Role of palladium precursors in morphology selective synthesis of palladium nanostructures

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ABSTRACT

In this study, the role of various palladium precursors for morphology selective synthesis of palladium nanomaterials in aqueous medium was investigated. Based on the different types of palladium precursors, we achieved the formation of rod shaped, spherical and fern leaf like morphologies of Pd nanomaterials. The reaction time for the synthesis of Pd nanostructures is relatively less as compared to the other existing methods. These Pd nanomaterials were characterized using X-ray diffractometer (XRD), field emission gun-scanning electron microscopy (FEG-SEM), energy dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) techniques. The XPS analysis confirms that Pd(II) was completely reduced to Pd(0) state. Furthermore the application of as synthesized Pd nanomaterials was tested for Suzuki cross-coupling reaction and it provides good catalytic activity for Suzuki reaction with the reusability of nanocatalyst.

1. Introduction

The syntheses of size and shape selective nanocrystals are fundamental to modern science and technology. The size and shape selectivity is most sensitive to the packing of atoms on the surface or the exposed facets of nanocrystals. The selective morphology of nanomaterials brings drastic changes in its physical and chemical properties. The attention of nanocrystals particularly palladium nanoparticles (Pd NPs) has been growing steadily in current research due to their potential tunability in terms of fascinating properties and catalytic activity [1]. Pd NPs are interesting because of their widespread applications in photonics, electronics and biomedical sensing [2], magnetizations and water treatment [3], surface enhanced Raman scattering and electrocatalysis [4], and heterogeneous catalysis [5,6].

Researchers have carried out the synthesis of Pd NPs using various methods such as chemical reduction [7], electrochemical method [8], sonochemical method [9], using solar energy [6], using supercritical CO_2 [10], and biological method [11]. However, most of these methods have some disadvantages like the use of harsh synthesis conditions like high temperature and pressure, use of toxic reagents and excess chemicals for synthesis, need of specialized instruments, long reaction time and requirement of external additives during the reaction. Hence, there is a need to develop the facile, rapid and convenient method for

the synthesis of Pd nanostructures. Recently, we have developed simple and economic methods for the synthesis of shape and size selective nanoparticles [12–16]. In current protocol we have synthesized morphology selective various Pd nanostructures with different Pd precursors using PEG-6000 as a stabilizing agent and hydrazine hydrate as a reducing agent. In literature, Nagaraju et al. reported the synthesis of graphene–palladium nanocomposites using hydrazine hydrate as reducing agent [17]. Kalbasi and Mosaddegh demonstrated the Pd-poly(N-vinyl-2-pyrrolidone)/KIT-5 nanocomposite using hydrazine hydrate [18]. Tang et al. synthesized poly(acrylic acid)-$Pd^{(0)}$ composite films using hydrazine hydrate [19], but these protocols have one or more of the same drawbacks as mentioned above.

Chemical reduction in aqueous medium is a simple, versatile and economic method for the synthesis of nanoparticles. In chemical synthesis, metal salt is reduced by a reducing agent forming a metal nucleus and the growth of the nucleus to a particle is controlled by a capping agent who also prevents aggregation by steric hindrance or electrostatic repulsion. The main objective of this work was to investigate the effect of various Pd precursors on the morphology of Pd nanomaterials. We report a facile, rapid and inexpensive synthesis of rod shaped, spherical and fern leaf like morphologies of Pd nanostructures using different Pd precursors via chemical reduction using PEG-6000 as a stabilizing agent and hydrazine hydrate as a reducing agent in aqueous medium. PEG-6000 helps to prevent the agglomeration and control the crystal morphology of Pd nanoparticles. Although several reports are available on Pd nanomaterial synthesis, there is no report on the study of the role of various palladium precursors to obtain different Pd nanostructures with various morphologies.

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2. Experimental section

2.1. Materials

The palladium precursors like palladium acetate, [Pd(OAc)$_2$], palladium chloride [PdCl$_2$], and palladium bromide [PdBr$_2$] were purchased from Parekh Industries Ltd. Mumbai, India. Polyethylene glycol (PEG-6000) and hydrazine hydrate (100%) were purchased from S. D. Fine chemicals Pvt. Ltd. India. All chemicals were pure and used without further purification.
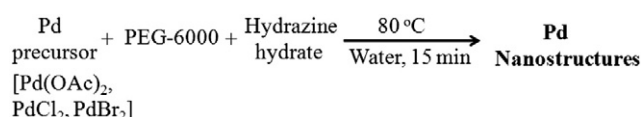
2.2. Synthesis of Pd nanostructures

In a typical synthesis, mixtures of 20 mg of Pd(OAc)$_2$ and 40 mg of PEG-6000 were dissolved in 5 mL distilled water. The obtained mixture was stirred for 5 min at 80 °C. Hydrazine hydrate (300 μL, 100%) was added drop wise in the above mixture and stirred for 10 min at 80 °C (Scheme 1). After completion of reaction, the color of the reaction mixture changes to black indicating the formation of Pd NPs. The product was deposited at the bottom of the reaction flask and separated by decanting the reaction solvent. The product was washed with distilled water and absolute ethanol several times and dried at 60 °C for 1 h in oven. The same procedure was repeated for PdCl$_2$ (20 mg) and PdBr$_2$ (20 mg) for the synthesis of Pd nanostructures.

