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Facile synthesis of palladium and gold nanoparticles by using dialdehyde nanocellulose as template and reducing agent

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ABSTRACT

Cellulose nanofibrils (CNFs) were firstly prepared by 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) oxidation and further oxidized to 2,3-dialdehyde nanocelluloses (DANCs) by periodate oxidation. Furthermore, by using DANCs as reducing as well as stabilizing agent, palladium (Pd) and gold (Au) nanoparticles (NPs) supported on nanocellulose (PdNPs@NC and AuNPs@NC) were synthesized, respectively. The reduction of Pd or Au ions to its metallic form by DANCs was confirmed by UV–vis spectra, XRD, and XPS. TEM results showed that Pd and Au NPs were homogenously deposited onto cellulose nanofibrils, respectively. The catalytic performance of PdNPs@NC was further investigated by Suzuki coupling reaction. The product yield of the Suzuki coupling reaction between aryl bromides and phenyl boronic acid was more than 90% after 1 h with 0.1 mol% PdNPs@NC catalyst, which demonstrated that the synthesized PdNPs@NC nanohybrid could be successfully applied in Suzuki coupling reaction with an efficient catalytic activity.

1. Introduction

Noble metal nanoparticles, being totally distinct from their bulk metal equivalents, have attracted considerable attention because of their unique properties such as optical (Wang, Ye, Iocozzia, Lin, & Lin, 2016; Yu et al., 2017), magnetic, and electronic activities (Loh, 2016) and their high catalytic performances in many chemical reactions (Dong et al., 2015; Long, Thi, Yong, Nogami, & Ohtaki, 2013; Sarina, Waclawik, & Zhu, 2013). The synthesis of noble metal nanoparticles has been an important research topic in the field of nanoscience over the past decades (Wu, Kuang, Zhang, & Chen, 2011). Palladium nanoparticles (Pd NPs) are well known for their excellent catalytic activity in C–C cross-coupling reactions including Suzuki, Heck, Sonogashira and Stille reactions (Phan, Van Der Sluys, & Jones, 2006; Xu, Wu, & Zhu, 2008). To date, such reactions have been frequently employed in the synthesis of pharmaceuticals, agrochemicals, dyes and other products (Hassan, Sévignon, Gozzi, Schulz, & Lemaire, 2002). Among various cross-coupling reactions, Suzuki cross-coupling reactions of aryl halides with arylboronic acids have become the prevailing technique, as it is one of the most efficient methods for construction of biaryl compounds in organic synthesis (Kumbhar, Jadhav, Kamble, Rashinkar, & Salunkhe, 2013). Likewise, gold nanoparticles (Au NPs) have attracted increasing interest due to their catalytic properties in various organic transformation reactions, including the CO oxidation, aerobic oxidation of alcohols, C−C coupling reactions and reduction reactions via transfer hydrogenation (Chen, Cao, Quinlan, Berry, & Tam, 2015; Chen, Kang, et al., 2015). However, both Pd and Au nanoparticles suffer from agglomeration in solution due to their large specific surface areas (Wu et al., 2013). One strategy to stabilize metal nanoparticles is by employing capping agents such as thiols, carboxylate ligands, surfactants and polyelectrolytes (Chen, Kang, et al., 2015). Most capping agents, however, are non-biodegradable polymers or potentially toxic chemicals (Shi et al., 2015). Another method to avoid agglomeration is by means of the immobilization of metal nanoparticles onto solid matrixes including carbon (Liu, Yang, Liu, Ye, & Wei, 2017), silica (Shimizu et al., 2004), metal oxide (Del Zotto & Zuccaccia, 2017), polymer, *etc.* (Yan et al., 2016). Polymeric supports are attractive due to a greater number of active sites such as carboxylate and amino in the structure (Chen, Kang, et al., 2015). As the most abundant organic polymer in nature, cellulose has been extensively used as bio-templates for metal nanoparticles (He, Kunitake, & Nakao, 2003; Li, Xu, et al., 2017; Y. Liu, Song, Shang, Song, & Wang, 2012; Van Rie & Thielemans, 2017).

