

Green synthesis, characterization and catalytic activity of palladium nanoparticles by xanthan gum

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Abstract Here, we report the synthesis, characterization and catalytic evaluation of palladium nanoparticles (PdNPs) using xanthan gum, acting as both reducing and stabilizing agent without using any synthetic reagent. The uniqueness of our method lies in its fast synthesis rates using hydrothermal method in autoclave at a pressure of 15 psi and at 120 °C temperature by 10 min time. The formation and size of the PdNPs were characterized by UV–visible spectroscopy, X-ray diffraction, Fourier transform infrared spectroscopy and transmission electron microscopy. The catalytic activity of PdNPs was evaluated on the reduction of 4-nitrophenol to 4-aminophenol by sodium borohydride using spectrophotometry.

Keywords Autoclave · Catalytic activity · 4-Nitrophenol · Palladium nanoparticle · Xanthan gum

Introduction

In the last decade, the importance of understanding of science at the nanometre scale has attracted the interest of number of groups all over the world and has led to the emergence of a new interdisciplinary field called nanoscience, because of the size-dependent optical, electronic, and catalytic properties of nanoparticles (Prashant et al. 2006), and even in biological and medical science applications (Salata 2004). There are enormous changes in physical and chemical properties, both quantitatively and qualitatively,

from those of bulk materials as these materials are derived by manipulation at the atomic or molecular levels and because of surface to volume ratio and quantum size effect (Roucoux et al. 2002; Rosi and Mirkin 2005; Yang et al. 2006). Palladium nanoparticles are of great interest owing to their application both in heterogeneous and homogeneous catalyses, their high surface-to-volume ratio and high surface energy (Narayanan and El-Sayed 2005). In addition, Pd is exploited as a catalyst in various coupling reactions like Heck coupling (Karimi and Enders 2006), Suzuki coupling (Klingensmith and Leadbeater 2003), and hydrogenation of allyl alcohols (Wilson et al. 2006). Till now, production of PdNPs involved different reducing chemicals such as NaBH₄ (Jana et al. 2000; Domenech et al. 2011), N₂H₄ (Yonezawa et al. 2001; Szilvia et al. 2007), ascorbic acid (Sun et al. 2007) and PEG (Luo et al. 2005; El-Houta et al. 2012). Over the past decade there has been an increased interest in the green chemistry (Roucoux et al. 2002; Raveendran et al. 2003). In the synthesis of metal nanoparticles by reduction of the corresponding metal ion salt solutions, there are three areas of opportunity to engage in green chemistry: (1) choice of solvent, (2) the reducing agent, and (3) the capping agent. There has also been increasing interest in identifying environmental friendly materials that are multifunctional (Nadagouda and Rajender 2008). Previously PdNPs were prepared through green methods using annona squamosa L peel extract (Roopana et al. 2012), banana peel extract (Ahok et al. 2010), cinnamom zeylanicum bark (Sathishkumar et al. 2009), broth of cinnamom camphora leaf (Yang et al. 2010) and gum acacia (Keerthi et al. 2011).

Xanthan gum (XG) is an extracellular polysaccharide secreted by the fermentation of the bacterium *Xanthomonas campestris* (Barrère et al. 1986). It is composed of pentasaccharide repeat units, comprising glucose,

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mannose, and glucuronic acid in the molar ratio 2.0:2.0:1.0 (Garcia-Ochoa et al. 2000). XG is used as a stabilizer, thickener and emulsifier. Due to its nontoxic and biocompatible properties, XG is widely used in food and pharmaceutical industries. In this paper, we report green synthesis of PdNPs using XG as both reducing and stabilizing agent without using any toxic chemicals. This reaction is carried out in an autoclave at a pressure of 15 psi and at 120 °C temperature for 10 min. This method is more efficient and rapid synthesis process compared to previously reported green methods mentioned above (Roopana et al. 2012; Sathishkumar et al. 2009; Yang et al. 2010) for the synthesis of Pd nanoparticles.

