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**Advances in Applied Science Research, 2013, 4(5):138-145**

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**ISSN: 0976-8610**
**CODEN (USA): AASRFC**

# Seed-mediated growth of palladium nanocrystals on ITO substrate and their characterization

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**ABSTRACT**

*In recent years, the seed-mediated growth method has been suggested as a new strategy to attach and grow metal nanoparticles on conducting substrates, such as indium tin oxide (ITO). In this method, Palladium nanoparticles can be fixed via a simple two-step immersion of the substrate into two different solutions at room temperature. In the first step, the nano-seed particles are inferred to attach on the surfaces by just immersing the substrates into the metal colloid solution (the seed solution) via the physi-sorption. In the second step, gradual nanocrystal growth from the nano-seed particles attached on the substrate is considered to occur via the chemical reduction of metal ions in the solution containing surfactants (the growth solution). After the growth treatment for 24 hr, PdNPs grew up to 60-80 nm, exhibiting crystal-like appearances. Thus prepared PdNPs tend to stick each other, so that the dense gathering of PdNPs was observed on the ITO surfaces. In present study, some details of our preparation methods of palladium nanoparticle-attached ITO electrodes, optical and electrochemical behaviour, other characterization like AFM, SEM, XRD of thus fabricated materials are summarized.*

**Keywords:** Nanoparticles, palladium, nanocrystal, PdNPs, ITO electrodes

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## INTRODUCTION

Nanotechnology literally means any technology performed on a nano-scale that has applications in the real world. Nanotechnology encompasses the production and application of physical, chemical and biological systems at scales ranging from individual atoms or molecules to submicron dimensions, as well as the integration of the resulting nanostructures into larger systems. Nanotechnology symbolizes the major get through of modern science that enabled materials of distinctive size, structure and composition to be formed. Such nanodimensional materials (1–100 nm size) are considered as a bridge between atomic and bulk materials and also have been shown to exhibit various unique physical, chemical and electronic properties or characteristics [1]. Nanotechnology is likely to have a profound impact on our economy and society in the early twenty-first century, comparable to that of semiconductor technology, information technology, or cellular, molecular biology, medicine, and material sciences [2]. As a novel approach, in the field of nanoscience and nanotechnology, the seed-mediated growth method has been extensively investigated to synthesize metal nanomaterials with a variety of morphology for decades [3; 4; 5; 6; 7]. In nanotechnology, researchers have focused on coinage metals [4]. Gold and silver are among the most studied metals. These days researchers have shown keen interest in other transition metal nanomaterials [8]. Palladium is also among the most efficient metals in catalysis [9; 10]. The preparation of palladium nanoparticles with well-controlled particle sizes and shapes of a high monodispersity is a key technology in producing materials that are more effective and efficient than the current state of the art [2; 11; 12]. Palladium nanoparticles have been widely used as the catalysts for a variety of reactions, including alkynol hydrogenation [13; 14; 15], as well as oxidation and reduction reactions involved in the operation of a fuel cell [16; 17; 18]. Palladium nanoparticles are also used for Suzuki coupling [14; 15]. Like many other catalysts, the activity and selectivity of palladium nanoparticles often have a

strong dependence on the size and shape (or more appropriately, the facets or surface structures). In principle, one could tailor these parameters to maximize the catalytic performance of a palladium catalyst in an effort to reduce the loading of this precious and rare metal. In this communication seed-mediated growth of palladium nanocrystals on ITO substrate has studied and characterized by UV-VIS spectrometry, electrochemical study (AC Impedence and Cyclic Voltametery), Atomic Force Microscopy (AFM) including roughness analysis and section analysis.

