



Heterogeneous Catalytic Degradation of Nitro-aromatic Compound using Highly Defect Spongy Surface Palladium Nanocatalyst

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ABSTRACT

Palladium nanoparticles (PdNPs) were successfully grown on an indium tin oxide (ITO) surface using a one-pot liquid phase deposition method. After the growth for 2 h, thick coat of PdNPs was observed on the ITO surfaces. Palladium nanoparticles exhibited spherical fibrous crystal-like appearance and tend to stick with each other and form flower like structure. After successful synthesis PdNPs were effectively applied as catalyst for degradation of Nitro-aromatic compound.

1. Introduction

Nitroaromatic compounds are widely used in the manufacturing of pharmaceuticals, pigments, dyes, plastics, pesticides and fungicidal agents, explosives and industrial solvent [1-2]. However, these compounds are highly hazardous on release in environment and have potential toxicity toward humans, animals and plants. United States Environmental Protection Agency (US-EPA) has listed out 129 organic chemicals, which are carcinogens and perilous to human beings as well as the environment. Among these, 4-nitrophenol (4-NP) is one of the organic pollutants, which is extensively used for the synthesis of drugs, dyes, insecticides and herbicides. Since it is readily soluble in water, 4-NP is abundantly present in the industrial effluents, soil and air. Further, it damages mitochondria and inhibits energy metabolism in human and animals [3]. 4-nitrophenol is stable in the environment and resists biodegradation. Therefore, it is highly desirable to develop the environmentally clean technology for treating such compounds in aqueous medium [4]

Nanoparticles have gained much attention for catalysis in recent years because of their high surface-to-volume ratios and unique electronic and surface properties [5-7]. Many reports are available on the application of metal nanoparticles as catalysts for the many organic reactions

and reduction of nitrophenols in the presence of NaBH₄. Au, Ag, Pd and Pt nanoparticles are most commonly used as efficient catalysts [8-15].

Palladium (Pd) is one of the important noble metals and since two decades extensively investigated by the scientist due to its potential applications in a broad range of scientific areas. Nanoscale palladium particles are useful and have drawn particular attention due to their electronic properties and for catalytic purposes [11, 16-20]. Recently a lot of research has been devoted to the preparation methods of PdNPs in solution phase [21-24]. In addition, shape-controlled wet synthesis of unique PdNPs, i.e. nanocubes and nanoplates, has been reported [25-26].

The fact that the catalysts is in a distinct phase with respect to the reaction medium, accounts for the major advantage of the heterogeneous catalysts over the homogenous as it makes the separation and re-utilization of heterogeneous catalysts simple and cheap compared to the homogenous catalysts [27].

Use of Pd nanoparticles as heterogeneous or semi-heterogeneous catalysts for C-C coupling reactions, such as Mizoroki- Heck, Suzuki-Miyaura and Sonogashira reactions, have been described in the literature [5, 28-37].

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We report, one-pot method of direct growth of solid highly energetic Pd nanoparticles on ITO substrate utilizing simple and efficient Liquid Phase Deposition (LPD) procedure. The crystal structure and morphology of Pd nanoparticles was confirmed by XRD and field-emission transmission electron microscopy, respectively.

2. Experimental

2.1 Materials

All the chemicals were purchased from the indicated companies and utilized as received without any further purification. Sodium dodecyl sulfate (Fluka), K_2PdCl_6 (Fluka) and formic acid 99.9% (Fluka). ITO-coated glass with the sheet resistance of 9-22 Ω per square was obtained from VinKarola instrument USA. Deionized water employed (conductivity 0.050 $\mu S/cm$) obtained utilizing a Milli-Q purification system.

2.2 Synthesis of Palladium Nanoparticles

Liquid Phase Deposition method is applied to prepare palladium nanoparticles as reported in our previous article [11]. ITO coated glass substrate was cleaned with acetone and ethanol in sequence through 30 minutes in ultrasonic bath and dried with continuous nitrogen flow.

In typical procedure, cleaned ITO substrate was dipped into the bottle containing 15 mL aqueous solution of precursor Pd salt, Sodium dodecyl sulfate (SDS) and formic acid. The growth process was carried out at optimized conditions e.g. 10 mM SDS, 0.5 mM Pd and 1.0 mM formic acid. The solution was continuously stirred during the growth process. The time for growth is about 2 hours and after 2 hours a homogenized black thick film appeared on the ITO surface. Then the coated substrate was washed with plenty of deionized water and afterward dried with nitrogen flow at room temperature.