Nitro phenols are important chemical materials which are widely used to manufacture explosives, drugs, insecticides and dyes, and also used as corrosion inhibitors of woods and rubber chemicals (Zhang et al. 2011). In addition, 4-nitrophenol (4-NP) is an intermediate in the synthesis of many organic compounds. Since 4-amino phenol (4-AP) is a potent industrial intermediate in the manufacturing of many analgesic (Sandip et al. 2010). Thus, being a common precursor material for 4-AP, a newer and cheaper method for catalytic hydrogenation of 4-NP is always in demand. The catalytic activities of PdNPs are tested on the reduction reaction of 4-NP by NaBH₄. The reaction was studied by spectrophotometric methods. In the present study, we report the catalytic activity of green synthesized PdNPs towards 4-NP reduction.

Experimental

Materials

Palladium (II) chloride, HCl, 4-NP, xanthan gum and sodium borohydride were purchased from S D Fine-chem Limited, Mumbai, India.

Preparation of PdNPs

Solutions were prepared with double distilled water. 0.0356 g of PdCl₂ was accurately weighed and dissolved in 100 ml of HCl (0.000413 M) to form an H₂PdCl₄ aqueous solution. An aliquot of 5 ml of the aqueous H₂PdCl₄ solution was mixed with 5 ml of a 0.2 % aqueous solution of XG in a boiling tube. This reaction is carried out in an autoclave at a pressure of 15 psi and at 120 °C temperature by 10 min time.

Catalytic activity

To monitor the homogeneous catalysis of 4-NP reduction by PdNPs, UNICAM UV–3600 UV–visible

Spectrophotometer (UV–Vis) (Thermo Spectronic) was used. To a 3-ml cuvette containing freshly prepared sodium borohydride (1 ml, 15 mM) solution, 2 ml of 4-NP (0.2 mM) solution was added. After adding PdNPs stabilized in XG (10 μl) solution, cuvette was shaken vigorously for mixing and kept in UV–Vis spectrophotometer to examine the reaction.

Characterization

To study the formation of palladium nanoparticles, the UV–Vis absorption spectra of the prepared solutions were recorded using an UNICAM UV-3600 spectrophotometer (Thermo Spectronic). Fourier transform infrared (FTIR) spectra of PdNPs stabilized in XG and XG alone were recorded in KBr pellets using FTIR spectrophotometer (Bruker optics, Germany) and the scan was performed in the range of 400–4,500 cm⁻¹. X-ray diffraction (XRD) measurement of PdNPs stabilized in XG was carried out on X'pert Pro X-ray diffractometer (Panalytical B.V., Netherlands) operating at 40 kV and a current of 30 mA at a scan rate of 0.388 min⁻¹. The size and morphology of the nanoparticles were determined by TEM using TechnaiG2 under 200 kv.

Results and discussion

UV–visible analysis

Present studies focus on the synthesis of PdNPs using XG as reducing as well as stabilizing agent without using any toxic chemicals, which is purely green approach. The reaction was carried out in an autoclave at a pressure of 15 psi and at 120 °C temperature. The yellow colour reaction mixture was converted to the characteristic black colour after the autoclaving. The appearance of black colour indicates the formation of PdNPs nanoparticles (Keerthi et al. 2011). Figure 1 shows the absorption peak at 412 nm, corresponding to mixture of H₂PdCl₄ and XG. After autoclaving formation of PdNPs the peak at 412 nm disappears confirming the reduction of Pd (II) ions to Pd (0).