## MATERIALS AND METHODS

As a novel approach to prepare metal NP-attached electrodes with wet chemical treatments, we are proposing a seed-mediated growth method for Palladium nanoparticles which is an alteration of the original seed-mediated method for preparing metal nanorods in solution. In actual, the nanoseed particles are attached on the surface by just immersing a piece of conducting substrate, such as indium tin oxide (ITO), into a seed solution containing metal NPs of ca. 4 nm. Then, by immersing the nanoseed-particle-attached substrate into the growth solution, which contained metal ions, ascorbic acid as reductant, and cetyl tri methyl ammonium bromide (CTAB), the crystal growth of metal NPs on the substrate's surface is possible. The first process is physisorption of small nanoseed particles, while the second process is chemical reductive growth.

In the present work, trials to fabricate metal-NP-attached electrodes, the attachment and growth of palladium NPs (PdNPs) on ITO surfaces are investigated using the same seed-mediated growth method.

**Synthesis Methodology for palladium nanoparticle (PdNPs)**
As the start of trials, a seed-mediated growth method for PdNPs was applied, as described earlier by some research workers for synthesizing Au nanorods in aqueous solution by the chemical reduction of HAuCl4 to the formation of AuNPs on the ITO surfaces [19; 20]. A piece of ITO coated glass was washed with sonication in acetone followed by distilled water. The washed ITO substrate was air dried and immersed in the seed solution which contains metal nanoparticles (NPs) followed by immersing the nanoseed-particle-attached ITO substrate into the Growth Solution (GS), which contains metal ions. Both the solutions were prepared in the double distilled water. The methodology is presented diagrammatically in **Figure 1**.

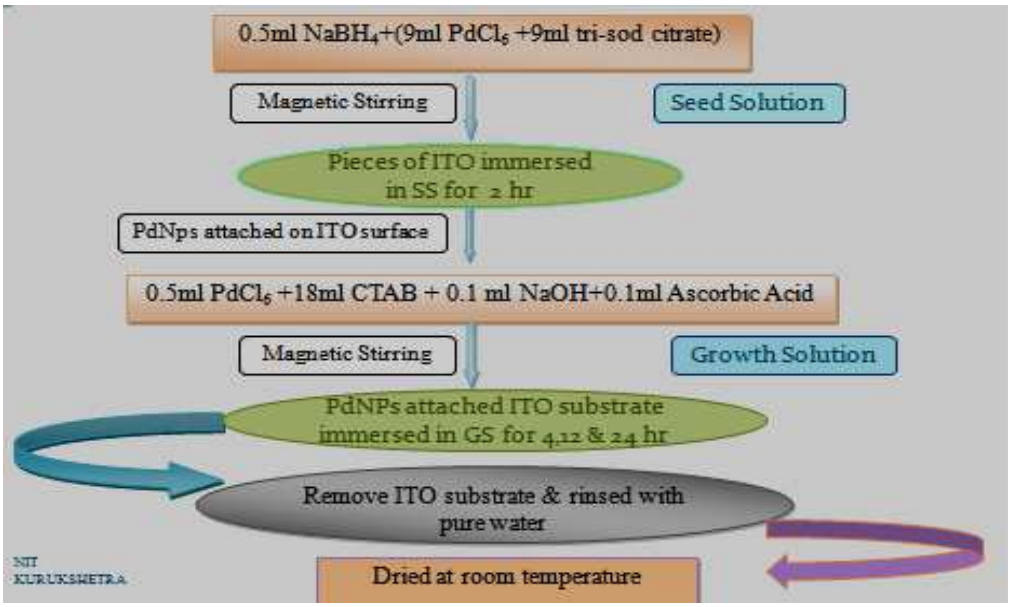


**Figure 1: Synthesis Methodology of Pd Nanocrystals [21].**

***Preparation of Seed Solution***
Seed solution was prepared by the mixing aqueous solution of 0.25M palladium chloride ($PdCl_6$) and tri-sodium citrate (0.25M) in ice-cold solution of 0.01 M sodium borohydride ($NaBH_4$). Solution was allowed to stir for some time .

Some pieces of ITO substrate were immersed in to the Seed Solution for two hours without particular treatments. Then, the ITO substrate was taken out from the seed solution, and the surface was washed carefully by flushing pure water over the surface for several times. The water remained on the surface was removed using tissue paper by just touching the edges of the glass. The palladium nanoseed particles were attached on the substrate's surface.

