

# Room temperature synthesis of polyvinyl alcohol stabilized palladium nanoparticles: Solvent effect on shape and electro-catalytic activity



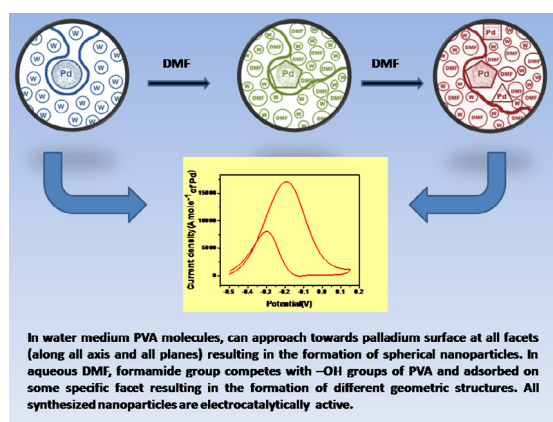
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## HIGHLIGHTS

- Synthesis of catalytically active palladium nanoparticles in different solvent media.
- By changing only the solvent anisotropy can be generated and particle size can be tuned.
- With increasing rate of formation of Palladium atom, smaller palladium nanoparticle is formed.
- Size dependent electrocatalytic property is observed.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Palladium nanoparticles have been synthesized at room temperature,  $25 \pm .5$  °C by the reduction of  $K_2PdCl_4$  using biocompatible polymer polyvinyl alcohol (PVA) as reducing and stabilizing agent in water and aqueous dimethyl formamide (DMF) media with varying composition of DMF. The effect of variation of composition of aqueous DMF on growth, morphology and size of palladium nanocrystals is explained. Different aqueous DMF mixtures furnish palladium nanoparticles of different shapes like triangular plates, cuboids, hexagon with different average edge length between (3–30 nm) indicating preferential interaction and blocking of DMF to some specific planes of nanocrystals leading to various shapes. The synthesized nanoparticles have been characterized by different spectroscopic, microscopic and electro-analytical studies like cyclic voltammetry (CV), chronopotentiometry (CP) and chronoamperometry (CA). The increase in electro-catalytic activity is found to decrease with the increased size of the embedded crystallites deposited on the support constituting the electrodes and hence on the precursor medium. The same order of the studied electrodes is found from mole normalized peak current density values ( $A\ mol^{-1}\ Pd$ ) in CV, transition time in CP and steady current density values in CA, on increasing the content of DMF in the aqueous DMF solvent system as expected. The outcomes are explained on the basis of the crystallite size, morphology of the surface, unequal development of certain planes and purity of the products as guided by the rate of nucleation and growth of the particles formed in different media.

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## 1. Introduction

Palladium nanoparticles attract much attention in the past five decades because of its versatile application in various fields like catalysis [1–3], drug delivery [4], electronics [5], sensing [6] etc.

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Comparatively cheap rate and sufficiently corrosion-resistant ability made it a perfect choice for fuel cell research [7–9] also. Since the catalytic properties of the crystal depend on the nature of the facets exposed which in turn are governed by the shape of a catalyst, a delicate shape control of Pd nano crystals is therefore highly desirable for tailoring their catalytic properties and high performance in various catalytic applications. Narrow size distribution and well defined morphology are two parameters which allow one to modify fundamental properties of nanoparticles and thereby enhance their performance for various applications [10,11]. Consequently, different synthetic protocols for palladium nanoparticles with small size and well defined morphology have become a challenging task and the need of various works.

The rate of reaction as guided by the change of synthetic protocol is an important parameter in controlling the nucleation and growth. When the rate of reduction of the precursor metal ion is high, more seeds would form at the initial nucleation stage. Obviously, these would lead to the formation of nano crystals with smaller size (particle-volume)  $s$ , since the amount of precursor is fixed and limited. On the other hand, anisotropy is generated by differentiating the nucleation and growth processes, changing the reaction from thermodynamic to a kinetically controlled pathway, e.g. slow down of precursor decomposition or reduction/oxidation via a weak (reducing/oxidizing) agent and Oswald ripening [12]. Other parameters such as concentration of each of metal precursor, stabilizer, foreign ion, and change of temperature can also control the relative growth rate on particular crystallographic surfaces during crystal growth resulting formation of various shapes of nanoparticles [13,14]. Finke and co-workers proposed a mechanism of nanoparticle-synthesis which involves a slow continuous nucleation step, followed by fast autocatalytic surface growth and bimolecular agglomerative growth [15,16]. Protic solvents and water, a versatile protic, green solvent provide only global nanoparticles from  $\text{PdCl}_4^{2-}$  in presence of polyvinyl alcohol (PVA) [17] but global structures have the least surface area among different geometric shapes. Protic-aprotic mixed solvents might develop different geometric shapes since mixed solvents sometime show completely different thermodynamic properties from that of the pure solvents [18,19]. Among different dipolar aprotic solvents, *N,N*-dimethyl formamide (DMF) is well-known for its potential use as a medium of synthesis due to its wide liquid temperature range, good chemical and thermal stability up to its boiling point, 153 °C, high polarity and wide solubility range for both organic and inorganic compounds [20]. DMF also possesses reducing capability at room temperature and convert Pd (+2) to Pd (0) [21]. Pure solvents were used extensively for synthesis of nanoparticles of Pt metals [22]. Since these particles possess well-behaved electronic and optical properties [23], it would be provocative to investigate the change in the nature, geometries and catalytic properties of the particles synthesized from the mixtures of these solvents.