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Nanocellulose (NC), produced via chemical or physical approaches from vegetal or bacterial cellulose, mainly includes three different types, i.e., cellulose nanocrystals (CNCs), cellulose nanofibrils (CNFs) and bacterial cellulose (BC). (Li et al., 2015; Li, Sirviö, Haapala, & Liimatainen, 2017; Sirviö, Visanko, & Liimatainen, 2015; Sirvio & Visanko, 2017; Suopajärvi, Sirviö, & Liimatainen, 2017; Visanko et al., 2017; Zhang et al., 2016). Nanocellulose has emerged as an attractive candidate for supporting metal NPs due to its high surface area, environmental sustainability and biodegradability (Hu, Meng, Liu, Fu, & Lucia, 2017; Kaushik & Moores, 2016; Wu et al., 2016; Xiong, Lu, Zhang, Zhou, & Zhang, 2013; Yan et al., 2016; Zhou et al., 2012). The most common preparation technique for the fabrication of noble metal NPs/nanocellulose hybrids is the treatment of noble metal salts with reducing agents in the presence of nanocellulose (Cirtiu, Dunlop-Briere, & Moores, 2011; Ghaderi, Gholinejad, & Firouzabadi, 2016; Koga et al., 2010; Liu et al., 2012; Van Rie & Thielemans, 2017). However, the reducing agents employed such as $NaBH_4$ and H_2 would be hazardous or dangerous (Wu et al., 2013; Wu et al., 2014). So far, several methods of reduction of metal nanoparticles by using nanocellulose as reducing agent have been reported (Benaissi, Johnson, Walsh, & Thielemans, 2010; Y. Dong, Liu, Liu, Meng, & Ma, 2017; Fu, Deng, Ma, & Yang, 2016; Hu, Meng, Liu, Fu, & Lucia, 2017). Rezayat et al. (2014) prepared Pd NPs through nanocellulose-induced reduction of Pd precursors in subcritical and supercritical carbon dioxide ($scCO_2$). Likewise, Pd and Au NPs were synthesized in a hydrothermal system by using neat nanocellulose as both supporting matrix and reductant (Wu et al., 2013; Wu et al., 2014). Nonetheless, these methods still require harsh or complicated conditions (in $scCO_2$ or hydrothermal system).

Nanocellulose surface possesses many reactive hydroxyl groups, which can be utilized for further chemical modification. 2, 3-dialdehyde cellulose (DAC) can be obtained by using periodate as oxidant to oxidize vicinal hydroxyl groups of cellulose at positions 2 and 3 to aldehyde groups (Liimatainen, Sirvio, Pajari, Hormi, & Niinimaki, 2013; Mou, Li, Wang, Cha, & Jiang, 2017; Sirvio, Liimatainen, Niinimaki, & Hormi, 2011). Wu, Kuga and Huang (2008) and Drogat et al. (2011) reported that Ag NPs could be produced and coated on nanocellulose while introducing DAC as reductant. As we know that the reduction potential of Pd (0.915 V) and Au (1.50 V) ion are higher than that of silver (0.8 V) (Nadagouda & Varma, 2008). Therefore, it would be possible to reduce Pd or Au ions to metallic forms by utilizing aldehyde groups on the surface of DAC. In the present study, cellulose nanofibrils (CNFs) were firstly prepared by 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) oxidation and further oxidized to 2,3-dialdehyde nanocellulose (DANCs) by sodium periodate. Pd NPs and Au NPs supported onto nanocellulose (PdNPs@NC and AuNP@NC, respectively) were successfully synthesized by employing DANCs as reducing agent as well as stabilizing template (Fig. 1). The catalytic activity of obtained PdNPs@NCFs nanohybrid for Suzuki coupling reaction was subsequently investigated. To our best knowledge, this paper is the first demonstration for the reduction of Pd(II) and Au(III) ions by DANCs. The present strategy provides a new way to synthesize Pd and Au NPs nanoparticles by cellulose based materials.