After drying the Pd nanoseed particles attached ITO substrate, it was immersed next in the Growth Solution.

***Preparation of Growth Solution***
Growth solution was prepared by the mixing of aqueous solution of CTAB (0.1 M), 0.01 M Palladium chloride ($PdCl_6$), Sodium hydroxide (1 M), and 0.1 M L-ascorbic acid ($C_6H_8O_6$). Solution was allowed to stir for some time.

ITO substrate attached with Pd nanoseed particles were immersed in growth solution for different time periods i.e. 4hr, 12hr, 20hr, and 24 hr to promote the growth of PdNPs. Then the ITO substrate fabricated with Pd nanocrystals were removed form the growth solution and rinsed with pure/ditilled water several times and then dried in the room temperature for characterization by scanning electron microscopy, X-ray diffraction, UV-VIS spectrophotometer, Atomic force microscopy and electrochemical measurements.

## RESULTS AND DISCUSSION

The characterization results of the synthesized palladium nanoparticle by the seed-mediated growth method on ITO substrate have been described in results and discussion. The characterization done by the UV-VIS spectroscopy, electrochemical measurements, atomic force microscopy, X-ray diffraction, scanning electron microscopy has been discussed.

**UV-VIS Spectrometry**
Absorption spectrum between seed and growth solution was observed which have different composition. As predicted from the **Figure 2**, the absorption peeks obtained at 275 nm for seed solution and absorption value lies at 0.27. Absorption peek for growth solution obtained at wavelength 265 nm and absorption value for lies at 0.61.

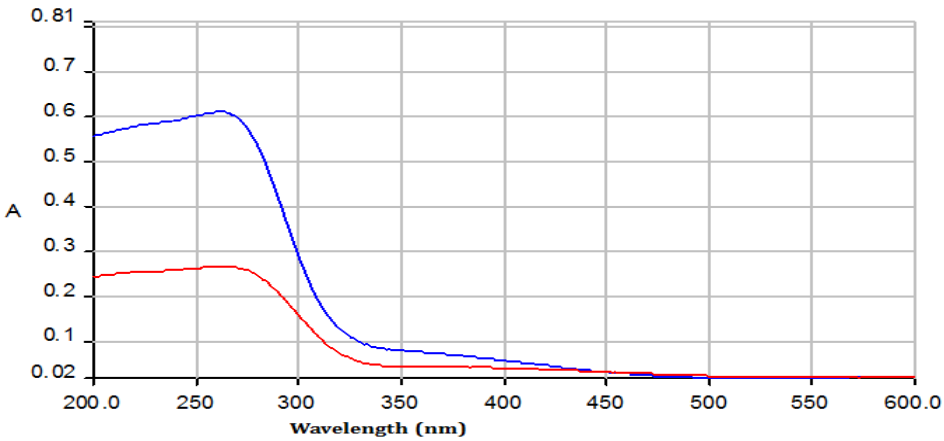


**Figure 2: Absorption spectra of seed & growth Solution**

**Electrochemical Study**
Electrochemical measurements were performed by AC impedence and cyclicvoltametery.

***AC* Impedence**
To evaluate the effect of Pd nanocrystals on the charge-transfer resistivity, the electrochemical impedance of the PdNP/ ITO electrodes were measured that were prepared with different growth periods. Electrochemical impedance spectra were recorded in 1M KCl & 0.5mM $Fe(CN)_6$ solution as depicted in **Figure 3**. The *R*ct values were observed to decrease with the increase in the growth period, reflecting the correlation of the $R_{ct}$ values with the degree of the crystal growth of PdNPs via different time period. For a reference, the $R_{ct}$ value of the Pd bulk electrode was 17 k Ω $cm^2$.

