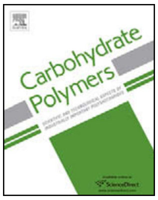
Carbohydrate Polymers 113 (2014) 525–531

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol



Catalytic reduction of *p*-nitrophenol by using platinum nanoparticles stabilised by guar gum

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ARTICLE INFO

Article history:
Received 5 May 2014
Received in revised form 8 July 2014
Accepted 14 July 2014
Available online 28 July 2014

Keywords:
Biopolymer
Guar gum
Metal nanoparticle
Green method
Catalysis
p-Nitrophenol

ABSTRACT

We report a facile and green method to synthesise highly stable dispersions of platinum nanoparticles (PtNPs) with an average particle size of ~6 nm. Natural, nontoxic, eco-friendly biopolymer guar gum was utilised as both the reducing and capping agent precursor in aqueous medium. The PtNPs that had been stabilised by guar gum (GG-*s*-PtNPs) were characterised by UV–vis spectroscopy, XRD, TEM and XPS. GG-*s*-PtNPs performed better in terms of catalytic activity for the liquid phase reduction of *p*-nitrophenol (*p*-NP) compared to *p*-aminophenol (*p*-AP). The efficiency of the catalytic reduction of *p*-NP over GG-*s*-PtNPs was found to be 97% in a total time of 320 s at room temperature. The mechanisms of the synthesis and catalytic reduction of *p*-NP are also discussed. The synthesis approach presented here does not require stringent conditions or toxic agents and thus is a straightforward, rapid, efficient, and green approach to the fabrication of highly active catalysts.

1. Introduction

Para-nitrophenol (*p*-NP) is one of the hazardous and toxic pollutants, which is known to cause adverse health effects in living organisms. It is known to be anthropogenic, toxic and inhibitory in nature. *Para*-nitrophenols are widely used in the manufacture of pesticides, insecticides, fungicides, synthetic dyes, pharmaceuticals and to darken leather (Agency for Toxic Substances and Disease Registry (ATSDR), 1990). Human exposure to *p*-NP takes place by three pathways, namely inhalation, ingestion (eating, drinking) and dermal contact. The severity of health effects after exposure to *p*-NP depends on exposure dose, duration, pathways and individual characteristics such as gender, nutritional status, family traits, lifestyle, and state of health. Short-term exposure of *p*-NP by the pathways of inhalation or ingestion causes symptoms such as headaches, drowsiness, nausea, and cyanosis. Contact with eyes results in irritation (U.S. Department of Health and Human Services (USDHHS), 1993). *Para*-nitrophenol is one of the most toxic derivatives of the parathion insecticide and is carcinogenic, hazardous, mutagenic and toxic (cytotoxic and embryo-toxic) to mammals (Banik, Prakash, & Upadhyay, 2008).

Para-Nitrophenol is known to be highly soluble and stable in water bodies such as freshwater, marine environments and in industrial wastewaters. Due to its solubility, traditional water purification methods to remove *p*-NP from contaminated wastewater are not effective. Scientists have therefore developed many techniques for *p*-NP removal which include adsorption, microwave-assisted catalytic oxidation, microbial degradation, photocatalytic degradation, electro-Fenton method, electrocoagulation, and electrochemical treatment (Marais & Nyokong, 2008; O'Connor & Young, 1989; Dieckmannand & Gray, 1996; Bo, Zhang, Quan, & Zhao, 2008; Modirshahla, Behnajady, & Mohammadi-Aghdam, 2008; Canizares, Sez, Lobato, & Rodrigo, 2004). However, all these techniques are energy-consuming and involve the use of organic solvents. Therefore, in the present scenario, it is very important to develop and employ aqueous phase conversion of *p*-NP to *p*-AP under mild conditions. *Para*-nitrophenol is converted to *p*-AP by catalytic reduction method. The reduction product (*p*-AP) obtained from the catalytic reduction of *p*-NP is effective in many useful applications such as analgesic and antipyretic drugs, photographic developer, corrosion inhibitor, anticorrosion lubricant, etc. (Shin, Choi, Park, Jang, & Kim, 2009).

The use of many noble metal–alloy nanoparticles for water treatment has been reported extensively in the literature, but reports on applications of precious-metal nanoparticles are quite limited in the literature. Precious-metal nanoparticles have been attracting a lot of interest recently because of their significant properties of high activity (Pandey, Goswami, & Nanda, 2012; Pandey, Goswami, & Nanda, 2013a), excellent efficiency, and higher Fermi potential which result in lowering of the reduction potential value, and hence metal nanoparticles act as active catalysts

