SHORT COMMUNICATION

Green Synthesis of Bimetallic PdAg Nanowires as Catalysts for the Conversion of Toxic Pollutants

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Abstract—The green synthesis of bimetallic PdAg nanowires which were created under ambient conditions and in the absence of any stabilizers and harsh reagents is herein reported. The straightforward synthesis involved a one-pot set-up containing only the HEPES buffer, metal salt and reductant. The PdAg nanowires were efficient catalysts toward the reduction of common and toxic nitrophenol pollutants. The nanowires exhibited high turnover frequency and were able to achieve total conversion of the starting material. The bimetallic materials were also superior catalysts relative to other materials reported in literature. Taken together, the method and material presented have the potential to be of great use and value to environmental catalysis.

Keywords—Environmental catalysis, bimetallic materials, PdAg nanowires, nitrophenol reduction

INTRODUCTION

Catalysis is an important component of environmental management since it has the capacity to offer realistic solutions to many ecological problems (Centi *et al*, 2002). Catalysts help the environment at two fronts: efficient use of resources that will lead to waste minimization; and reduction of the harmful effects of toxic pollutants through degradation. Hence, it can be said that developing efficient catalytic systems will directly benefit the environment. One of the approaches in developing more efficient catalysts is utilizing bimetallic systems. Bimetallic nanostructures exhibit higher catalytic activity over their monometallic counterparts due to the synergism that exists between the two metals (Singh and Xu, 2013). Among the different bimetal combinations, palladium and silver bimetallic materials are highly sought after since both metals complement each other. Palladium is an important element in catalysis, wherein it is involved in numerous reactions such as the different C-C couplings (Balanta *et al*, 2011). Palladium however has very weak optical properties, in contrast to silver which often exhibit strong surface plasmon resonance (SPR) within the visible range. SPR refers to the collective oscillations of the surface electrons of the metal at specific wavelengths (Stewart *et al*, 2008). Hence, silver nanostructures are often used as sensors that exploit this phenomenon (Homola 2003). Thus, by combining the two important metals together, nanostructures with high catalytic performance and adequate optical properties may be achieved (He *et al*, 2010). Colloidal-based methods are the common routes in which bimetallic nanostructures are prepared (Gu *et al*, 2012). Stabilizers are essential constituents of the synthesis since they prevent aggregation and influence the shape formation of the nanostructures. Common stabilizers used in the formation of PdAg nanostructures include sodium bis(2-ethylhexyl)sulfosuccinate (AOT) (Chen *et al*, 2006), cetyltrimethylammonium bromide (CTAB) (He *et al*, 2010), among others. Taking into consideration the environmental impacts of the synthesis, it is more desirable to devise a minimalist method which will involve less components and benign reaction conditions. Bearing this in mind, we report here the green synthesis of bimetallic PdAg nanowires which were created in the absence of any stabilizers and harsh reagents, less amount of reagents and under ambient conditions. The PdAg nanowires exhibited excellent catalytic activity towards the conversion of common toxic pollutants.

METHODOLOGY

Nanomaterial Synthesis

The synthesis of the bimetallic materials was carried out in aqueous environment and under normal atmosphere, pressure and room temperature. In a 20 mM HEPES-buffered solution at pH 7.4, K_2PdCl_4 was added to yield a final concentration of 30 μM. The palladium ions were reduced upon the addition of 200 μM $NaBH_4$. After ten minutes, 30 μM of $AgNO_3$ was added and the solution was allowed to stand for 90 minutes. Reduction was stopped through the 10-fold dilution of the resulting solution. Characterization of the materials involved bright field- scanning electron microscopy (BF-STEM), energy dispersive X-ray spectroscopy (EDX) and UV-Vis spectrophotometry. For BF-STEM and EDX, 5 μL of the diluted sample was introduced onto a carbon coated copper disk. For UV-vis measurements, the diluted sample was placed inside a glass cuvette.