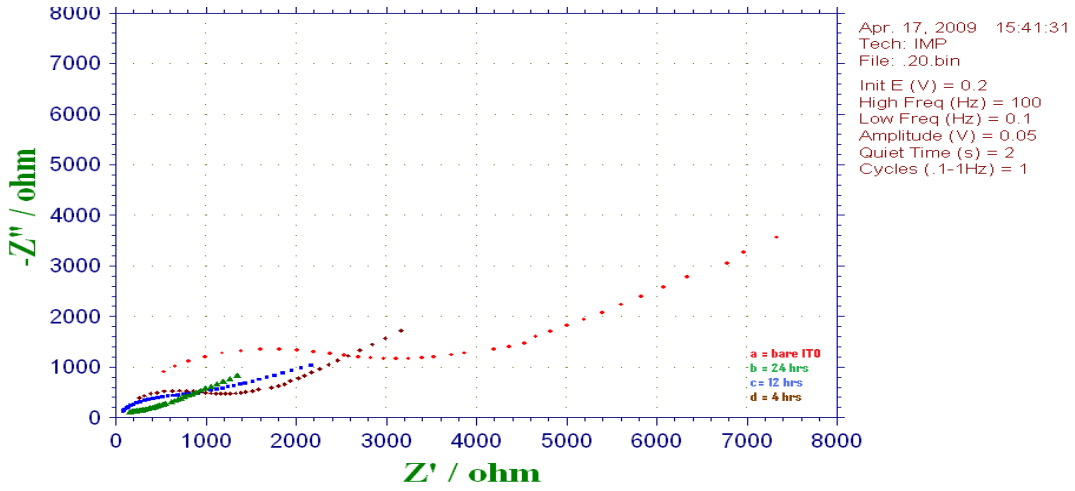


**Figure 3: ECI Spectra in 1M KCl & 0.5mM $Fe(CN)_6$ solution with Bare ITO electrode and PdNP/ITO electrode prepared via 4 hr, 12 hr and 24 hr Growth**

***Cyclic Voltametery***

To investigate the applicability of the PdNP/ITO electrode for typical redox systems, cyclic voltammograms of [Fe(CN)6]4- were observed in 1.0 M KCl and 0.1 M phosphate buffer solution. The PdNP/ ITO electrode was prepared after 4 h of growth and of Pd nanoseed particle attached ITO electride via 2 hr immersion in Seed solution. The results are depicted in **Figure 4**.

In the redox reaction of [Fe(CN)6]4-/[Fe(CN)6]3-, the responses should be governed by the diffusion processes, and the diffusion layer is expected to be far more than the thickness of the layer of PdNPs. Thus, the improvement characteristics of the PdNP/ITO electrode cannot be explained with changes in the increased surface of Pd in PdNPs. By attaching on the surface of ITO, PdNPs are inferred to change the nature of the interfaces to reduce the charge-transfer resistivity. In addition, the porous surface of PdNPs may reduce the adsorption of phosphate ions.

At any rate, as the most noticeable feature here, it was found that the PdNP/ITO was superior to the Pd bulk electrode in terms of the reversibility. If it is assumed only the surface of Pd is working as electrode on the PdNP/ITO, such a difference is difficult to consider. Thus, it is inferred that a unique interface could be fabricated by attaching PdNPs on the ITO surface.