Thereafter the morphology of particles including shape and particle size was investigated by Zeiss Supra 55VP field emission SEM. X-ray diffraction (XRD) was performed to study the crystallinity of nanoparticles employing Bruker D8 system with a $CuK\alpha$ irradiation. The machine was operated at a scanning rate of 0.025°/s and at 30 kV.

2.3 Heterogeneous Catalytic Application

The catalytic property of the PdNPs was evaluated by the degradation of nitroaromatic compound i.e. 4-Nitrophenol using small amount of sodium borohydride as hydrogen source under ultra sonic waves. In typical procedure, the porous Pd-NPs coated ITO substrate was introduced into a glass vial containing 15 mL of mixed-aqueous solution of 0.005 mol L^{-1} of 4-Nitrophenol and 1.0×10^{-4} mol L^{-1} sodium borohydride. The solution was continuously irradiated under sonication during the reaction for 5 min. To obtain the catalytic effect of the Pd NPs in the reduction of 4-Nitrophenol, absorption

spectrum of the solution was recorded every 15 seconds time by taking approximately 3 mL portion of the solution. The results of 4-Nitrophenol degradation to 4-Aminophenol are shown in Fig. 4. The solution was transferred into a quartz cuvette for absorption spectrum measurement using a Biochrom Libra S22 UV-Visible spectrophotometer. Reduction reaction was continued for 5 min.

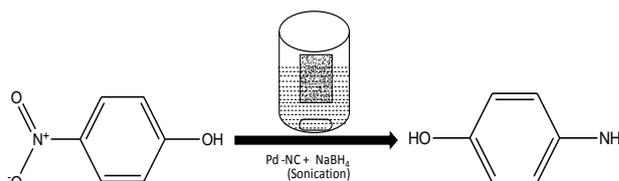


Fig. 1: Catalytic degradation of 4-Nitrophenol

3. Result and Discussion

A successful growth of highly defect spongy surface palladium nanocatalyst was obtained by LPD process using formic acid as reducing agent in presence SDS surfactant system on ITO substrate. After 2 hours reaction a homogenized black thick film is formed on the surface of transparent ITO substrate. The structure and shape is confirmed by FESEM image as shown in Fig. 2.

As shown in Fig. 2 shape controlled Pd nanoparticles are obtained with particle size of about 10-30 nm. It can be observed in FESEM image, that well distributed and high density Pd nanocrystals are grown with rough surface. High magnification FESEM image Fig. 2(B) shows that nanospheres are composed of small clusters which could be due to high energy surface of Pd-particles. Pd NPs appeared as flower like structure having fibrous and rough morphology, it is probable to have an improved mobility of charge carriers to different reaction position and more effective reaction approach can be achieved by two ways e.g. (a) process of interaction between reacting species and intermediates created from the diverse crystal planes involved in a short range region (b) the steric environment provided by different (111) planes sharing common boundaries and its effect on the surface coverage of the catalyst. High resolution FESEM image (Fig. 2B) further confirms that palladium (Pd) nanocrystals grown on the ITO surface have irregular shapes with rough surfaces. After FESEM image analysis of the synthesized nanostructures the elemental composition was checked by Energy Dispersive X-Ray Spectroscopy (EDX). Fig. 2 C represents the EDX spectrum of PdNPs deposited on ITO slide. This figure shows the prominent and intense peaks of five elements palladium, indium, tin, oxygen and carbon. Peaks of indium, tin and oxygen corresponds to the ITO substrate and carbon peak which came from the sample support carbon tape. This confirmed that our sample is highly pure and free from any sort of impurities.

Afterward the crystallinity was confirmed via X-ray diffraction and the results are shown in Fig. 2. Two main peaks at 38.38 and 45.15 degrees are the reflection of plane (111) and (200), respectively.

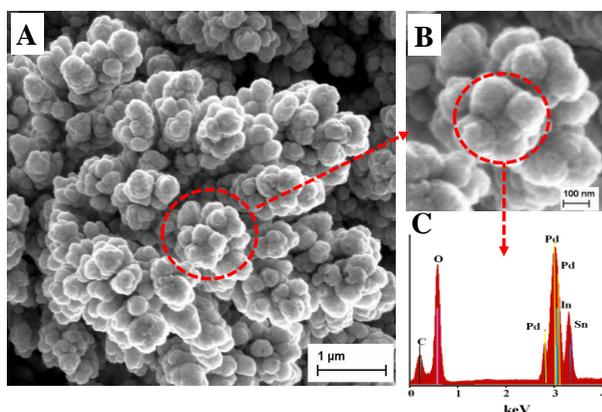


Fig. 2: A and B is Low and high-resolution FESEM image of Pd-Nanocatalyst respectively. (C) EDX spectrum of Pd-Nanocatalyst

The main characteristic peak of Pd (200) at 45.15 degree validates the successful reduction of Pd metal complex to Pd. This diffraction spectrum was found to agree well with JCPDS card No. 05-0681 for fcc Pd crystal. Therefore, the present treatment is considered as a practical method to gather Pd nanocrystals on the supporting material with high density.