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http://dx.doi.org/10.1016/j.carbpol.2014.07.047
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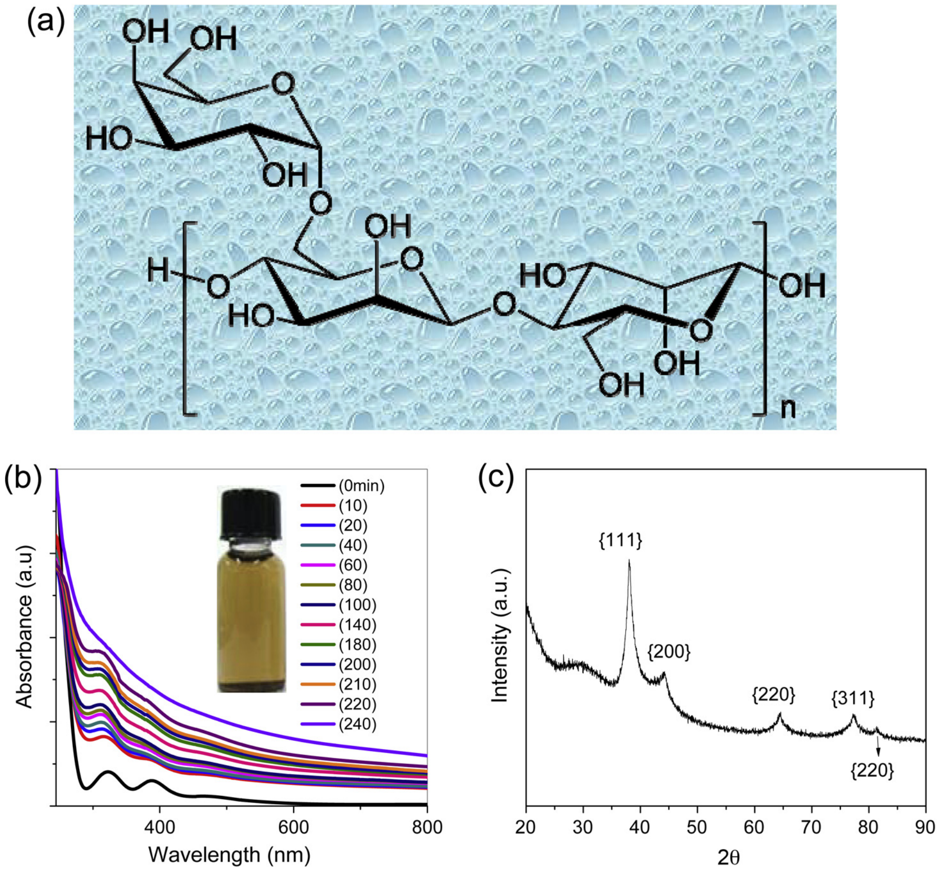

Fig. 1. (a) Structure of guar gum; (b) spectral changes of the GG-*s*-PtNPs at various time intervals (10 min to 240 min) recorded using UV–vis spectroscopy (GG-*s*-PtNPs solution is shown in the inset); and (c) XRD pattern of GG-*s*-PtNPs.

for many electron-transfer reactions (Ismail et al., 2011; Ismail & Bahnemann, 2011; Ghosh, Mandal, Kundu, Nath, & Pal, 2004). There are various methods for the synthesis of precious-metal nanoparticles such as electrochemical synthesis, radiation, chemical reduction, photochemical reduction, etc. However, the focus in this article is on the green method for the synthesis of precious-metal nanoparticles (PtNPs) by using guar gum (GG). Guar gum is a high-molecular-weight polysaccharide that is abundantly available in nature; its backbone is a linear chain of β-D(1 → 4) mannopyranosyl units with 1 → 6 linked α-D-galactopyranosyl units as side-chains. The structure of GG is shown in Fig. 1(a).

The catalytic properties of precious-metal nanoparticle catalysts depend on the size and distribution of the nanoparticles and on the interactions between the metal nanoparticles and the nature of the support (Tian, Zhang, Tong, & Chen, 2008; Hervés et al., 2012; Sen, Maity, & Islam, 2013; Xu et al., 2014). Catalytic reduction of *p*-NP in the presence of $NaBH_4$ has already been performed using Au nanoparticles deposited on poly(methyl methacrylate) (PMMA) (Kuroda, Ishida, & Haruta, 2009), Au/polypyrrole nanotubes (Qiu et al., 2012), Pd/Al_2O_3 (Arora, Kapoor, & Singla, 2010), Pd/polypyrrole nanocapsules (Hwang, Sang-Ho, Hoon, Kim, & Choi, 2008), and Ag/SBA-15 (Zhang et al., 2012). Dubey et al. (2014) fabricated graphene–carbon sphere hybrid aerogel decorated with silver nanoparticles (G/AgCS) for the catalytic reduction of *p*-NP in the presence of $NaBH_4$, while Jan, Chuang, Chen, and Teng (2011) used layer-by-layer polypeptide assemblies to mediate the synthesis of Au/mesoporous silica nanotubes with the apparent rate constant of 3×10^{-4} and $8 \times 10^{-4}\,s^{-1}$ for Au/SNTs obtained from $(Lys340/Glu125)_5$ and $(Lys340/PLT)_5$ coated membranes.

Herein, we demonstrate a simple, environmentally friendly, and cost-effective method for preparing highly stable dispersions of nanosized platinum particles derived from a natural biopolymer. The reaction is carried out in an aqueous medium solution and guar gum is used as both reducing and capping agent to prevent the aggregation of platinum nanoparticles. No other chemical is added to avoid any adverse effect on the performance of the products. Additionally, these GG-*s*-PtNPs were successfully used in the catalytic reduction of *p*-NP as a model reaction. To the best of our knowledge, this is the first report on spherical PtNPs formed with guar gum (GG); details of the synthesis and characterisation of the novel GG-*s*-PtNPs are provided, as are the results of the investigation into their catalytic activities.

2. Experimental

2.1. Materials

Potassium tetrachloroplatinate(II), (K_2 $PtCl_4$ 98%) was purchased from Sigma-Aldrich (USA) and used without further purification. Guar gum (GG), *p*-nitrophenol (*p*-NP) and sodium hydroxide (NaOH) were purchased from Merck (South Africa). All aqueous solutions were made up using ultrahigh deionised (DI) water purified using a Milli-Q Plus system (Millipore Co.).

2.2. Preparation of PtNPs stabilised with guar gum (GG-s-PtNPs)

All glassware used during synthesis was cleaned in a bath of freshly prepared aqua regia solution (HCl: HNO_3, 3:1), and rinsed thoroughly with deionised water prior to use. For the synthesis of GG-*s*-PtNPs, a stock solution of 2.5 mM was prepared by adding K_2PtCl_4 (0.0415 g) in DI water. Thereafter the K_2PtCl_4 solution was mixed with GG solution followed by the addition of a few drops of