XRD analysis

The crystalline nature of resulting PdNPs synthesized can be seen in Fig. 2, in which all the peaks are clearly distinguishable. The broad peak at 39.73 is characteristics peak of the (111) indices of Pd (0) which is a face-centred cubic structure. Three other peaks at 2θ values of 46.09, 67.82, 81.52, 86.87 were observed corresponding to the major reflections of the (200), (220), (311), (222) crystal planes, respectively (Ramesh et al. 2012). Broadening of the diffraction peaks was observed

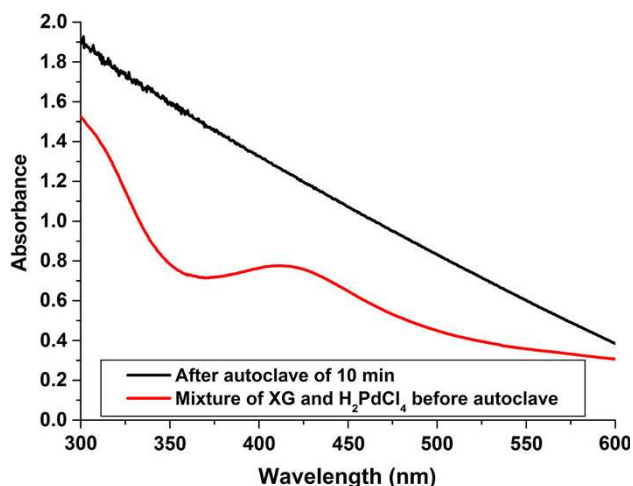


Fig. 1 UV–visible spectra of reaction mixture of H_2PdCl_4 and xanthan gum solution before and after autoclaving

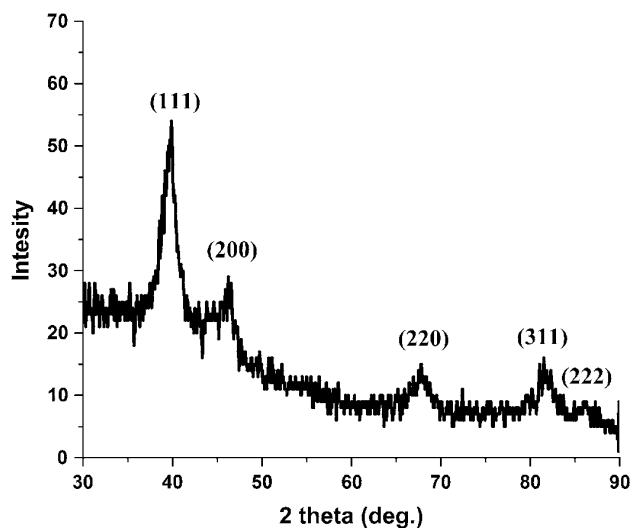


Fig. 2 Typical XRD pattern of the palladium nanoparticles stabilized in xanthan gum

owing to the effect of the nano-sized particles. The crystallite size of palladium nanoparticles is 10 nm which was calculated using peak broadening profile of (111) peak at 40° using Sherrer's formula given below

$$d = 0.94 (\lambda) / \beta \cos \theta$$

where λ is wavelength (1.5418 Å) and β is full-width half-maximum (FWHM) of corresponding peak. The calculated crystallite size of the synthesized palladium nanoparticles is 10 nm.

FTIR spectra analysis

FTIR analysis was used to identify the role of XG for the reduction and the capping of NPs surfaces. Figure 3 shows

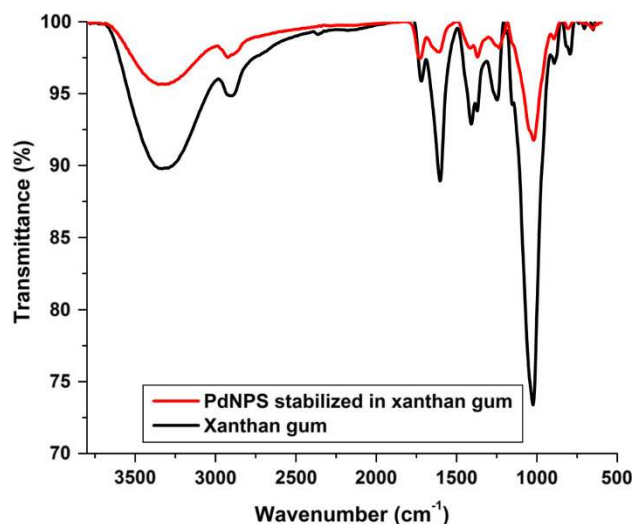


Fig. 3 FTIR spectra of palladium nanoparticles stabilized in xanthan gum and pure xanthan gum

