Synthesis of decorated carbon nanotubes with Fe₃O₄ and Au nanoparticles and their application in catalytic oxidation of alcohols in water

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1. Introduction

Hybrid composite materials, incorporating metal and metal oxide nanoparticles, have attracted much attention due to their uses in photonic crystal, surface-enhanced Raman scattering and plasmon resonance [1–5]. Amongst the various materials that are used for the fabrication of metal nanoparticles, carbon nanotubes have attracted much attention [6–8]. Carbon nanotubes are sheets of six-membered carbon atom rings rolled up into cylinders which one layer are known as single-walled CNTs (SWCNTs) and with two-walls CNTs (DWCNTs) and more layers are known as multi-walled CNTs (MWCNTs). MWCNTs is one of the most used carbon nanostructures due to its easy availability, affordable price, chemical inertness and ability to be functionalized easily. More significantly, MWCNTs have large surface area with high reactivity which can be covalently modified with functional groups such as thiols, phosphines, carboxylic acids and amines that results in their ability to be decorated with metal nanoparticles [9,10]. Magnetic nanoparticles (MNPs) have attracted much attention due to their uses in immobilization of cells and enzymes, magnetic resonance imaging and therapeutical agents for the diagnosis of many diseases, gene and drug delivery [11–15]. The magnetic properties of MNPs allow the remote control of their accumulation by means of an external magnetic field and coupling with drugs, poroteins and nucleic acids, in combination with an external magnetic field to target the nanoparticles has additionally emerged as a promising strategy of delivery [23].

Gold nanoparticles have been in focus of both academic and industrial research in the past few decades due to their unique properties in various fields ranging from catalysis, electrocatalysis and optical kits for cancer therapy and drug delivery [16–22]. The fabrication of gold nanoparticles on colloidal carbon nanotubes can be achieved in a number of various methods such as electrodeposition, chemical decoration π–π stacking, sonochrome, wet impregnation and other means which a chemical reduction is most commonly and convenient [24–26].

In contrast to the widely studied gold nanoparticles coated on various functionalized materials [27], relatively few papers have been reported on the preparation of controlled size of nano gold particles on simple functionalized carbon nanotubes [28–30], although there is evidence that these nanocomposites are applicable in oxidation reaction of alcohols [31–33]. Pratia and co-
workers reported liquid phase oxidation of alcohols by a nitrogen functionalized CNT prepared by direct amination of CNT with ammonia gas for the supporting of Au-Pd nanoparticles [31]. Recently a self-assembly of amphiphilic nitrotriacetic-diyne lipid on CNT has been reported by Doris and co-workers for the synthesis of novel carbon nanotube-gold nanohybride catalyst for oxidation of alcohols [32]. More recently, Wang and co-workers reported preparation and applications of gold nanoparticles loaded on nitric acid-pretreated carbon nanotubes for the selective oxidation of cellubiose by molecular oxygen to gluconic acid in aqueous medium at 145 °C [33].

In this study, we report preparation and characterization of a novel pyridine functionalized magnetic carbon nanotubes supported gold nanoparticles. The magnetic CNT supported gold nanoparticles was also applied as a catalyst for the aerobic oxidation of alcohols in water.

2. Materials and methods

2.1. Oxidative treatment of MWCNTs

The commercial MWCNTs (CAS: 308068-56-6 from Aldrich O.D.xL = 6–9 nm x 5 μm, Fig. 1) were oxidized according to the literature by stirring the MWCNT in concentrated nitric acid at 60 °C for 12 h [34].

2.2. Preparation of Fe3O4/MWCNTs (m-MWCNTs)

The magnetic nanoparticle composite of Fe3O4/MWCNTs was prepared according to our recently report and the literature with slight modification [23,35]. Oxidized MWCNTs (1.0 g) was added to a solution mixture of (NH4)2Fe(SO4)6H2O (1.7 g, 4.33 mmol) and NH4Fe(SO4)2·12H2O (2.51 g, 8.66 mmol) in water (200 mL) at 50 °C under N2 atmosphere. The solution was sonicated for 10 min and then NH4OH (10 mL, 8 M) was added dropwise to precipitate the iron oxides while the mixture solution was sonicated. The pH of the final mixture should be in the range of 11–12. The precipitate was isolated by an external magnet and the supernatant was separated from the precipitate by decantation. Fe3O4/MWCNTs were washed with doubly distilled water (500 mL). The obtained Fe3O4/MWCNTs nanocomposite (m-MWCNTs) was then washed with absolute alcohol (150 mL) for three times and then dried under vacuum.

