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High catalytic activities of palladium nanowires synthesized using liquid crystal templating approach

Mohit Chawla, Raj Kumar, Prem Felix Siril *

School of Basic Sciences and Advanced Materials Research Centre, Indian Institute of Technology Mandi, Mandi 175005, Himachal Pradesh, India

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ABSTRACT

Synthesis of palladium (Pd) nanoparticles of various morphologies using swollen liquid crystalline (SLC) phases as structure directing templates is described in the present paper. The Pd precursor, bisdibenzyledene acetone palladium ($Pd(DBA)_2$) was dissolved in the oil phase of a hexagonal lyotropic liquid crystalline phase. The characteristic nature of the hexagonal mesophase was confirmed using polarized optical microscopy. The hexagonal mesophases were exposed to hydrogen gas for the synthesis of Pd nanoparticles. The nanomaterials were characterized using UV–vis spectroscopy, X-ray diffraction (XRD) and transmission electron microscopy (TEM). These nanowires showed very good catalytic activity for reduction of 4- nitrophenol to 4-aminophenol when compared to the spherical Pd nanoparticles. A comparative study revealed that the catalytic activity of the nanowires was much better than even very small Pd nanoparticles that are reported in the literature. The nanowires also had a very good catalytic activity in Suzuki-Miyaura coupling reactions for the synthesis of biphenyl even using aryl chlorides as reactant.

1. Introduction

Nanostructured metals are gaining importance due to their potential applications in catalysis, sensing, electronics and optics [1–4]. The morphology controlled synthesis of metallic nanomaterials for different applications such as catalysis and electro-catalysis is very important as their activity strongly depends on the size and shape [5]. Thus, synthesis of shape and size controlled nanomaterials is being explored in order to enhance the performance of catalysts [6,7]. Pd nanostructures have attracted considerable attention in research concerned with noble metals over the last decade [8–11]. They can be employed as highly efficient nanocatalysts [12–15], bio/chemical sensors [16–20], hydrogen storage media and switches [21,22]. Pd nanostructures have very good catalytic activities in hydrogenation [14], carbon–carbon coupling [23–25], electrochemical oxidation and reduction reactions [26–28] and reduction of automobile pollutants [29]. Recently, it was found that Pd nanoparticles can catalyze organometallic reactions in living cells without interfering with native biochemical processes [30]. Morphology controlled syntheses of Pd nanostructures has been investigated extensively [31–38]. There are numerous reports on the synthesis of different Pd nanostructures viz. spherical nanoparticles [31,32], nanoballs [33], nanowires [34–36], nanosheets [37] and mesoporous ball-shaped structures [38]. The possibility to synthesize Pd nanostructures with a variety of shapes provides an opportunity to systematically evaluate their electrical, plasmonic, and catalytic properties. The present work describes a template assisted sysntheis of Pd nanowires and detailed studies on their catalytic activities vis-à-vis Pd nanoparticles of other morphologies.

One of the most widely used model reactions in the evaluation of nanomaterials as catalysts is the conversion of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) by sodium borohydride [39–41]. Nitrophenols are hazardous waste and priority pollutants which are generated or released from agricultural and industrial manufacturers. The conversion of nitrophenols to aminophenols is vital because aminophenols are one of the major starting materials for photography, pharmaceutical and chemical dye industries [42,43]. Moreover, this reaction is considered to be a model reaction because there are no byproducts formed. The presence of an isosbestic point in the Ultraviolet (UV)-visible absorption spectrum suggests that there is only one reaction product observed in solution [44]. The reaction gained interest because it is easy to monitor the progress with simple spectroscopic techniques such as the UV–vis absorption spectroscopy or stopped flow. Recently, Clergeaud et al. reported the synthesis of ultra small monodispersed Pd nanoparticles via polyol using 1-glycerol as both reducing

* Corresponding author.
E-mail addresses: prem@iitmandi.ac.in, spfelix@yahoo.com (P.F. Siril).

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and stabilizing agent and proved that their Pd nanoparticles are catalytically active in the reduction of 4-NP [45].

Pd as a catalyst also plays a crucial role in C—C coupling reactions like Suzuki-Miyaura, Heck, Stille and Sonogashira [24,46–49]. Suzuki-Miyaura coupling reaction has become one of the most influential methods for the synthesis of biaryls which constitute a wide range of natural products and pharmaceutical drugs [50,51]. The Pd nanowire was found to have very good catalytic activity for the Suzki-Miyaura coupling reaction. Most of the studies on the catalytic activities of Pd nanoparticles are limited to assessing the effect of particle size, composition modification using alloying or core shell nanostructure formation and presence of stabilizing agents [52–58]. However morphology of the catalyst can often lead to interesting enhancement in catalytic activities [59]. Hence, the effect of morphology of the Pd nanoparticles on their catalytic activities was studied by preparing Pd nanoparticles having different morphologies and the results are presented in this paper.

Walter et al. synthesized electrodeposited Pd nanowires for hydrogen gas sensing [60]. There are a number of other reports on the synthesis of Pd nanowires for electrocatalytic applications [35,61–64]. Teng et al. successfully synthesized ultrathin Pd nanowires and studied their magnetic properties [65]. Gao et al. prepared Pd nanowires in thiol functionalized ionic liquids for Sonogashira coupling reactions having 100% conversion up to 2nd cycle [66]. Jiang et al. prepared nanocontact induced Pd nanowires for Suzuki coupling reactions [67]. Chen et al. synthesized seed-mediated Pd nanorods for Suzuki coupling reactions [68]. Here we report a facile synthesis of Pd nanowires in hexagonal mesophases and the catalytic behavior of the synthesized nanowires for 4-NP reduction and Suzuki-Miyuara coupling.