So in this study, we report room temperature synthesis of Pd nanoparticles in water and aqueous DMF solvents of varying composition in presence of PVA which acts as a reducing agent and steric stabilizer and co-solvent DMF as an adsorbing agent to get the nanoparticles of various geometries. Moreover, the synthesized particles are characterized including their catalytic properties in reference to oxidation of ethanol.

## 2. Experimental section

### 2.1. Materials

Palladium Chloride ( $\text{PdCl}_2$ ) with a purity of 99% Pd was purchased from Arora Matthey Limited. KCl from Mark, India was used to prepare  $\text{K}_2\text{PdCl}_4$  solution. PVA (number average molecular weight = 125,000) from Lab Rasayan Co., India was used as reducing and stabilizing agent. The solvents used are of spectroscopic

grade (spectrochem). All the other reagents were of AR grade from Mark, India and used without further purification. Millipore water was used throughout.

### 2.2. Synthesis of colloidal palladium nanoparticles

Colloidal palladium nanoparticles were prepared at room temperature in pure water and aqueous solvents containing different percentage of DMF.  $\text{K}_2\text{PdCl}_4$  solution was prepared by dissolving  $\text{PdCl}_2$  (0.0246 g, 0.1387 mmol) and KCl (0.0192 g, 0.2575 mmol) in a 25 mL volumetric flask and the volume was made up to the mark with water. To obtain the clear solution the aqueous mixture was sonicated for about 30 min. Then PVA (0.5 g, 0.004 mmol) was dissolved in about 25 mL of hot water. Then five different sets of 1 mM solution of  $\text{K}_2\text{PdCl}_4$ , each containing 1 mass % of PVA were prepared in different aqueous DMF mixed solvents containing 0, 10, 20, 30, 40 volume percent of DMF by appropriate mixing of  $\text{K}_2\text{PdCl}_4$  solution, PVA solution and pure DMF.

To remove the impurities and unchanged  $\text{PdCl}_2$  if any, colloid purification was applied to the Pd/PVA system. The dispersed phase consisting of Pd/PVA nanoparticles was separated from the solvent medium on treatment with excess ethanol repeatedly. Then nanoparticles trapped into the PVA matrix were collected by centrifugation, washed several times with water and re-dispersed in water with the further formation of a Pd hydrosol. UV-visible spectroscopy confirmed the unchanged nanostructure of the sol.

### 2.3. Characterization of the palladium nanoparticle

The Ultraviolet-visible (UV-Vis) absorption spectra of the synthesized sol were recorded using a UV-visible spectrophotometer (UV-1800/Shimadzu, Model TCC-240A) between 250 and 800 nm with quartz cells. After each of definite time intervals, a small amount of Pd sol undergoing the reaction was transferred to a quartz cell of 1 cm path length, and UV-Vis spectrum was recorded with baseline subtracted against the corresponding water-DMF mixture as blank reference solvent.

X-ray powder diffraction (XRD) studies were carried out using a (Bruker D8 Advance) diffractometer equipped with a  $\text{CuK}\alpha$  radiation source ( $\lambda = 1.5418 \text{ \AA}$  generated at 40 kV and 40 mA). For this purpose each solution of palladium nano-crystallites was adsorbed on a small amount of activated charcoal and then dried by keeping it overnight inside vacuum desiccators.

High resolution transmission electron microscope (TEM) (JEOL 2010, operating at 200 kV) was used to reveal the shape and size of the particles. The reaction was frozen to collect cooled samples. Samples for TEM imaging was prepared by irradiating diluted and cooled palladium sol with ultrasonic waves, using a sonicator (D-compact, SL No.-1482) for about 45 min. No apparent change of colour and absorbance was observed at the end of the sonication which eliminated the possibility of further reaction. A drop of the resulting sol was cast on a 300 mesh carbon-coated copper grid, and then blotted off with soaking paper after 10 s of contact, followed by natural evaporation of the solvent at room temperature.

The protection of PVA and PVA-solvent interaction was investigated using Fourier transform infrared (FTIR) spectroscopy. For the measurements, dry solid nano composite were mixed thoroughly with a KBr pellet and analysed using an FTIR spectroscope (Perkin Elmer, SN-74514).

The electrocatalytic behaviour of palladium nanoparticles synthesizing in water and aqueous DMF medium was verified using cyclic voltammetric (CV), chrono potentiometric (CP) and chrono amperometric (CA) studies in reference to oxidation of ethanol in alkali medium. For this, each Ni-supported electrode was prepared from the respective Pd hydrosol by chemical solution deposition

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