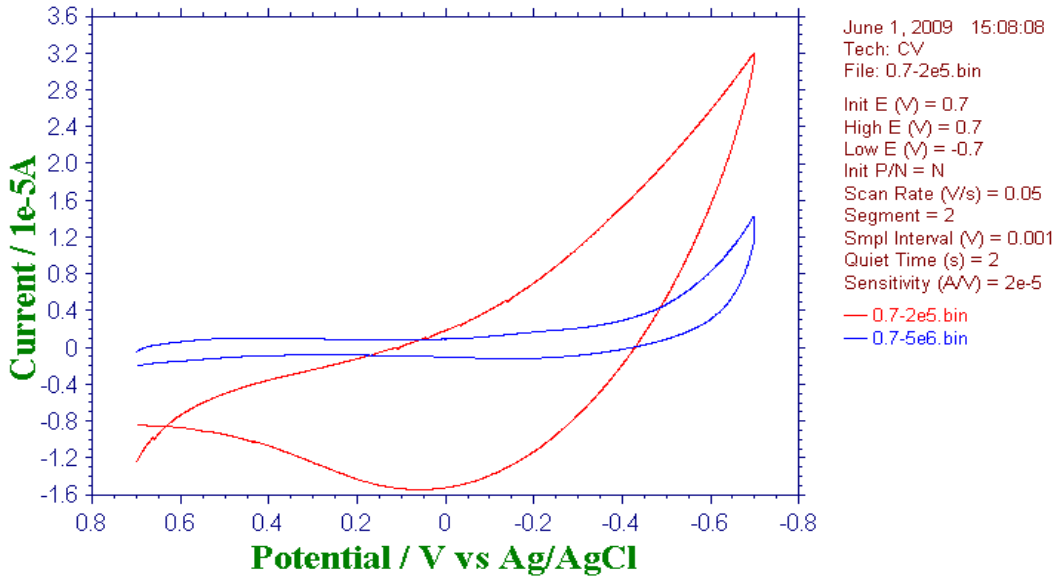


**Figure 4: Cyclic Voltammogram of 1mM $Fe(CN)_6$ in Buffer Sol. (pH 7) with PdNP/ITO electrode via 2 hr Seed Solution immersion & 4 hr Growth in GS**

Glucose Oxidase coated on PdNP/ITO electrode via 4 hr and 24 hr growth and allow to dry at room temp for one hour.Then the CV was taken of $Fe(CN)_6$. In phosphate buffer solution that current in the 4 hr growth is lower than the current in 4 hr growth of PdNP/ITO electrode (**Figure 5 and Figure 6**). The voltammograms shows the variation of current & voltage in different electrodes as shown in the **Figure 5** and **6**.

