



# Synthesis, characterization, and catalytic activity for hybrids of multi-walled carbon nanotube and amphiphilic poly(propyleneimine) dendrimer immobilized with silver and palladium nanoparticle

E. Murugan\*, G. Vimala

Department of Physical Chemistry, School of Chemical Sciences, University of Madras, Maraimalai Campus, Guindy, Chennai 600 025, Tamil Nadu, India

## ARTICLE INFO

### Article history:

Received 29 October 2012

Accepted 26 December 2012

Available online 30 January 2013

### Keywords:

Multi-walled carbon nanotubes based nanohybrid catalysts

Amphiphilic poly(propyleneimine) dendrimers

Silver nanoparticles

Palladium nanoparticles

4-Nitrophenol reduction

## ABSTRACT

Four types of new multi-walled carbon nanotube (MWCNT) based nanohybrid catalysts were prepared through simple methods. Initially, MWCNT was functionalized with carboxyl group and subsequently bonded with amphiphilic poly(propyleneimine) dendrimer (APPI) having generation (G2) and (G3). They are abbreviated as MWCNT–APPI (G2) and MWCNT–APPI (G3). Silver nanoparticles (AgNPs) and palladium nanoparticles (PdNPs) were separately immobilized to each hybrid to obtain four types of MWCNT based nanohybrid catalysts. The pseudo-first order rate constants for reduction of 4-nitrophenol revealed that among the four types of MWCNT nanohybrid catalysts, MWCNT–APPI (G3)–PdNPs was more efficient than the other catalysts with five-fold higher efficiency than the homogeneous PPI (G3)–PdNPs. For the same reaction with MWCNTs–APPI (G3)–PdNPs catalyst, the variation of [catalyst] and [NaBH<sub>4</sub>] was directly proportional to  $k_{obs}$ . The study of reusability of MWCNT–APPI (G3)–PdNPs proved no loss in activity even after recycling the catalyst for five times.

© 2013 Elsevier Inc. All rights reserved.

## 1. Introduction

Carbon nanotubes (CNTs) have attracted a lot of interest since their discovery in 1991 due to their unique structural, mechanical, and electronic properties. In the catalytic field, CNT have received extensive attention since they represent a novel class of advanced materials for catalytic applications [1–4]. Compared to different support materials like polymers, dendrimers, ionic liquids, and surfactants for the preparation of heterogeneous catalysts CNT are advantageous in some catalytic reactions [5–8]. For the use of nanotubes in many applications, there is a need to introduce different functional groups to CNT, specifically onto the surface of CNT. For instance, the attachment of organic molecules to CNT improves its solubility and brings extensive applicability in prominent fields like biomedicine and catalysis [9–12]. The highly branched 3-dimensional macromolecules like “dendrimers (DEN)” [13–17] can also be grafted to CNT and thus exploited different studies. Especially, DEN grafted MWCNT hybrids are considered to be prominent supports for the preparation of heterogeneous catalyst. Similarly, zero-dimensional metal nanoparticles (MNPs) have also been attracting considerable attention of chemists, physical scientists, engineers, and even biologists due to their unique photonic,

electronic, magnetic, biologic, and catalytic properties, which are recognized to be dependent strongly on their sizes and shapes. As a result, size-control of NPs is always of special interest and a handful of organic molecules has been adopted as protectors or stabilizers to control the sizes of MNPs [18–21].

Recently, it has been realized that the integration of CNT with MNPs can generate a new family of novel materials with more advanced properties and applications than the pristine precursors. As a result, hybrid materials of CNT with MNPs have attracted greater attention due to their promising applications in electronics, catalysts, and biosensors [22–25]. Although CNT supported metal nanoparticles exhibit greater catalytic efficiency than their bulk counterparts, because of high surface-to-volume ratio, there are some difficulties in dispersing metal nanoparticles on the surface of pristine CNT due to their hydrophobic nature as well as their tendency for agglomeration. In order to overcome these problems and to favor a high loading of nanoparticles, grafting well-defined polymers known as dendrimers can act as macromolecular coupling agents carrying multiple binding sites [26–37]. The continuous demand has strived the researchers/industrialist to prepare new heterogeneous nanoparticle catalysts with the property for easy recovery and recycling. Mainly, nanometer-scale silver (Ag) NPs have attracted extensive attention due to their potential utility in electrocatalysis, chemical sensors, catalysis, and optical devices [38–40]. Similarly, nanoscale palladium (Pd) NPs have drawn particular attention due to their catalytic and electronic

\* Corresponding author. Fax: +91 44 22300488.

