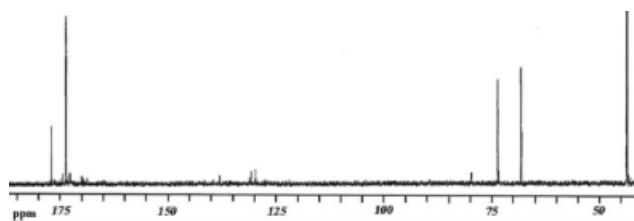
Figure 4(a) shows the IR spectra of MWCNT-COOH. In this figure, the absorbance band of acidic and alcoholic hydroxyl functional groups are appeared at 3600–3200 cm<sup>-1</sup>. The absorbance band at 1700 cm<sup>-1</sup> is assigned to the carbonyl groups and two absorbance bands at 1590 and 1400 cm<sup>-1</sup> are related to the C=C aromatic bonds of MWCNT. Figure 4(b) shows the IR spectra of MWCNT-g-PCA hybrid materials in which a broad absorbance band at 3620–2700 cm<sup>-1</sup> is appeared for hydroxyl functional groups of grafted PCA. In these spectra two absorbance bands of carbonyl groups of citric acid



**Figure 4** IR spectra of MWCNT-g-PCA. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 5** <sup>1</sup>H-NMR spectra of MWCNT-g-PCA in D<sub>2</sub>O.

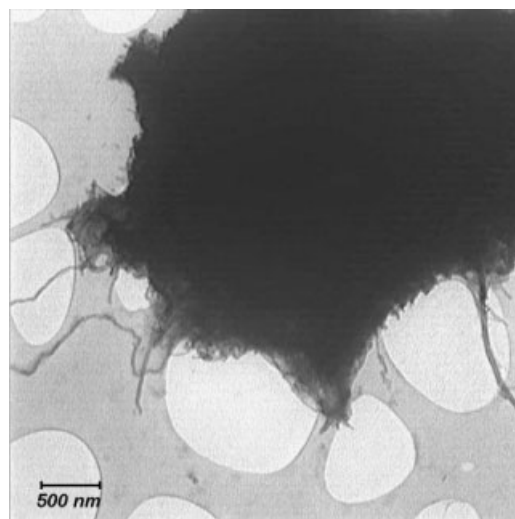


**Figure 6**  $^{13}\text{C}$ -NMR spectra of MWCNT-g-PCA in  $\text{D}_2\text{O}$ .

are appeared at  $1730$  and  $1660\text{ cm}^{-1}$ . The absorbance band of  $\text{C}=\text{C}$  bonds is appeared at  $1590\text{ cm}^{-1}$ .

The structure of MWCNT-g-PCA hybrid materials was further evaluated using NMR spectroscopy. Figure 5 shows the  $^1\text{H}$ -NMR spectra of MWCNT-g-PCA hybrid materials in which two signals at 4.8 and 3.5 ppm are assigned to the hydroxyl functional groups of PCA, because they disappeared on addition  $\text{D}_2\text{O}$ . In this figure two AB systems can be recognized for methylene groups of citric acid building blocks. An AB system at 3.3–3.1 ppm is related to the citric acids units in the backbone of PCA and another 2.8–2.9 ppm is related to the citric acid units in the surface of polymer shell. Figure 6 shows the  $^{13}\text{C}$ -NMR spectra of MWCNT-g-PCA hybrid materials in which signals of carbonyl groups at 177–173 ppm can be seen clearly. In this spectra, weak signals for  $\text{C}=\text{C}$  bonds can be seen at 143–129 ppm and signals of citric acid are appeared at 74, 68, and 48 ppm.