2.3. Pyridine functionalized m-MWCNTs (mf-MWCNTs)

NaNO2 (0.490 g, 7.10 mmol) was dissolved in water (0.7 mL) and added dropwise to a cooled solution of 4-aminopyridine (0.658 g, 6.99 mmol) in HCl (5 mL, 4 M). The resulting solution was stirred for 30 min at 0 °C. The solution was added to a sonicaed dispersed mixture of m-MWCNTs (20 mg) in DMF (20 mL) and the mixture was stirred for 4 h at 0 °C and 15 h at room temperature. The precipitate was isolated by external magnet and the supernatant was separated from the precipitate by decantation. The solid was dispersed in HCl (100 mL, 2 M) and again isolated by external magnet and the composite was washed with water (500 mL). The resulting solid material was dispersed in NaOH (100 mL, 2 M) and stirred overnight to ensure deprotonation of the pyridinium salt to free pyridine and the mf-MWCNT composite was then isolated by an external magnet, washed with water, THF (2 × 30 mL), acetone (2 × 30 mL), and ethanol (2 × 30 mL), respectively. The composite dried overnight at 80 °C to afford purified mf-MWCNT [36,37].

2.4. Preparation of mf-MWCNTs stabilized gold nanoparticles (AuNPs/mf-MWCNT)

To an aqueous solution of HAuCl4 (1 mM, 35 mL) was added 14 mg of mf-MWCNT. The mixture was stirred for 30 min at 0 °C. Then, an aqueous solution of NaBH4 (100 mM, 5 mL) was rapidly sprayed into the reaction mixture with a syringe under vigorous stirring. The mixture was further stirred for 1 h. The precipitate AuNPs/mf-MWCNT was isolated in the magnetic field, and the supernatant was separated from the precipitate by decantation. The AuNPs/mf-MWCNT were subsequently washed with deionized water to remove inorganic impurities. The composite was dispersed and isolated by the magnetic field in ethanol and dried overnight at 80 °C [38].

2.5. Oxidation of benzyl alcohol catalysed by AuNPs/mf-MWCNT

AuNPs/mf-MWCNT (3 mg, 1.88 mmol Au/g catalyst) in distilled water (2 mL) was dispersed for 5 min by ultrasound. K2CO3 (0.08 g, 0.6 mmol) and benzyl alcohol (20 μL, 0.2 mmol) was added into the reaction mixture and the mixture was stirred under an atmospheric of oxygen for 16 h at 50 °C. The catalyst were collected by external magnet and washed three times with deionized water. The solution

Fig. 1. TGA of MWCNT composite.
was neutralized with 0.1 M HCl (pH = 3–4) and extracted with AcOEt (3 × 7 mL). The extracted organic layer was dried over Na2SO4 and then analyzed by gas chromatography. The GC yield was obtained from the calibration curve.

3. Results and discussion

Pyridine groups through lone-pair on their nitrogen atoms and also benzene ring in MWCNTs are ideal stabilizers for gold nanoparticles [31,39]. Although gold has been reported as a poor catalytic metal, its nanosized in nanocomposites have been shown to be able to catalyze chemical transformations [40–42]. The preaparation of magnetic CNTs opens new possibilities in nanotechnology applications [43]. Therefore we decided to prepare pyridine functionalized magnetic decorated MWCNTs to synthesize gold nanoparticles on their surface. Scheme 1 shows a schematic illustration of the step-by-step approach for the preparation of AuNPs/mf-MWCNT.

The magnetic nanoparticles of MWCNTs (m-MWCNTs) hetero-structures were achieved by the co-precipitating of iron metal ions within a dispersion of MWCNTs [35]. In order for the functionalization of m-MWCNTs with pyridine groups, aryldiazonium salts were found as a convenient precursor [36]. Therefore, the next step (pyridine functionalization) was achieved by direct reaction of the m-MWCNTs with 4-pyridinediazonium salt.

The functional groups of nanomaterials were characterized by FT-IR spectroscopy (Fig. 2). First of all, the vibration band of Fe-O appeared at 540–700 cm⁻¹ wave number range. The pyridine groups of mf-MWCNTs were measured at about 1600–1700 cm⁻¹ wave number range. The assignments for mf-MWCNTs are concordant with the Tuci reported on pyridine functionalized CNTs [38]. Therefore by FT-IR analysis, it can be concluded that Fe₃O₄ nanoparticles and pyridine groups have been bonded successfully on the surface of MWCNTs.