E-mail addresses: [dr.e.murugan@gmail.com](mailto:dr.e.murugan@gmail.com), [dr.e.murugan@unom.ac.in](mailto:dr.e.murugan@unom.ac.in) (E. Murugan).

properties. The use of PdNPs in automobile catalytic converters, various hydrogenation reactions, and Suzuki coupling reactions is well studied [41–47].

4-Nitrophenol (4-NP) is one of the most important refractory pollutants that can occur in industrial and agricultural wastewaters. In order to eliminate this pollutant, the concerned waste water has been treated with different catalysts and converted 4-NP into 4-aminophenol and thus used as a precursor for the manufacture of many analgesic and antipyretic drugs such as paracetamol, phenacetin, and acetanilide. It is also used as a potential intermediate in pharma industry and finds applications in photographic developer, anti-corrosion lubricant inhibitor, corrosion inhibitor, hair-dyeing agent, etc. Therefore, due to the wider applications of 4-aminophenol, there is always a greater demand for the direct catalytic hydrogenation of 4-NP. The conventional method for catalytic hydrogenation of 4-NP involves use of iron/acid as a reducing agent at high temperature and pressure and hence this technique bears a lot of inconvenience. However, other metallic reagents containing Zn, Al, and Sn have leads to produce the undesirable metal oxides [48–50]. In view of these backgrounds, there is a need for an alternative, effective, and eco-friendly method for the reduction of 4-NP.

In our previous study [51], we developed new nanohybrids viz., MWCNT functionalized with amphiphilic poly(propyleneimine) (APPI) dendrimer carrying silver nanoparticles (AgNPs) and demonstrated high dispersability and antimicrobial activity. We also developed an amphiphilic MWCNT polymer hybrid with improved conductivity and dispersability produced by functionalization with poly(vinylbenzyl)triethylammoniumchloride [52]. Though different researchers have developed different heterogeneous nanoparticle catalysts using dendrimers and CNT immobilized with various metal NPs, none of them developed MWCNT nanohybrids through effective functionalization of MWCNTs with generation 2 and 3 (G2)/(G3) derived APPI dendrimers decorated with different MNPs. Therefore, in the present study, we reported a novel MWCNT–APPI (G2)–AgNPs, MWCNT–APPI (G3)–AgNPs, MWCNT–APPI (G2)–PdNPs, MWCNT–APPI (G3)–PdNPs nanohybrid catalysts, and their effective catalysis for the reduction of 4-nitrophenol (4-NP).

## 2. Experimental

### 2.1. Materials

MWCNT with purity higher than 95% was obtained from Sigma–Aldrich. The diameter of MWCNT was 110 nm and length 70–80  $\mu\text{m}$ . Potassium permanganate ( $\text{KMnO}_4$ , Merck), methylene chloride ( $\text{CH}_2\text{Cl}_2$ , Merck), tetrabutylammoniumchloride (TBAB, Alfa aesar), acetic acid ( $\text{CH}_3\text{COOH}$ , 99.8%, Merck), poly(propyleneimine) dendrimer (PPI G2 and G3, Symo-chem, Netherland), N,N'-dicyclohexylcarbodiimide (DCC, Aldrich), 2-chloroethylisocyanate (Alfa Aesar), N,N-dimethyl acetamide (Alfa Aesar), dimethyldodecylamine (SRL), toluene (SRL), acetone (Merck), silver nitrate ( $\text{AgNO}_3$ , Merck), palladium acetate ( $\text{Pd}(\text{OAc})_2$ , Merck), methanol ( $\text{CH}_3\text{OH}$ , Merck), 4-NP (Merck), and sodiumborohydride ( $\text{NaBH}_4$ , Merck) were analar grade (99% purity) and used as received.

### 2.2. Synthesis

#### 2.2.1. Functionalization of MWCNT

Pristine MWCNT (200 mg) and 15 ml  $\text{CH}_2\text{Cl}_2$  were taken in a 100 ml round-bottomed flask, and the mixture was dispersed in ultrasonicator (Cole Parmer) for 10 min. Then, 0.25 g of TBAB in 5 ml  $\text{H}_2\text{O}$ , 5 ml acetic acid, and 0.065 g  $\text{KMnO}_4$  in 5 ml  $\text{H}_2\text{O}$  were mixed together, and the resulting solution was added to the flask

[52]. Then, the resulting mixture was stirred vigorously at 25 °C for 48 h. Then, it was diluted with 1000 ml of deionized water, and the resulting product was filtered under vacuum by 0.2 m Teflon membrane. The dispersion, washing, and centrifugation of resulting functionalized materials were performed continuously until the pH of the filtrate showed 7 (at least 10 cycles were required). The resulting filtrate was dried in vacuum and thus obtained 0.198 g of functionalized MWCNT (MWCNT–COOH).