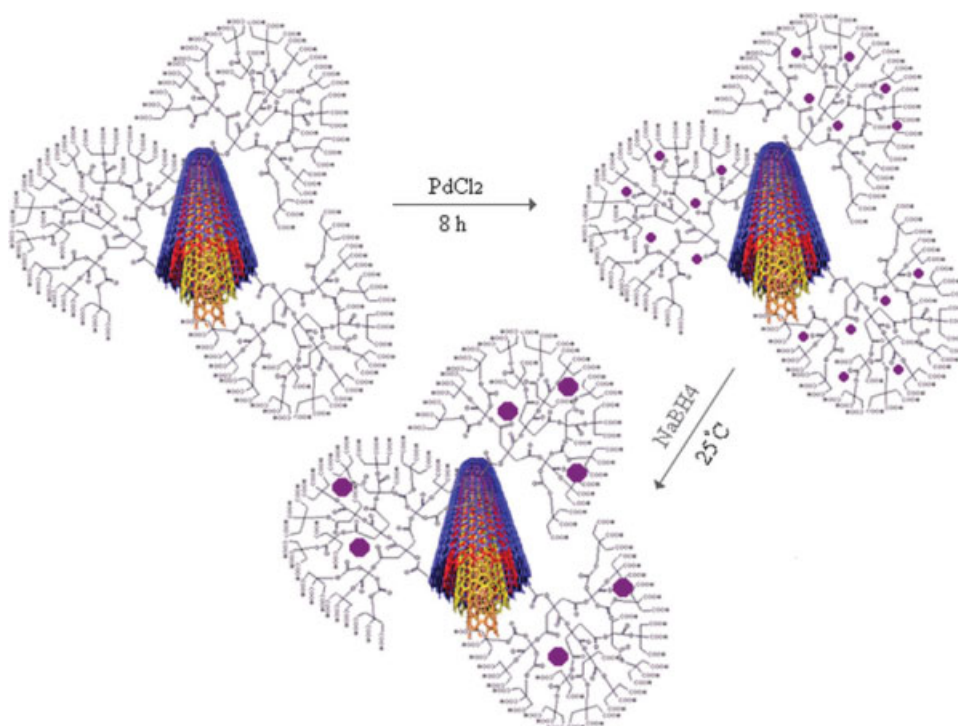
TEM experiments were performed to evaluate the structure and morphology of MWCNT-g-PCA



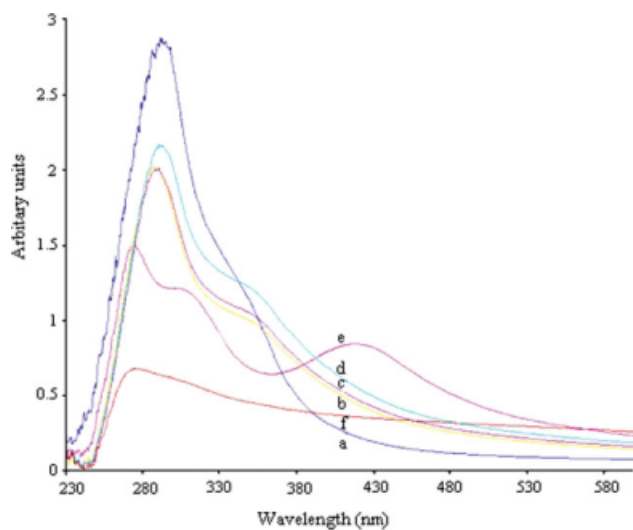
**Figure 7** TEM image of MWCNT-g-PCA hybrid materials.

hybrid materials. Based on this experiments MWCNTs are held by PCA shell (Fig. 7), hence polymeric shell dominate the chemistry of MWCNTs. For example due to the presence of numerous carboxyl functional groups on the surface of MWCNT-g-PCA hybrid materials, they were able to anchor, support and transport palladium nanoparticles.

Encapsulation of palladium nanoparticles by polymeric shell of MWCNT-g-PCA hybrid materials was achieved through reduction of MWCNT-g-PCA-