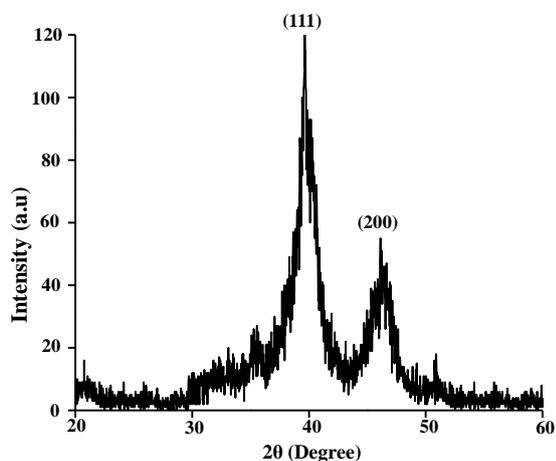


Fig. 3: XRD pattern of Pd-nanocatalyst

After successful synthesis, the Pd nanostructures were applied for the catalytic degradation of Nitro-aromatic compounds due to the large surface area or porous characteristics under sonication. Fig. 4 shows the results of 4-nitrophenol degradation to 4-aminophenol. The complete degradation was achieved in about 2 minutes of reaction time. Decrease in absorbance at 400 nm was observed as the Pd-NPs catalyst was introduced in the solution and the new peak at 300 nm was appeared. Peak

at 300 nm corresponds to the production of 4-aminophenol from the degradation of 4-nitrophenol. As the degradation proceed further the peak at 400 nm decreases while the peak at 300 nm increases. Sonication also appeared to significantly activate the reduction for 4-nitrophenol to 4-aminophenol along with catalyst by reacting rapidly with hydrogen source and resulting in 99 % reduction. The known surface cleaning effect of ultrasonic waves may explain the beneficial effect of ultrasounds [38]. Since the in situ generation of hydrogen is a very important part of the reaction mechanism. Sodium borohydride is used in very small amount as source of hydrogen because the 4-nitrophenol reduction depends only on the concentration of 4-nitrophenol and it is independent of the concentration of NaBH_4 .

Hence the resultant Pd nanocatalyst possess a unique large surface area, an extremely high aspect ratio, high mechanical strength, and excellent durability and therefore exhibit remarkably high and stable catalytic activity toward the reduction of 4-NP as shown in Fig. 4. These features, coupled with the simplicity of the process shows the suitability of the method for large-scale degradation of Nitrophenol.

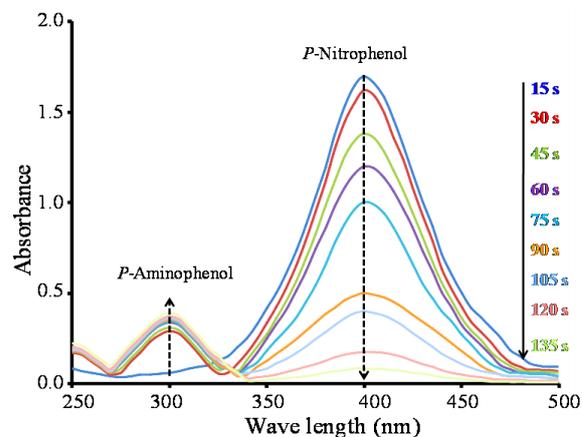


Fig. 4: Optical absorbance of 0.005 mol L^{-1} 4-NP during the photocatalytic degradation under sonication using $1.0 \times 10^{-4} \text{ mol L}^{-1}$ sodium borohydride as hydrogen source and in the presence of one slide of ITO containing Pd-nanocatalysts.

3.1. Investigation of Kinetics and Reaction Mechanism

Two models namely Pseudo first order and Pseudo second order were applied to investigate the kinetics rate/order of reaction of heterogeneous catalytic degradation of 4-Nitrophenol.