Catalytic Activity Determination

The reduction of nitrophenol into aminophenol was used as the probe reaction wherein the three different kinds of isomers were used as the substrate (2-nitrophenol, 3-nitrophenol and 4-nitrophenol). In a glass cuvette with a micro stirring bar, 50 μM of the nitrophenol substrate and 10 mM of $NaBH_4$ were added. Upon the addition of the bimetallic material which corresponds to 0.8 mol% with respect to both metals, the colored substrate immediately faded signifying that reduction has taken place. The progress of the reaction was monitored for five minutes by time-resolved UV-vis measurements at the following wavelengths: 2-nitrophenol = 414 nm; 3-nitrophenol = 391 nm; 4-nitrophenol = 398 nm. $NaBH_4$ is necessary for the reduction to take place. In the absence of any catalyst however, the reaction does not take place even after 30 minutes to 24 hours as signified by
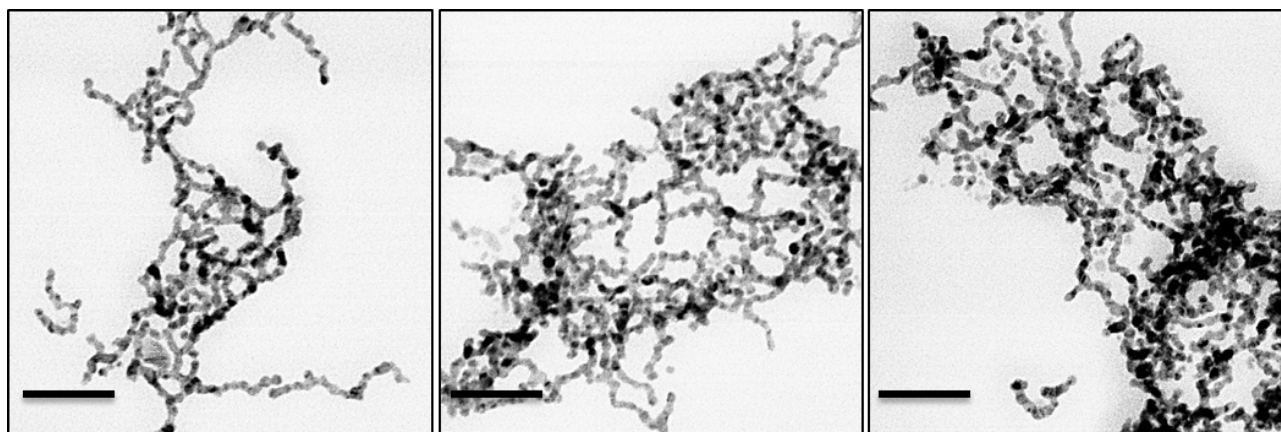
Figure 1. BF-STEM images of PdAg bimetallic nanowires. Scale bar = 50 nm

the unchanged absorbance readings of the starting material at their respective wavelengths. Catalytic activity was assessed by calculating the rate constant and turnover frequency.

RESULTS AND DISCUSSION

The nanostructures formed are characterized as having slender and elongated morphologies (Figure 1). The nanowires form networks and branch off at several points. The composition of the nanowires was determined to be a mixture of both palladium and silver according to UV-vis and EDX measurements. The UV-vis spectrum of the PdAg nanowires is different from the typical spectra of monometallic Pd and Ag nanostructures (Figure 2). The obtained UV-vis spectrum has an increasing absorbance from 400 – 800 nm and a weak peak at 350 nm. The absorption spectrum of the nanowires appears to be a combination from that of Pd and Ag. This is because Pd nanostructures of different shapes and sizes usually have a featureless absorption spectrum from 200-800 nm (Janairo and Sakaguchi, 2014). On the other hand, silver nanostructures exhibit surface plasmon resonance (SPR) upon irradiation with light (Wiley *et al*, 2006). This leads to a UV-vis spectrum characterized by having a strong absorption at the wavelength in which the surface electrons resonate with. Moreover, the obtained UV-vis spectrum shares similarities with that of the PdAg nanostructures produced by He *et al* (2010). The EDX spectrum of the PdAg nanowires supports the UV-vis spectrum and confirms that indeed the obtained structures were bimetallic (Figure 3). The faint signals of palladium and silver from the K line are conclusive evidence in addition to the overlapping signals from the L lines. The strong copper signal is from the copper grid in which the sample was placed. It should be noted that the synthesis of the PdAg nanowires was carried out in environmentally-friendly conditions. Stabilizers and harsh reagents were not utilized, in addition to very dilute conditions. This demonstrates efficient use of materials which will have minimal wastes. In the absence of any stabilizers, non-aggregated structures were still formed. The presence of the HEPES buffer may have helped stabilize the structures since the presence of a buffer influences nanostructure formation (Janairo and Sakaguchi, 2014). This is possible since HEPES possesses sulfonic acid and hydroxyl moieties that have the ability to bind with metal surfaces. The buffer may thus be involved in capping the growth of the nanostructure resulting in the regulation of its morphology. The HEPES buffer also regulates nanostructure growth by maintaining the pH since the rate of metal reduction is dependent on the pH (Li *et al*, 2015).
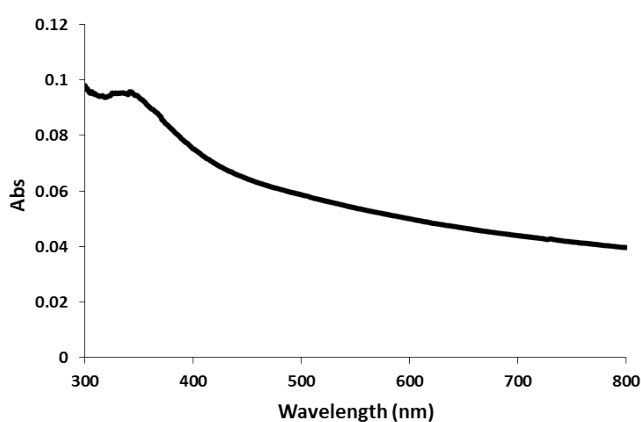