**Scheme 2** Synthesis route of MWCNT-g-PCA-EPN. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

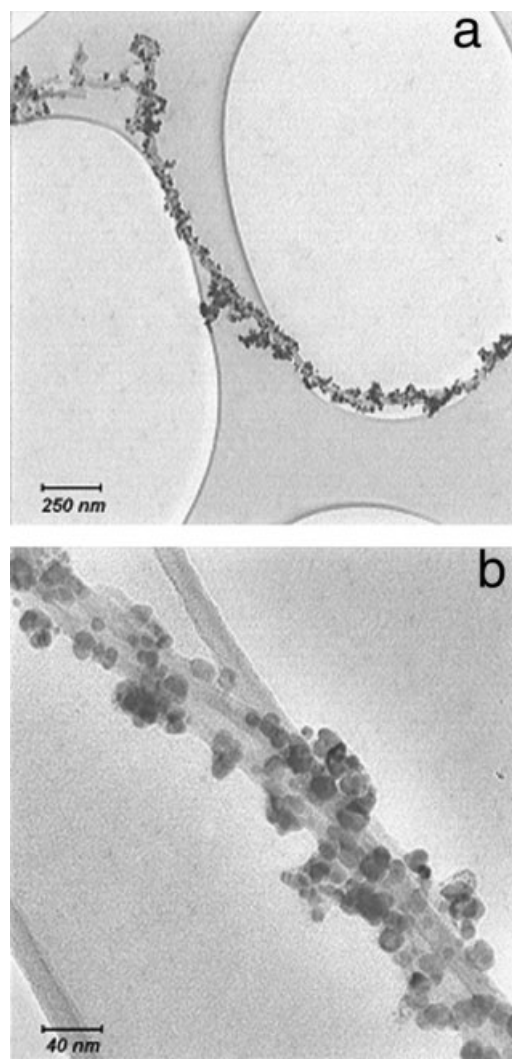


**Figure 8** UV spectra of dilute aqueous solution of (a) fresh solution of MWNTs-g-PCA and MWCNTs-g-PCA+PdCl<sub>2</sub> after (b) 30 min, (c) 1 h, (d) 2 h, (e) PdCl<sub>2</sub> solution, (f) Reduced solution. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

PdCl<sub>2</sub> hybrid materials by NaBH<sub>4</sub> (Scheme 2). Due to the complexation of Pd<sup>2+</sup> by poly(citric acid) shell, the intensity of absorption peak of palladium chloride at 420 nm, in UV-vis, was decreased over addition a water solution of MWCNT-g-PCA to a water solution of PdCl<sub>2</sub>. However an absorption peak for ligand to metal charge transfer (LMCT) at 360 nm was appeared and its intensity increased over the time (Fig. 8).

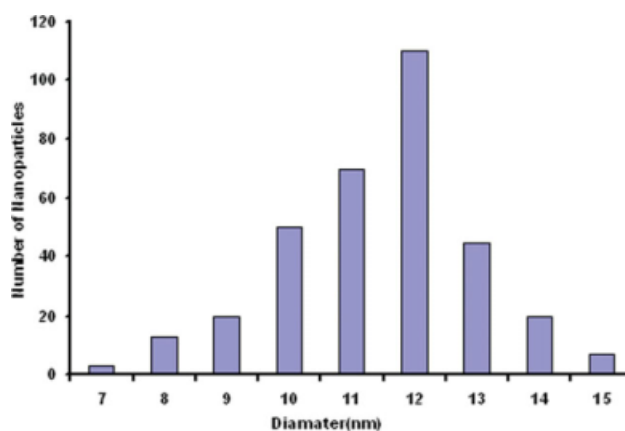
Based on TEM experiments it was found that palladium nanoparticles were uniformly dispersed on the surface of MWCNTs [Fig. 9(a)]. This is due to existence of a large number of oxygen-containing groups, as anchoring sites, on the surface of MWCNT. Figure 9(b) shows the TEM image of MWCNT-g-PCA-EPN in which palladium nanoparticles are encapsulated in the PCA branches of the MWCNT-g-PCA. Figure 10 shows the size distribution of encapsulated palladium nanoparticles in the polymeric shell of MWCNT-g-PCA. We found that the main average size is around 10–12 nm and the size distribution is relatively narrow. Because of the multifunctionality of opened MWCNTs and citric acid, intra- and intercrosslinking can occur during polycondensation. Figure 11(a) shows crosslinking of different parts of a MWCNT (intracrosslinking) and formation of cyclic hybrid materials. Here different parts of a single MWCNT are conjugated together through citric acid as a crosslinker.

Figure 11(b) display the crosslinking of two different MWCNTs. In these figure functional groups of two different MWCNTs are conjugated together by citric acid as an intermediate.



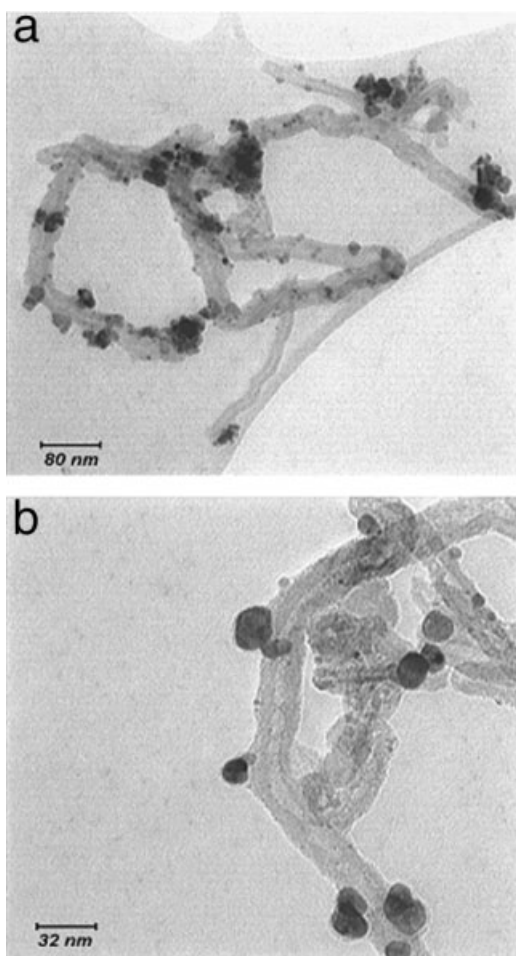
**Figure 9** TEM images of MWCNT-g-PCA-EPN.