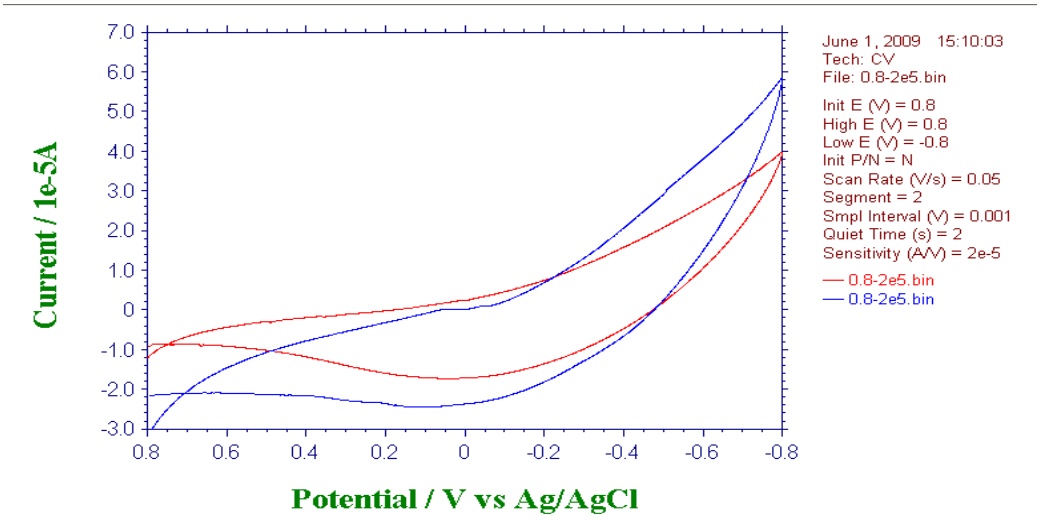


**Figure 5: Cyclic Voltammogram of buffer solution with PdNP/ITO electrode via 4hr & 24hr growth**

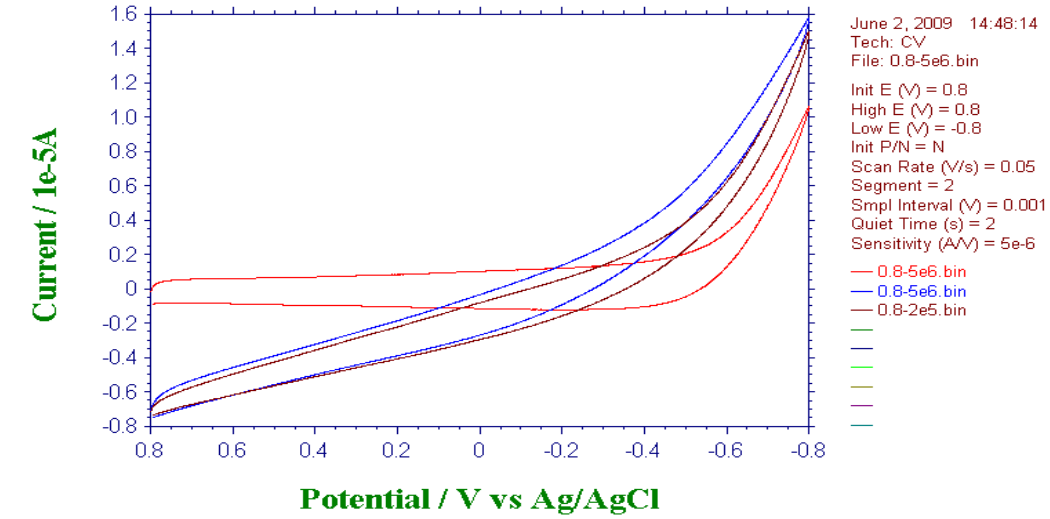


**Figure 6: Cyclic voltammogram of buffer solution with Blank ITO and PdNP/ITO electrode via & 4Hr,12 Hr growth**

**Atomic Force Microscopy (AFM)**

Atomic force microscopy was used for detailed characterization of synthesized palladium nanoparticles. The AFM characterization of the Palladium nanoparticle attached on the ITO substrate has been shown in **Figure 7-10**. AFM characterization was done on different sections like 2-D image, 3-D image, Roughness analysis & Section analysis.

In **Figure 7**, two dimensional image was recorded and the palladium nanoparticles were observed on the basis of color. The color scale is shown in the graph. Mostly nanoparticles are 10-15 nm size. Some PdNPs are of 20 nm size as shown in the Figure. Scan rate was 5.086 Hz.