Figure 2. UV-vis spectrum of the PdAg nanowires

The catalytic activity of the PdAg nanowires towards the conversion of pollutants was assessed using nitrophenol isomers as the substrates. All three nitrophenol isomers are common toxic pollutants that are by-products of industrial wastes (Megharaj *et al*, 1991). The catalytic reduction of nitrophenol into aminophenol is well-known and often used to study the properties of catalysts. It follows an adsorption-reaction-desorption mechanism which makes it ideal to be used to study catalytic surfaces (Blaser *et al*, 2009). This reaction has been often
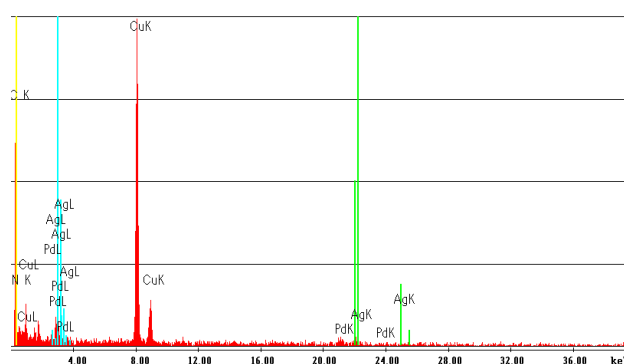

Figure 3. EDX spectrum of the PdAg nanowires

used to study catalytic systems such as Pt-Ni bimetallic structures (Ghosh *et al*, 2004), composites of silver/iron oxide (Chiou *et al*, 2013), among others. It follows pseudo-first order reaction kinetics, provided that NaBH4 is in a large excess amount compared to the substrate. Once the pseudo-first order kinetic state is reached, increasing the amount of NaBH4 will not affect the reaction. Table 1 shows the calculated catalytic parameters for the PdAg nanowires. The calculated rate constants for the PdAg nanowires for all substrates were much higher than the monometallic Pd nanostructures at identical catalyst loading and reaction conditions (Janairo *et al*, 2014). This signifies that alloying palladium with silver did enhance the catalytic activity of the resulting nanostructures. Furthermore, the calculated turnover frequency values of the PdAg nanowires for all substrates were also superior relative to other nanocatalysts reported in literature (Table 2). This indicates that the prepared PdAg nanowires are efficient catalysts for the conversion of common nitrophenol pollutants. In addition to the synergistic effect of alloying, the unique overall architecture of the nanowires may have endowed the material with excellent catalytic properties. The layers and networks formed by the PdAg nanowires provided an overall porous structure for the material which can aid in enhancing the catalytic properties of the material (Rolison, 2003). Porous materials have high surface areas, therefore more exposed surface ready to accommodate reactions (Fang *et al*, 2012). Aside from this, the porosity of the materials aids catalytic activity by facilitating the passivity and diffusion of the reagents (Bhandari and Knecht, 2011).

Table 1. Comparison of the pseudo-first order rate constant ($\times 10^{-3}$ s^{-1}) of the PdAg nanowires and previously synthesized Pd nanoparticles at identical reaction conditions.

	2-nitrophenol	3-nitrophenol	4-nitrophenol
PdAg Nanowires	14.8 ± 5.3	56.5 ± 3.3	96.6 ± 11.7
Pd nanoparticles (Janairo *et al*, 2014)	1.97 ± 0.06	4.07 ± 0.85	4.23 ± 0.21

CONCLUSION

In summary, we have presented a simple and straightforward approach in synthesizing catalytically active bimetallic PdAg nanowires. The synthesis involves very ambient and environmentally-friendly reaction conditions. The nanowires were characterized by BF-STEM, UV-Vis spectrophotometry and EDX which revealed the slender and elongated structures made up of both metals. The PdAg nanowires were efficient catalysts toward the reduction of common and toxic nitrophenol pollutants. The bimetallic materials were also superior catalysts relative to other materials reported in literature. Taken together, our method and material have the potential to be of great use and value to environmental catalysis.

Table 2. Comparison of turnover frequency (h^{-1}) of PdAg nanowires with other materials reported in literature.

Material	2-nitrophenol	3-nitrophenol	4-nitrophenol	Reference
PdAg nanowires	1266 ± 61	3630 ± 190	2527 ± 83	This work
PdNP / SiO$_2$-IL	281	281	281	Li et al, 2011
Cu-Nano-ZSM5	-	13.5	13.2	Kaur et al, 2013
Pd/CN	879.5	-	-	Wu et al, 2013
SiO2@Fe$_3$O$_4$/C@Au	1044	-	-	Zeng et al, 2013

CONFLICTS OF INTEREST

None

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