According to TEM experiments it was found that some of palladium nanoparticles are encapsulated by the cavity of MWCNT-g-PCA hybrid materials.



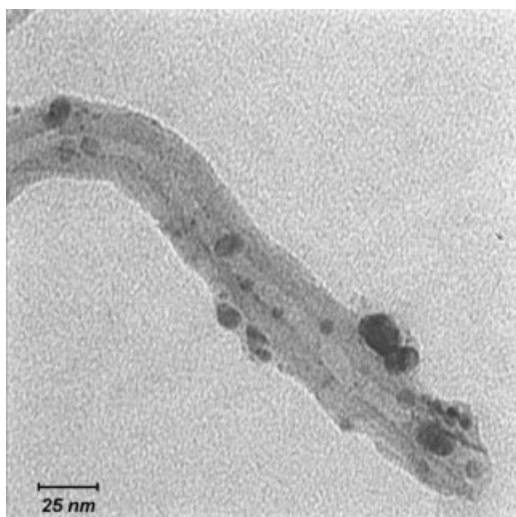
**Figure 10** The size distribution of encapsulated palladium nanoparticles. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



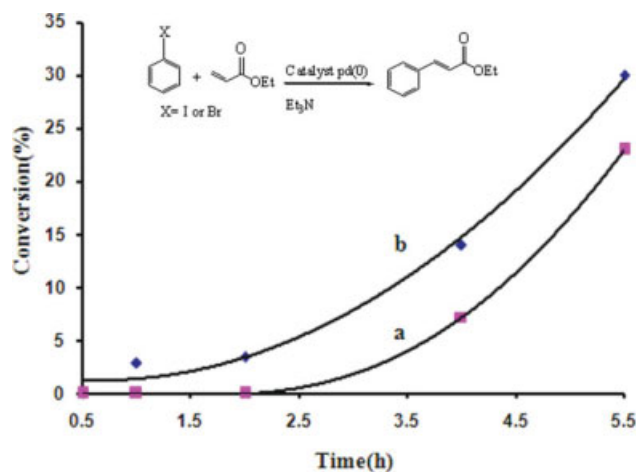


**Figure 11** (a) Intra- and (b) intercrosslinking of MWCNTs.

The reason for this observation is the high solubility of MWCNT-g-PCA hybrid materials in water, which causes an extended conformation for MWCNT-g-PCA hybrid materials and a possibility to intro-



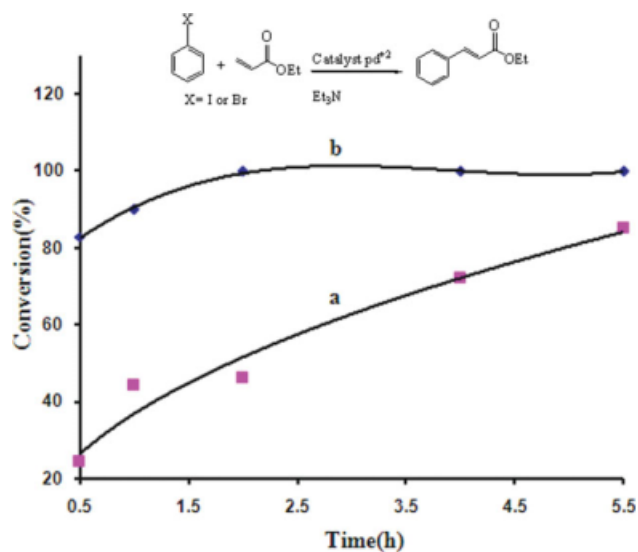
**Figure 12** TEM image of MWCNT-g-PCA-EPN.



**Figure 13** Product yield for Heck reaction in presence MWCNT-g-PCA-EPN as catalysts at (a) 106°C, (b) 120°C. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

duce palladium nanoparticles inside the cavity of MWCNT (Fig. 12).