Worm-like cylindrical micelles that are formed by the self-assembly of highly concentrated surfactant solutions in water can be assembled further to form mesophases. The diameter of the surfactant cylinders can be varied by tuning the oil to water ratio, ionic strength of salts in the aqueous medium and the concentration of the co-surfactant [69,70]. Hence, the mesophase assembly is called 'swollen' liquid crystals. Due to their ordered assembly and the tight confinement provided by SLCs, they can be used as versatile 'soft' templates for the synthesis of nanostructures of noble metals and polymers [31,35–37,70,71]. The Pd nanowires were synthesized in the oil phase of the mesophase by decomposing the dissolved $Pd(DBA)_2$ salt using hydrogen gas. The prepared nanowires were found to have very good catalytic activity in 4-NP reduction and Suzuki-Miyaura coupling reactions.

2. Experimental

2.1. Materials

Cetyltrimethyl ammonium bromide (CTAB), sodium dodecyl sulfate (SDS), toluene, 1-pentanol and thin layer chromatography (TLC) plates were purchased from Merck, India. Bis-dibenzyledene acetone Palladium(0) ($Pd(DBA)_2$), silica gel, chlorobenzene, bromobenzene, iodobenzene, pottasium carbonate (K_2CO_3), phenylboronic acid, hexane, ethyl acetate, 4-NP and sodium borohydride ($NaBH_4$) were purchased from Sigma Aldrich. All the chemicals were used as received. Ultra pure water (18.2 MΩ-cm) from double stage water purifier (ElgaPurelab Option-R7) was used throughout the experiments.

3. Preparation of mesophases

For the preparation of the mesophase, CTAB (1.5 g) was first dissolved in brine (3 ml, 0.1 M), to give a transparent and viscous micellar solution. The subsequent addition, under vortex mixing of toluene with $Pd(DBA)_2$ (4.5 ml, 10^{-3} M) into the micellar solution led to a light pink unstable emulsion. The cosurfactant, 1-pentanol (35 μl) was then added to the mixture, which was strongly vortexed for a few minutes to form the mesophase. SDS (1.2 g) was used to make another mesophase while keeping the ingredients and their concentration same as that was used to make the mesophase with CTAB.

3.1. Preparation of Pd nanoparticles

The $Pd(DBA)_2$ doped mesophases were incubated for a week and then subjected to hydrogen gas treatment for preparing the Pd nanoparticles. In a typical procedure, the mesophases were initially sealed in a pyrex glass culture tube with a rubber septum. The hydrogen gas was passed through the mesophases for 15–20 min at fixed time intervals of 6 h and the reaction was completed in 18 h. The mesophases were then destabilized with *iso*-propyl alcohol, centrifuged and washed 4–5 times to remove any undissolved reactants.

3.2. Characterization techniques

The polarized optical microscopy (POM) imaging of the mesophases was done with a Nikon LV100POL polarization microscope. A small quantity of the mesophase was sandwiched between a glass slide and a cover slip, and the edges were sealed using vacuum grease. X-ray diffraction (XRD) patterns of Pd samples were recorded using Smart Lab X-ray diffractometer (Rigaku, Japan) using Cu Kα radiation as an X-ray source (λ = 0.1542 nm, 40 mA, 45 kV) at room temperature in the 2θ angle range of 35–90°. TEM imaging of the samples was done using FEI Tecnai G^2 20 S-Twin model operating at 200 keV. A Bruker SDD detector attached with the TEM was used to carry out the EDX analysis. A Fischione HAADF STEM detector was used for collecting the STEM data along with elemental mapping. The ^1H and ^{13}C spectra of the product of coupling reactions were recorded using JEOL JNM ECX 500 MHz NMR system in $CDCl_3$. Catalytic reduction of 4-NP was studied using a Shimadzu 2400 series UV–vis spectrophotometer.

3.3. Catalytic activities of Pd nanowires

Catalytic activity of the Pd nanowires was tested in NP reduction and Suzuki-Miyaura coupling reactions.

3.3.1. Catalytic reduction of 4-nitrophenol (4-NP)

Catalytic activity of Pd nanowires for the conversion of 4-NP to 4-AP was carried out as per Scheme 1(a). The reaction proceeded in a 3 ml quartz cuvette under ambient conditions. Typically, 4-NP (0.5 ml, 0.01 M), aqueous solution of freshly prepared $NaBH_4$ (0.2 ml, 0.1 M) solution was added into a quartz cuvette followed by the addition of required amount of Pd nanowire (0.005 mg/ml) catalysts. Deionized water was then accordingly added to make up the total volume to 3 ml. The change in color of the mixture solution from bright yellow to colorless was monitored using UV–vis spectroscopy, and the decrease in absorbance at 400 nm was recorded with time. The overall reaction process for the conversion of 4-NP to 4-AP by $NaBH_4$ is depicted in Scheme 1(b).

The Suzuki-Miyaura coupling in presence of Pd nanowires as catalyst was carried out as per Scheme 2 shown below. Typically, halobenzene (1 mM), phenyl boronic acid (1.5 mM), K_2CO_3 (3 mM) and the catalyst (0.01 M%) was added to a 50 ml round bottom flask containing toluene (5 ml). The reaction mixture was then refluxed in an oil bath under magnetic stirring at 90 °C for 13 h. The reaction progress was monitored using TLC. The product was extracted