FTIR spectrum of XG and PdNPs stabilized in XG. The major absorbance bands present in the spectrum of XG were at 3,334, 2,906, 1,719 and 1,603 cm^{-1} . The broad bands observed at 3,334 and 2,906 cm^{-1} could be assigned to the stretching vibrations of O–H groups and $-\text{CH}_2$, $-\text{CH}_3$ aliphatic groups in XG. The bands found at 1,719 and 1,603 cm^{-1} could be due to the characteristic asymmetrical stretch of carboxylate group and carbonyl group. The peak at 1,024 cm^{-1} is due to the C–O stretching vibration of alcoholic groups. The band at 3,334 cm^{-1} shifted to 3,320 cm^{-1} in the presence of PdNPs. These observations clearly show the interaction of Pd with the OH group of XG. The interactions among the resultant Pd nanoparticles and oxygen atoms of O–H, $-\text{COO}^-$ and $-\text{CO}$ become stronger. This can lead to corresponding changes both in the positions and in the strengths of FTIR spectra of XG. The variations in the shape and peak positions of the $-\text{OH}$ stretching vibration, $-\text{COO}^-$ group, $-\text{CO}$ group and $-\text{OH}$ bending vibration at 3,334, 1,719, 1,603 and 1,024 cm^{-1} , respectively, are observed, because of the contribution of XG towards the reduction and stabilization process (Venkatesham et al. 2014).

TEM analysis

The size distribution, shape and morphology of the PdNPs stabilized in XG were studied by high-resolution transmission electron microscopy. The TEM image of PdNPs stabilized in XG is shown in Fig. 4a. The TEM image shows that the PdNPs are spherical and are well distributed in the gum polymer matrix. To obtain size distributions of PdNPs, approximately 38 particles were counted and then converted into histograms. Figure 4b presents a histogram

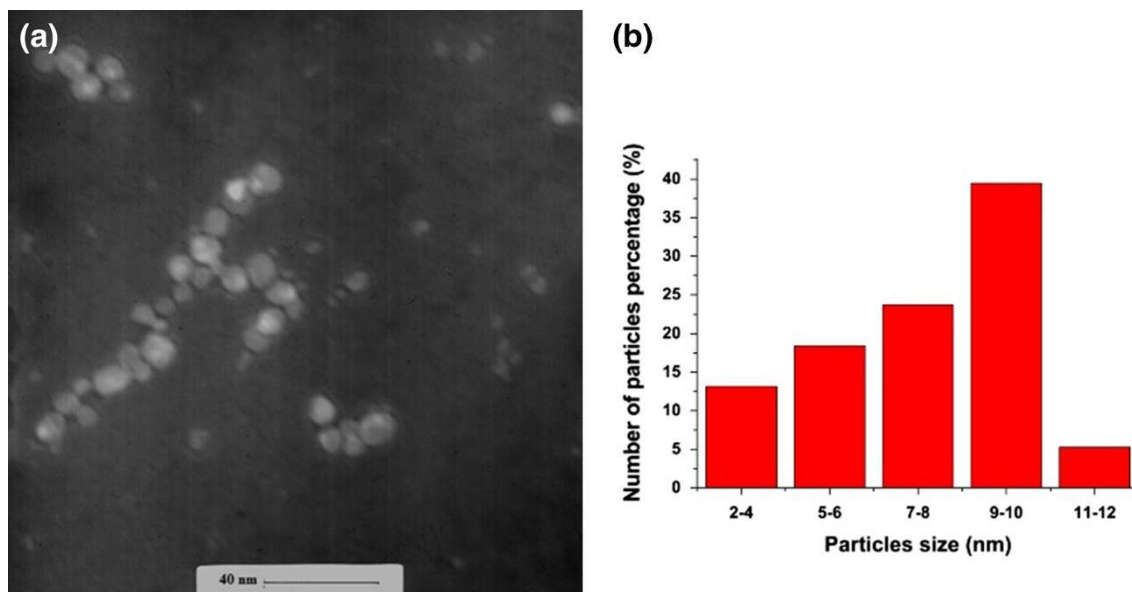


Fig. 4 **a** Typical TEM image of PdNPs in aqueous system using xanthan gum as reducing and stabilizing agent. **b** Histogram showing the size distribution of PdNPs