MWCNT-COOH-PdCl<sub>2</sub>, MWCNT-DPN, MWCNT-g-PCA-PdCl<sub>2</sub> and MWCNT-g-PCA-EPN systems were used to catalyze Heck coupling of iodobenzene and bromobenzene with ethyl acrylate in water and DMF solvents. No catalytic activity was observed for MWCNT-COOH-PdCl<sub>2</sub> and MWCNT-DPN at 106°C and 120°C in both water and DMF solvents whereas MWCNT-g-PCA-PdCl<sub>2</sub> and MWCNT-g-PCA-EPN systems were able to catalyze this reaction in DMF. Figures 13 and 14 show the conversion of these reactions versus time at 106 and 120°C respectively. According to these results the rate of reaction



**Figure 14** Product yield for Heck reaction in presence MWCNT-g-PCA-PdCl<sub>2</sub> as catalysts at (a) 106°C, (b) 120°C. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

catalyzed by MWCNT-g-PCA-PdCl<sub>2</sub> is much higher than that of MWCNT-g-PCA-EPN. For MWCNT-g-PCA-PdCl<sub>2</sub> conversation at 106°C after 4 h was 72% whereas for MWCNT-g-PCA-EPN it was 7%. In the same time but at 120°C the yields of reaction for MWCNT-g-PCA-PdCl<sub>2</sub> and MWCNT-g-PCA-EPN were 100% and 14% respectively.

A study to evaluate the influence of solvents on the Heck reactions catalyzed by our systems suggested that DMF is the best solvent in this case.

Heck reactions using homogeneous and heterogeneous palladium catalysts have widely been studied and several informative reviews describing the state of the art along with the reaction mechanism are available.<sup>25,26</sup> It is important to know the influence of various reaction parameters on the reaction rate. In this work the kinetic for Heck coupling between iodobenzene and ethyl acrylate in the presence of triethylamine as a base for homogenous and heterogeneous systems in DMF solvent were studied.

The reaction rate constant  $k$  is expressed by the Arrhenius equation:<sup>27</sup>

$$K = A \exp(-E_a/RT)$$

where  $k$  is the rate constant in the rate law,  $A$  is a constant for the reaction at all temperatures and concentrations,  $E_a$  is the activation energy,  $R$  is the universal gas constant,  $T$  is the temperature of the reaction in Kelvin.

Experimentally, we need to focus on the effect of  $E_a$  on the rate constant. Since  $E_a$  is mathematically tied to  $T$  (reaction temperature), Heck reactions were performed at 106 and 120°C temperatures and rate constants were calculated using below equation.

$$\frac{1}{a[A]_0 - b[B]_0} \ln \frac{[A]}{[A]_0} = Kt$$

$\ln(\text{Rate})$  as  $y$  (The vertical coordinate on the graph) was plotted versus  $(1/T)$  as  $x$  (the horizontal coordinate on the graph) and  $-E_a/R$  as slope was obtained.

$$y = b + (\text{slope})x$$

$$\text{where : } y = \ln(\text{Rate})$$

$$x = 1/T$$

$$\text{Slope} = -E_a/R$$

Activation energy was found to be 4 and 10 J/mol for MWCNT-g-PCA-PdCl<sub>2</sub> and MWCNT-g-PCA-EPN catalysts respectively. According to these

results the rate of reaction catalyzed by MWCNT-g-PCA-PdCl<sub>2</sub> is higher than that for MWCNT-g-PCA-EPN. It seems in the MWCNT-g-PCA-PdCl<sub>2</sub> system, palladium ions are only complexed by functional groups on the surface of MWCNT and they are accessible in atomic scale while in MWCNT-g-PCA-EPN palladium ions are reduced to elemental palladium and some of palladium atoms are not accessible.

However these systems are comparable or in some cases better than reported other systems in literatures.<sup>24,28</sup>

## CONCLUSIONS

Citric acid is a nontoxic, cheap and polyfunctional molecule, which is soluble in aqueous and some of polar organic solvents. Due to its high functionality and water solubility it has been used as capping agent to produce nanoparticles copiously. Hence polycondensation of citric acid on the surface of MWCNT leads to water soluble hybrid materials which are able to stabilize and encapsulate metal nanoparticles. According to TEM images the transport capacity of MWCNT-g-PCA hybrid materials is high. CNTs containing palladium ions and nanoparticles show a high catalytic activity toward Heck reactions, but the catalytic activity of supported palladium ions is much higher than that for supported palladium nanoparticles.

Hybrid materials consisting of CNTs, poly(citric acid) shell and metal nanoparticles are multidisciplinary materials with interesting properties which can be used in different fields ranging from catalysis to nanomedicine.

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