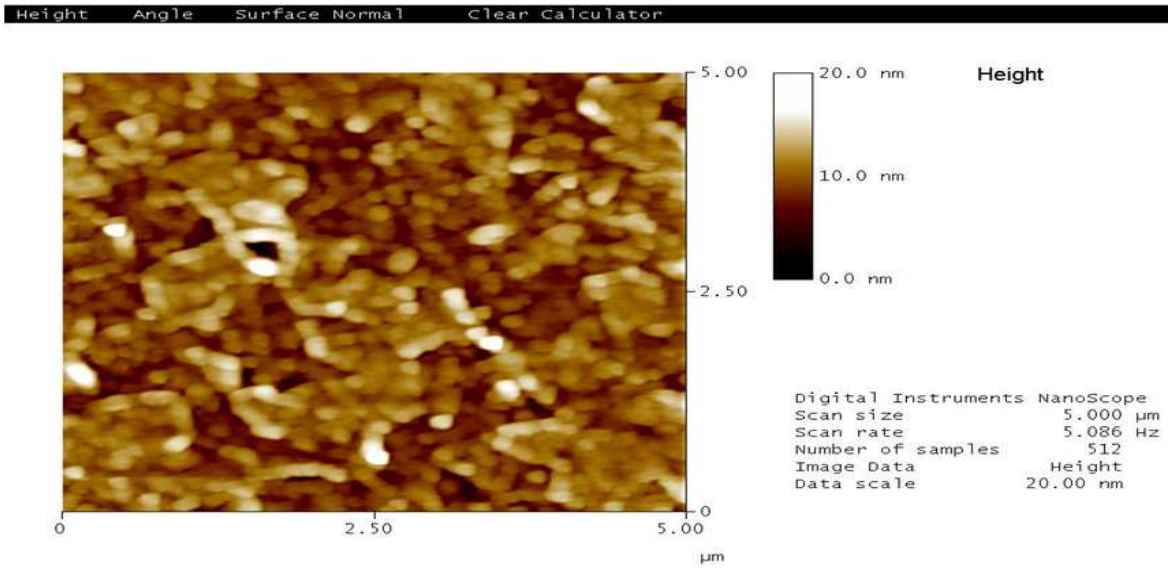


**Figure 7: Typical AFM image of PdNPs after the 12 hr growth**

In **Figure 8**, three dimensional image (3 D) has been shown and palladium nanoparticle exhibit like the crystal. According to color scale the nanoparticles are of the size 10-15 nm and some nanoparticles were 20 nm size. Scan rate was also 5.086 Hz in this case.

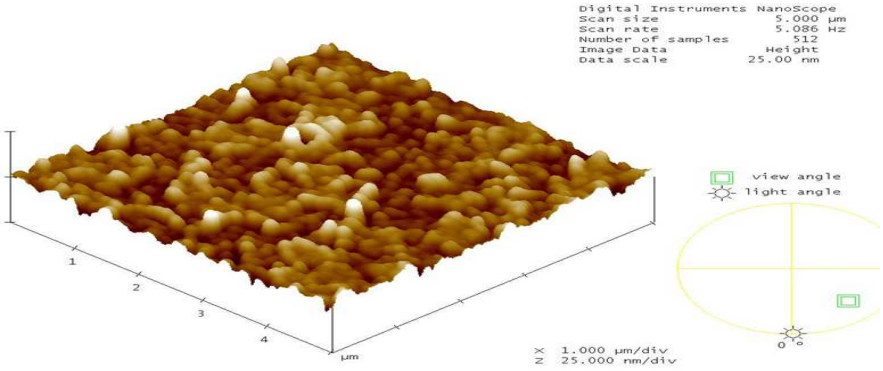


**Figure 8: Typical 3-D image of PdNPs after 12 hr growth**

In **Figure 9**, roughness of palladium nanoparticles is shown. According to analysis the mean roughness is found to be 1.629 nm.

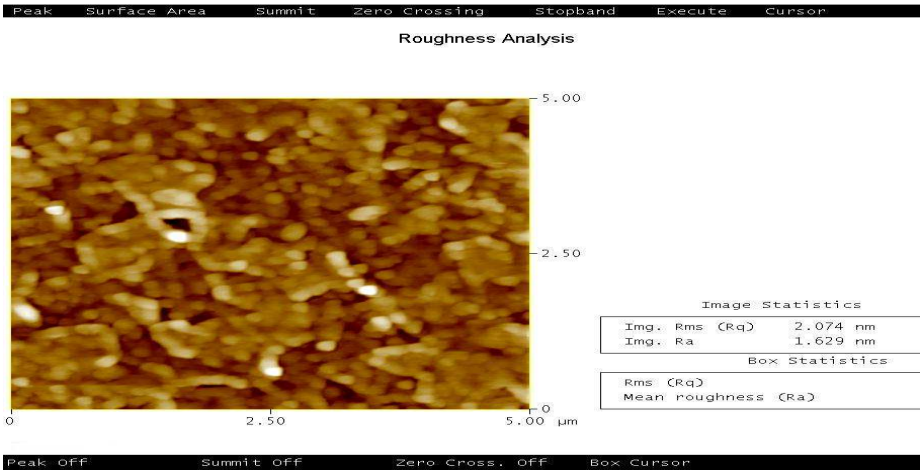


**Figure 9: Roughness analysis of PdNPs after 12 hr growth**

In **Figure 10**, section analysis of palladium nanoparticle attached on ITO substrate is shown. In this various parameters are shown like surface distance, horizontal & vertical distance, angle, spectral period etc. The vertical distance observed from the graph is 0.033, 0.363, 0.441 nm.