AuNPs/mf-MWCNT were prepared by sonication of mf-MWCNTs in distilled water, followed by the addition of HAuCl₄·3H₂O aqueous solution and treatment with ice-cooled NaBH₄ solution, as a reductant, at room temperature with vigorous stirring for 1 h. The morphology and structure of the prepared AuNPs/mf-MWCNT was characterized by SEM, TEM, EDS, XRD and atomic absorption analyses, which confirmed the successful preparation of AuNPs/mf-MWCNT.

The SEM image of the AuNPs/mf-MWCNT is shown in Fig. 3. Fig. 3 shows the CNT nanowires decorated with Fe₃O₄ and Au nanoparticles.

Also, elemental analysis for m-MWCNTs and mf-MWCNT confirm successfully attachment of pyridine and Fe₃O₄ groups on mf-MWCNTs. The elemental analysis of mf-MWCNTs showed that the C/N and C/Fe ratio is 115/1 and 28/1 respectively. The content of Au in AuNPs/mf-MWCNT was measured by atomic absorption spectrometry (1.87 mmol of Au per 1 g of the catalyst). The analysis (EDS) confirmed the presence of Au, Fe, and N in the nanocomposite (Fig. 3). EDS quantitative microanalyses indicates that the nanocomposite has a composition of Au, Fe, O, N, and C.

TEM was used to obtain direct information about the structure and morphology of novel composite. Fig. 3 shows the TEM image of prepared AuNPs/mf-MWCNT. In TEM, black dots indicate Au NPs and pale gray dots indicate iron oxide NPs [44]. TEM showed that the mean diameter of Au nanoparticles is about 15 nm.

In the XRD spectrum of AuNPs/mf-MWCNT (Fig. 4), all diffraction peaks and positions match well with those from the JCPDS card (No. 01–1172) for the face-centered cubic gold and cubic Fe₃O₄ (JCPDS card no. 75–0449) on the surface of mf-MWCNTs. The average crystallite sizes of Fe₃O₄ nanoparticles estimated using Scherrer’s equation is ~23 nm. Comparing the XRD spectrum of AuNPs/mf-MWCNT with XRD of m-MWCNT [23], showed that the Au nanoparticles decorated on the surface of MWCNT. The average crystallite sizes of Au nanoparticles estimated using Scherrer’s equation is ~18 nm for AuNPs/mf-MWCNT.

Catalytic oxidation of alcohols using oxygen as oxidant in water in the presence of recyclable and reusable gold supported catalysts, is one of the most economical and environmentally-friendly advanced oxidation process [45–47]. The catalytic oxidation activity of the nanocomposite was assessed using benzyl alcohol as a model compound under an atmospheric of oxygen. Since reported analogous supported gold nanoparticles for the oxidation of alcohols usually require reaction conditions such as heating and oxygen pressure, in a preliminary screening, oxidation of benzylalcohol (0.2 mmol) in the presence of AuNPs/mf-MWCNT catalyst (3 mg) in water (2 mL) was performed under an atmospheric of oxygen at room temperature. The results showed that after 24 h no products (benzaldehyde or benzoic acid) were observed (Table 1 entry 1). The conversion proceeded to only 40% with the addition of certain base (K₂CO₃, 3 equiv) to the reaction mixture at room temperature. The conversion increased to 100% with increasing the reaction temperature to 50 °C (entries 2–4). By screening of different bases (3 equiv) we found that K₂CO₃ was the best (entries 5–9). The oxidation reaction catalyzed by AuNPs/mf-MWCNT in the presence of K₂CO₃ is highly selective to benzoic acid, found as the sole product (entry 4). When the oxidation reaction was performed under an aerobic condition at 50 °C, the conversion was decreased to 16% (Table 1, entry 12). Hydroxide ions play an important role during oxidation and no activity is seen over Au catalysts without

![Scheme 1. Schematic illustration of the step-by-step approach for the preparation of AuNPs/mf-MWCNT.](image-url)
Fig. 2. FT-IR spectrums of mf-MWCNTs.

Fig. 3. The SEM, EDS and TEM of AuNPs/mf-MWCNT
adding a base (Table 1 entry 1). The mechanism of the over-oxidation of benzyl alcohol to benzoic acid was occurred via the formation of the gem-benzidiol \( \text{PhCH(OH)}_2 \) intermediate \[48\]. On the other hand, for Au catalysts, particle size and support composition had negligible effect on the rate or selectivity of the oxidation reactions \[49\].

The recyclability and reusability are very important points for heterogeneous catalysis systems. The recycling experiments were examined for the catalytic oxidation of benzyl alcohol with less selectivity for the benzaldehyde product. The catalyst was also applicable for the oxidation of 1-phenyl ethanol, as a secondary alcohol, to acetophenone in high yield. The catalyst are efficiently recovered and reused for next run with negligible gold leaching to solution.