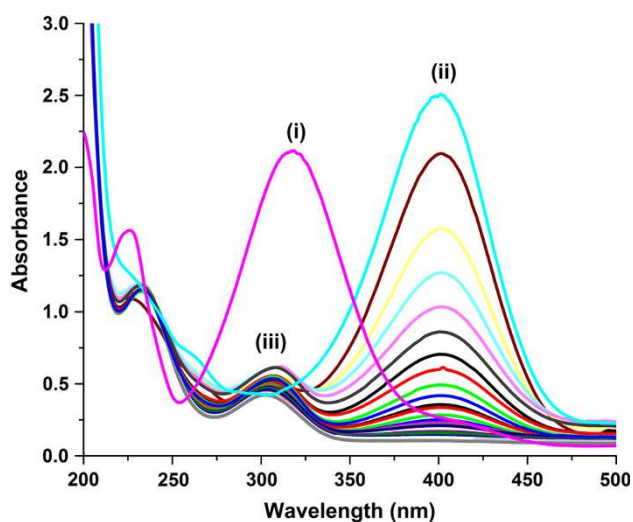


Fig. 5 UV-visible spectra of *i* 4-nitrophenol, *ii* successive reduction of nitrophenolate ion with a time interval of 1 min, and *iii* 4-aminophenol

of the particle size distribution of PdNPs. Most of the particles were in the size around 10 nm.

Catalytic reduction of 4-nitro phenol

As Pd is recognized to be an excellent catalyst for hydrogenation reactions, we tried the PdNPs stabilized in XG for the reduction of 4-NP to 4-AP using borohydride. In a typical catalytic reaction, freshly prepared NaBH₄ (1 ml, 15 mM) solution, taken in a 3-ml cuvette, was added to the aqueous 4-NP solution (2 ml, 0.2 mM). The 4-NP shows

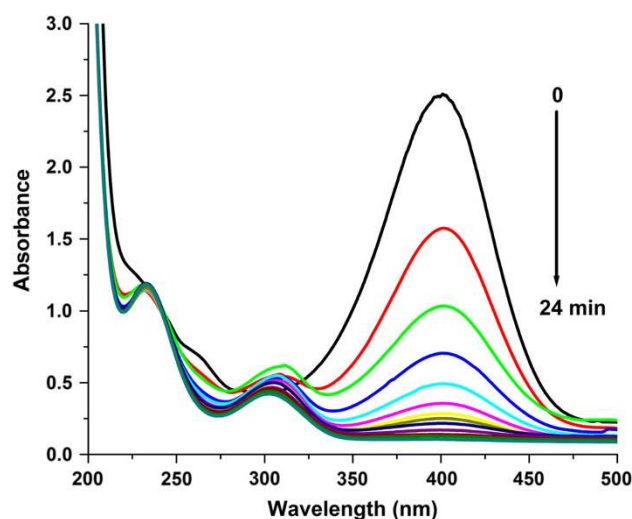


Fig. 6 The conversion percentage of 4-nitrophenol to 4-aminophenol with time

an absorbance peak at 317 nm, which shifts to 400 nm (red shift) in the presence of NaBH₄ due to the formation of 4-nitrophenolate ion (Fig. 5). In the absence of catalyst, the 4-nitrophenolate ions cannot be reduced further, even in the presence of strong reducing agent like NaBH₄ (Venkatesham et al. 2014). However, immediately after adding 10 μl of PdNPs to the reaction mixture, the intensity of the absorbance band at 400 nm successively decreased with increasing reaction time. At the same time a new band with increased absorbance intensity appears at 300 nm, which is known to be due to absorption of 4-AP.