2. Materials and methods

2.1. Materials

Bleached sugarcane bagasse sulphite pulp was obtained from Jiangmen sugarcane chemical factory (group) Co.,Ltd. The cellulose content was 94% and the rest was mostly hemicelluloses. 2,2,6,6-tetramethylpiperidinyl-1-oxy radical (TEMPO), 4-nitrophenols (4-NP), odium bromide (NaBr), sodium hypochlorite solution (NaClO, 15%), sodium periodate ($NaIO_4$), potassium carbonate (K_2CO_3), palladium chloride ($PdCl_2$), gold chloride tetrahydrate ($HAuCl_4{\cdot}4H_2O$), HCl, and NaOH were supplied by Sigma–Aldrich and used without further purification. Bromobenzene, bromoanisole, bromobenzonitrile *p*-bromonitrobenzene and phenylboronic acid were all purchased from Aladdin reagent Co., Ltd. (Shanghai, China).

2.2. Methods

2.2.1. Isolation of cellulose nanofibrils (CNFs) by TEMPO-mediated oxidation

Bleached sugarcane bagasse sulphite pulp was used as a cellulose raw material and cut into small pieces by a crusher. TEMPO-mediated oxidation employing 7 mmol NaClO per gram of cellulose and ultrasonic treatment (sonicating for 30 min with an output power of 450 W and 6 mm probe tip diameter) were subsequently performed as reported before to obtain CNFs (Zhang et al., 2016). The carboxyl content of CNFs obtained was determined to be 1.38 mmol/g cellulose by conductometric titration.

2.2.2. Preparation of 2, 3-dialdehyde nanocelluloses (DANCs) by periodate oxidation

0.4 g $NaIO_4$ was dissolving in 20 mL of aq. 0.6 wt.% CNFs suspension in a brown bottle. The mixture was stirred and reacted under 25 °C for 72 h in the dark. The suspension of DANCs was finally obtained after dialyzing against distilled water for 5–7 days to remove excess unreacted sodium periodate (Lu, Li, Chen, & Yu, 2014). The aldehyde content of DANCs was evaluated via the titrimetric method based on Schiff base reactions with hydroxylamine. 0.12 g freeze-dried DANCs was added in a hydroxylamine hydrochloride solution (1 g in 50 mL methanol) with thymol blue as indicator. The mixture was stirred at 40 °C for 4 h and then immediately titrated using 0.03 mol/L NaOH methanol solution until a faint pink color was obtained. The aldehyde group content of the synthesized DANCs was 3.8 mmol/g cellulose.

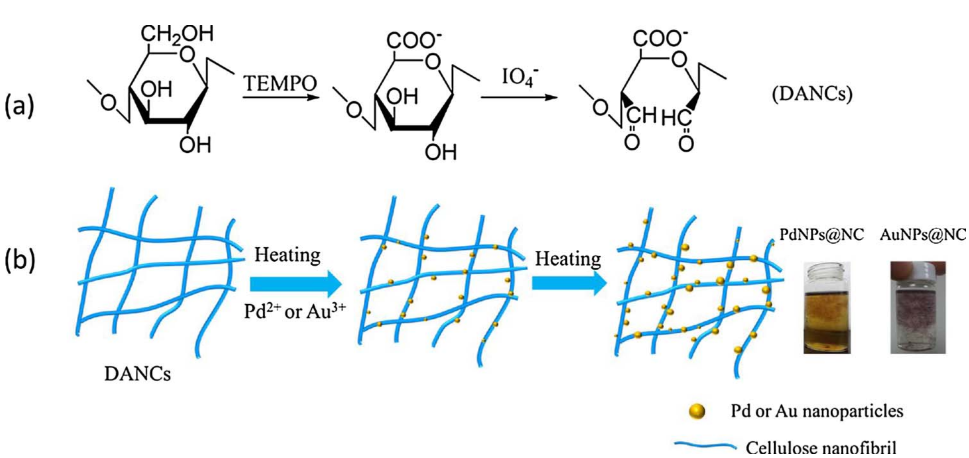

Fig. 1. Schematic illustration of preparation of (a) dialdehyde nanocellulose (DANCs) and (b) PdNPs@NC or AuNPs@NC.