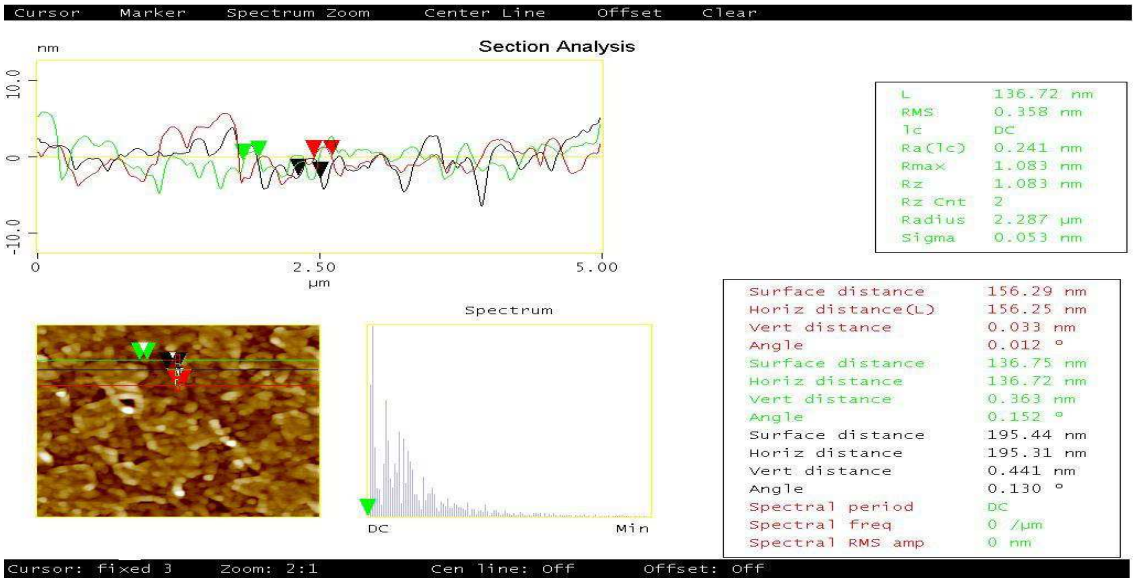


**Figure 10: Section analysis showing various parameters**

## CONCLUSION

In the present work, Pd nanocrystals were successfully attached and grown on the ITO surfaces using the seed-mediated growth method. While some short nanorods were formed as a minor product, the PdNPs having crystal-like appearance, whose size was 60-80 nm, were densely modified on the ITO surface after 24 h of growth. Because the PdNPs tend to stick to each other in the growth treatment, which is particular to Pd, the ITO surfaces could be modified with a kind of porous structure composed of Pd nanocrystals. The electrochemical impedance measurement of the PdNP/ ITO electrode showed a significant decrease of the charge transfer resistivity, which is comparable to the cases of AuNPs and AgNPs. Despite the high resistivity of Pd in comparison with Au or Ag, the dense modification by Pd nanocrystals is inferred to improve the charge transferring situations at the interface. Thus, the PdNP/ITO electrode can be regarded as a unique modified electrode in which the NPs at the interface promote the electron-transfer reactions. The cyclic voltammetric measurements showed some characteristics due to the limited volume and the dispersed state of PdNPs. Palladium thin films have been utilized in some applications. As discussed in introduction section, the palladium nanoparticles have wide application potential and this study can help to further execute research on palladium nanoparticles.

**Acknowledgement**
Anurag Sangwan acknowledges the facilities provided by the NIT, Kurukshetra and CSIO, Chandigarh, India to execute this research work.

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