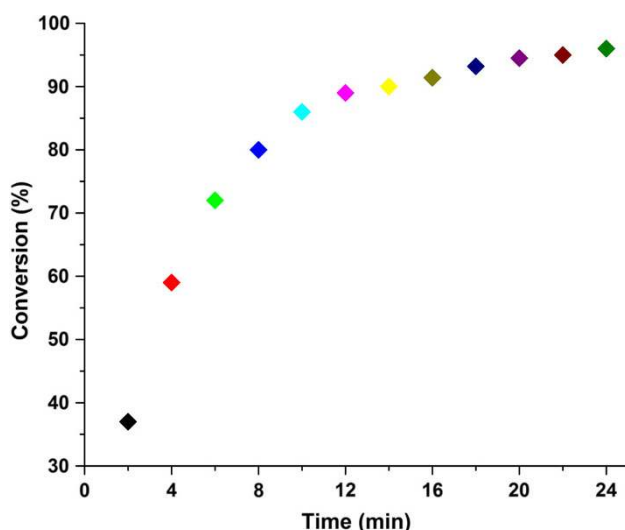


Fig. 7 Reduction of UV–Vis spectra of 4-nitrophenol using PdNPs stabilized in xanthan gum with time of interval 2 min

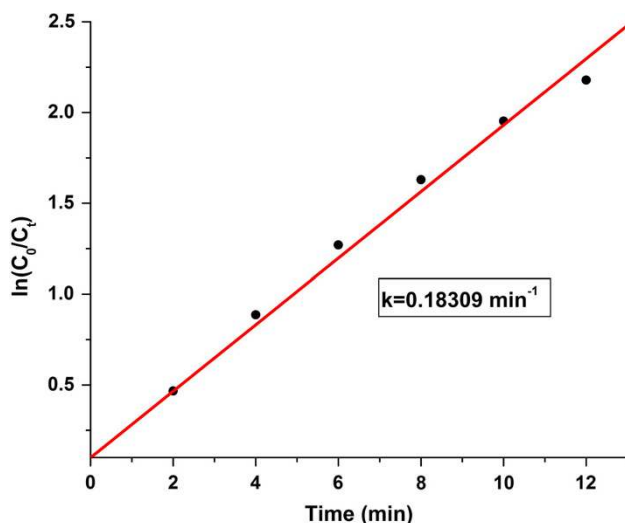


Fig. 8 The plot of $\ln C_0/C_t$ versus time for the reduction of nitrophenol to aminophenol

The absorbance at time $t = 0$ (A_0) and at t (A_t) is proportional to the initial concentration C_0 and concentration at time t (C_t) of 4-NP, respectively. The conversion percentage (α) of 4-NP to 4-aminophenol was calculated by the formula:

$$\alpha = \frac{(C_0 - C_t)}{C_0} \cdot 100.$$

The conversion percentage of 4-NP to 4-AP is shown in Fig. 6.

It has been found that the reduction of 4-NP to 4-AP by sodium borohydride in the presence of PdNPs as catalyst follows pseudo first-order rate equation with respect to 4-NP; the concentration of sodium borohydride was too high

as compared to 4-NP. So, concentration of sodium borohydride was considered constant throughout the reaction. UV–Vis spectra of successive reduction of 4-NP to 4-aminophenol using PdNPs stabilized in XG with time interval of 2 min are shown in Fig. 7. The rate equation can be written as

$$k = \frac{\ln(C_0/C_t)}{t}.$$

Figure 8 shows a good linear correlation of $\ln(C_0/C_t)$ versus time and the rate constant of the reaction is obtained as 0.18309 min^{-1} for PdNPs stabilized in XG.

Conclusions

The present study reports the green the synthesis, characterization and catalytic evaluation of PdNPs from aqueous H_2PdCl_4 solution using XG. The adapted method is compatible with green chemistry principles as the XG serves as a matrix for both reduction and stabilization of the PdNPs synthesized. The PdNPs stabilized in XG exhibited a very good catalytic activity and the kinetics of the reaction was found to be pseudo first order with respect to the 4-NP.

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