#### 2.2.2. Synthesis of MWCNT–APPI (G2) and MWCNT–APPI (G3)

The obtained MWCNT–COOH was further functionalized with PPI (G2) and PPI (G3) dendrimer individually. That is, in two different 100 ml RB flasks, 60 mg of MWCNT–COOH was taken and then 50 mg of PPI (G2) and 50 mg of PPI (G3) were added to the respective container. Subsequently, 0.96 g (8 equiv) of DCC was added in the respective flasks and then refluxed for 48 h under nitrogen atmosphere. It yielded the corresponding condensed products viz., MWCNT–PPI (G2) and MWCNT–PPI (G3) hybrids with yield having 0.07 g and 0.073 g, respectively. Further, to generate amphiphilic character, 50 mg of resulting MWCNT–PPI (G2) and MWCNT–PPI (G3) hybrids was taken in 100 ml RB flask individually and treated with 20 ml of anhydrous toluene, 14 ml of anhydrous N,N-dimethylacetamide and  $7.79 \times 10^{-2}$  g of 2-chloroethylisocyanate were added drop wise to each container and stirred both the mixtures for 24 h at room temperature, and they yielded the corresponding chlorinated product of MWCNT–PPI (G2) and MWCNT–PPI (G3). These two different chlorinated products was again quaternized by reacting with 1.52 g ( $6.87 \times 10^{-3}$  mol) of dimethyldodecylamine, 5 ml of N,N-dimethylacetamide, and 5 ml of toluene separately at 80 °C for 72 h in oil bath. The resulting product in the respective mixture was filtered and washed with acetone and dried in vacuum at 60 °C and thus obtained APPI functionalized black colored solid MWCNT nanohybrids viz., MWCNT–APPI (G2) (**7**) and MWCNT–APPI (G3) (**8**) [51] (Scheme 1).

#### 2.2.3. Preparation of four types of MWCNT–APPI (G2) and (G3) derived nanohybrid catalysts

Fifty milligrams of MWCNT–APPI (G2) (**7**) and 50 mg of MWCNT–APPI (G3) (**8**) were dispersed in 10 ml of deionized water separately in 100 ml round-bottomed flask using Cole parmer ultrasonicator for 10 min. Further, 10 ml of silver nitrate aqueous solution (0.1 M) was added drop wise to each flask. The respective solution mixture was then refluxed and stirred magnetically for 30 min. It was then centrifuged and the residue was thoroughly washed with deionized water. The as-produced blackish filtrate was dried in vacuum at 60 °C to obtain the corresponding catalysts viz., MWCNT–APPI (G2)–AgNPs (**9**) and MWCNT–APPI (G3)–AgNPs (**10**) (Scheme 2).

Similarly, 50 mg of MWCNT–APPI (G2) (**7**) and 50 mg of MWCNT–APPI (G3) (**8**) were dispersed in 10 ml of deionized water separately in 100 ml RB flasks using Cole parmer ultrasonicator for 10 min. 10 ml of palladium acetate in methanol (0.1 M) was added drop wise into each container and then stirred magnetically for 1 h at 25 °C. Subsequently, 0.1 ml of sodium borohydride (0.1 M) was added to each container and stirred again for 30 min. The resulting solution was centrifuged to obtain blackish filtrates. These filtrates were dried in vacuum at 60 °C and thus obtained two types of catalysts viz., MWCNT–APPI (G2)–PdNPs (**11**) and MWCNT–APPI (G3)–PdNPs (**12**) (Scheme 2).

### 2.3. Characterization

Fourier transform infrared (FTIR) spectra were recorded on a Bruker Tensor-27 FTIR spectrophotometer with OPUS software and the sample for analysis was prepared by taking equal amounts of each sample and KBr (1:1 ratio), and the corresponding pellet

Download English Version:

<https://daneshyari.com/en/article/7000118>

Download Persian Version:

<https://daneshyari.com/article/7000118>

[Daneshyari.com](https://daneshyari.com)