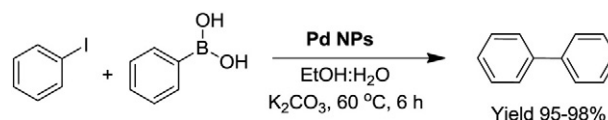### 2.3. Characterization of Pd nanostructures

The synthesized Pd NPs were characterized by X-ray diffractometer (Shimadzu XRD-6100 using Cu Kα radiations = 1.5405 Å) with a scanning rate of 2°/min and 2 theta (θ) angle ranging from 20° to 80° with current 30 mA and voltage 40 kV. The morphology of the samples was examined using field emission gun-scanning electron microscopy (FEG-SEM) analysis on Tescan MIRA 3 model with secondary electron (SE) detector between 10.0 kV and 20.0 kV and transmission electron microscopy (TEM) using Philips CM-200, operating voltage at 200 kV. The energy dispersive X-ray spectrum (EDS) was recorded using INCA x-act Oxford instrument (Model 51-ADD0007). X-ray photoelectron spectrum (XPS) was monitored by using PHI 5000 versa probe scanning ESCA microprobe. Gas chromatography (GC) was done on Perkin Elmer Clarus 400 equipped with a capillary column (Elite-1, 30 m × 0.32 mm × 0.25 μm) and a flame ionization detector (FID). Gas chromatography–mass spectrometry (GC–MS) was performed on Shimadzu GCMS-QP 2010 instrument (Rtx-17, 30 m × 25 mm ID, film thickness 0.25 μm df) with column flow − 2 mL/min, 80 °C to 240 °C at 10°/min rise).

2.4. Typical procedure for Suzuki cross-coupling reaction

In a typical synthesis, 10 mL sealed tube was charged with iodobenzene (1 mmol), phenylboronic (1.2 mmol), K$_2$CO$_3$ (1.5 mmol), Pd NPs (1 mol%, 1.06 mg) in EtOH:H$_2$O (1:1, 2 mL) as a solvent. The reaction mixture was stirred at 60 °C for 6 h (Scheme 2). After completion of the reaction, the reaction mixture was poured onto 15 mL water and the product was extracted with ethyl acetate (3 × 10 mL). The reaction solvent was dried over Na$_2$SO$_4$ and evaporated under vacuum. The product was confirmed by GC and GC–MS analyses and compared with literature data.

Scheme 1. Synthesis of Pd nanostructures in aqueous medium.

Scheme 2. Various Pd nanostructures catalyzed Suzuki cross-coupling reaction of iodobenzene with phenylboronic acid.

3. Results and discussion

3.1. Characterization of Pd nanostructures

The general representation for the synthesis of Pd nanostructures was shown in Scheme 1. The phase identification of Pd nanomaterials was carried out using an X-ray diffractometer (Fig. 1). The XRD spectrums of Pd nanomaterials synthesized using Pd(OAc)$_2$, PdCl$_2$ and PdBr$_2$ as precursors are shown in Fig. 1a, b and c respectively. All XRD pattern shows diffraction peaks at 2 theta values in the region of 40°, 47°, 68°, 82° and 87° which correspond to the (111), (200), (220), (311), and (222) phases for Pd nanomaterials. The obtained results from XRD confirm the formation of Pd NPs and are in good agreement with JCPDS card 05-0681 of Pd NPs [4].

The morphological analysis of Pd nanostructures was carried out by FEG-SEM and TEM analyses. Fig. 2 shows the FEG-SEM and TEM analyses of Pd NPs synthesized using Pd(OAc)$_2$ as a precursor. FEG-SEM images clearly indicate the size and shape of the nanoparticles synthesized
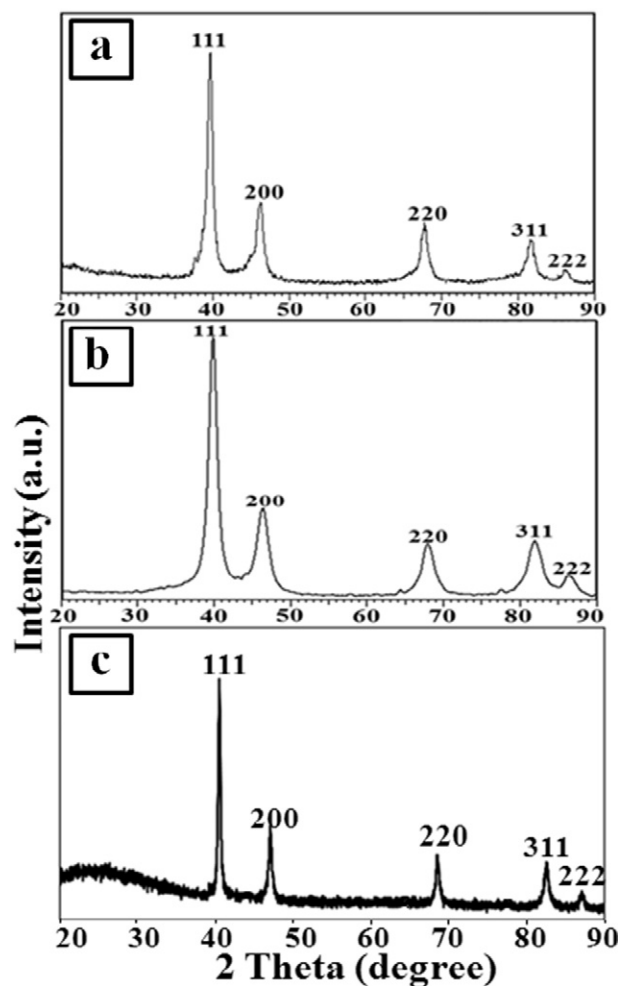
Fig. 1. XRD pattern of Pd NPs synthesized from (a) Pd(OAc)$_2$, (b) PdCl$_2$, and (c) PdBr$_2$ precursors.