Pseudo first order Eq. (1) and pseudo-second order Eq. (2) models are expressed as follows:

$$\ln(q_e - q_t) = \ln q_e - \frac{k_1 t}{2.303} \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

where q_t and q_e are the amount of reactants (mg g^{-1}) at time ' t ' and at equilibrium, k_1 is the rate constant of the pseudo-first order process (min^{-1}). Straight line plots of $\ln(q_e - q_t)$ against t were used to determine the rate constant k_1 , and adsorption capacity (Fig. 5). Whereas the plots of t/q_t versus t in equation (2) for pseudo-second order kinetics did not give a straight line. Good straight lines ($R^2 = 0.990$) was achieved in pseudo-first order as compared to the plot of pseudo-second order ($R^2 = 0.628$). As the pseudo first order model data fall on the straight line, it is concluded from these results that the heterogeneous catalytic process on Pd-NPs follow pseudo-first order kinetics.

Therefore it was concluded that the pseudo first order kinetic model provided a better correlation for the adsorption of reactants molecule on Pd NPs with rate constant $k = 5.51 \times 10^{-1}$ at different initial concentration compared to the pseudo second order model.

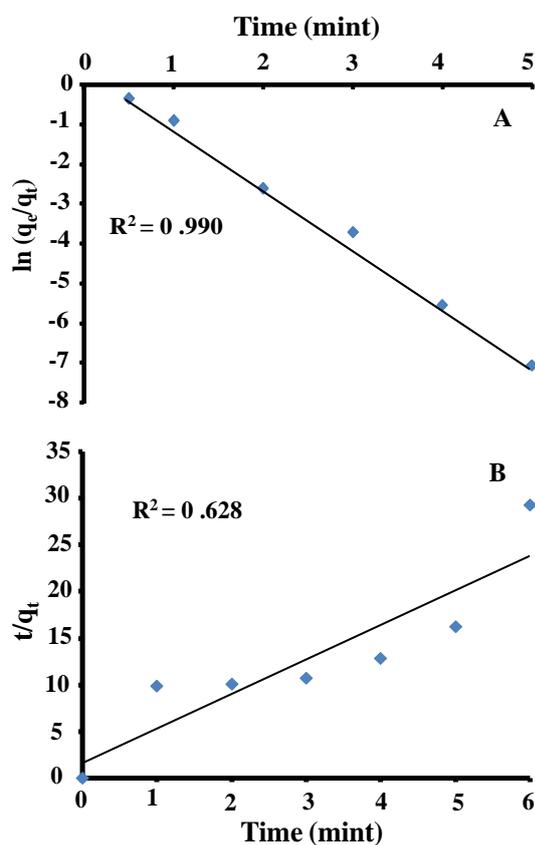


Fig. 5. Catalytic degradation kinetic rate of 4-NP over Pd-nanocatalyst. (A) Pseudo first order (B) Pseudo second order

3.2 Reusability of Catalyst

After successful application of palladium nanocatalyst for degradation of 4-nitrophenol, the catalyst efficiency was checked for next fresh reaction. In typical protocol, the ITO substrate containing Pd nanocatalyst was take out from first reaction vessel, washed with deionized water

and dried under nitrogen atmosphere. For 2nd cycle of catalyst the fresh solutions of 4-nitrophenol were taken into the reaction flask and the same procedure was followed as discussed in section 3. After the completion of reaction it was observed that 97% reduction is achieved in second cycle of the catalyst. Afterward the catalyst was consecutively applied for 3rd and 4th cycle in fresh 4-nitrophenol reduction reaction. It is examined that, the Pd nanocatalyst degradation efficiency was slightly decreased (92.6 and 85.0%) in 3rd and 4th cycle, respectively as shown in Fig. 6.

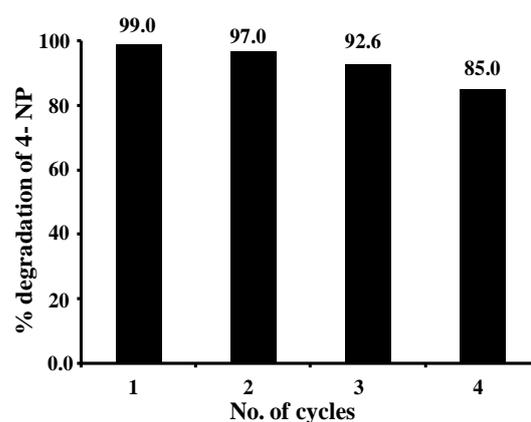


Fig. 6: Reusability of Pd-nanocatalyst for degradation of 4-Nitrophenol.

4. Conclusion

High-efficiency heterogeneous catalytic degradation of 4-nitrophenol has been demonstrated using spongy-porous palladium nanocatalyst grown on ITO substrate. The system effectively degrade 4-nitrophenol and convert to the 4-aminophenol with a degradation yield as high as 99 % in a reaction time of 2 minutes. The highly porous and spongy structure with high surface defect is considered a major factor for the excellent performance of the nanocatalyst in this heterogeneous process.

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