Using the new nanocomposite described here conversion yield for the oxidation of 1-heptanol is excellent with quantitatively yield and selectivity achieved for the desired acid product (Scheme 2). Such selectivity and efficacy is far superior to other AuNPs supported on CNTs catalysts (For example Doris and co-workers reported yield of only <5% for aliphatic alcohols \[32\]).

To further extend the scope of the reaction, secondary alcohol 1-phenyl ethanol was also studied under similar conditions. 1-Phenyl ethanol was also oxidized to the corresponding ketone with 100% yield (Scheme 2).

Interestingly, no reaction occurred under inert atmosphere of \( \text{N}_2 \) with both benzyl alcohol and 1-phenyl ethanol. The results showed that the oxidation reaction needs the molecular oxygen as an activator. Moreover, the conversion of the oxidation reaction of benzyl alcohol in THF was decreased to 25% and the major product was benzaldehyde (17%). Thus the presented catalytic system has selectivity depending on the reaction conditions.

### Table 1

**Oxidation of benzyl alcohol by AuNPs/mf-MWCNT composite.**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Base(^a)</th>
<th>Temperature (°C)</th>
<th>Conversion (%)(^b)</th>
<th>Selectivity (%)(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>–</td>
<td>25</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>( \text{K}_2\text{CO}_3 )</td>
<td>25</td>
<td>40</td>
<td>8</td>
</tr>
<tr>
<td>3</td>
<td>( \text{K}_2\text{CO}_3 )</td>
<td>40</td>
<td>60</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>( \text{K}_2\text{CO}_3 )</td>
<td>50</td>
<td>100</td>
<td>–</td>
</tr>
<tr>
<td>5</td>
<td>( \text{Na}_2\text{CO}_3 )</td>
<td>50</td>
<td>16</td>
<td>4</td>
</tr>
<tr>
<td>6</td>
<td>KOH</td>
<td>50</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>7</td>
<td>NaOH</td>
<td>50</td>
<td>98</td>
<td>–</td>
</tr>
<tr>
<td>8</td>
<td>( \text{N}(*\text{Et})_3 )</td>
<td>50</td>
<td>24</td>
<td>5</td>
</tr>
<tr>
<td>9</td>
<td>( \text{Na}_2\text{CO}_3 )</td>
<td>50</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>10</td>
<td>( \text{K}_2\text{CO}_3 )</td>
<td>50</td>
<td>9</td>
<td>6</td>
</tr>
<tr>
<td>11</td>
<td>( \text{K}_2\text{CO}_3 )</td>
<td>50</td>
<td>68</td>
<td>2</td>
</tr>
<tr>
<td>12</td>
<td>( \text{K}_2\text{CO}_3 )</td>
<td>50</td>
<td>16</td>
<td>7</td>
</tr>
</tbody>
</table>

\(^{a}\) Reaction condition: 0.6 mmol base under \( \text{O}_2 \).

\(^{b}\) Conversion and selectivity determined by GC.

\(^{c}\) 0.3 mmol of \( \text{K}_2\text{CO}_3 \).

\(^{d}\) 2 mg of AuNPs/mf-MWCNT.

\(^{e}\) Oxidation reaction under an aerobic condition.

The recyclability and reusability are very important points for heterogeneous catalysis systems. The recycling experiments were examined for the catalytic oxidation of benzyl alcohol under an atmospheric of oxygen at 50 °C in the presence of \( \text{K}_2\text{CO}_3 \) as a base. After the first run, the catalyst were collected by external magnet and washed three times with deionized water. The catalyst were reused without significant loss of activity. Atomic absorption analysis of recovered catalyst showed that Au amount decreased to 1.7 mmol of Au per gram of the catalyst after fifth run. Results showed a negligible Au leaching occurred after fifth run from the catalyst.

4. Conclusions

We reported here a successful preparation of novel functionalized MWCNTs containing gold nanoparticles. Transmission electron microscopy (TEM), scanning electron microscopy (SEM) images, XRD and EDS analysis confirmed that the Au nanoparticles were successfully immobilized on the mf-MWCNTs. This novel composite exhibited a catalytic activity in the oxidation reaction of benzyl alcohol with less selectivity for the benzaldehyde product. The catalyst was also applicable for the oxidation of 1-phenyl ethanol, as a secondary alcohol, to acetophenone in high yield. The catalyst are efficiently recovered and reused for next run with negligible gold leaching to solution.

![Fig. 4. XRD from AuNPs/mf-MWCNT composite.](image)
References