

# Synthesis of Pd@ZnO Core-shell Nanoparticles with Different Size and Their Gas Sensing Properties

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**Abstract:** Two different sizes of Pd@ZnO core-shell nanoparticles (NPs) have been prepared by using two different sizes of Pd NPs (15 and 50 nm) as metal cores and applied for acetaldehyde gas sensing. Transmission electron microscopy images revealed that the overall size of two sensing materials such as Pd<sub>15</sub>@ZnO and Pd<sub>50</sub>@ZnO core-shell NPs are 80-100 nm and 100-120 nm, respectively. X-ray-diffraction pattern revealed that the oxidation of Pd metal core was started from 300°C. The spherical shape and size are maintained after the Pd@ZnO core-shell NPs was calcined at 500°C for 2 h. PdO<sub>15</sub>@ZnO core-shell NPs showed higher response to acetaldehyde. The maximum response of PdO<sub>15</sub>@ZnO core-shell NPs to 100 ppm of acetaldehyde at 350 °C was 75, whereas the maximum response of PdO<sub>50</sub>@ZnO core-shell NPs to 100 ppm of acetaldehyde was 28 as compared to the pure ZnO NPs (R<sub>s</sub>=18). The high response of PdO<sub>15</sub>@ZnO core-shell NPs than PdO<sub>50</sub>@ZnO core-shell NPs is due to the smaller size of PdO core, which has more catalytic activity than 50 nm sized PdO core.

## 1 INTRODUCTION

The advancement in science and technology has resulted in rapid growth of urbanization, industrialization and automobiles. The dark side of the rapid growth in these sectors is the release of many toxic gaseous pollutants in the environment which are not only causing environmental pollution but also serious health problems. The severe condition of air pollution due to toxic and flammable gases resulted in rapid growth of gas sensor technology (Balouria, 2013). Among various gas sensors, metal oxide semiconductor (MOS) gas sensors are believed to be the best sensing materials so far owing to their simple sensing mechanism, low cost and ability to detect number of gases (Korotcenkov, 2007). However, there are certain issues, such as low sensitivity, poor selectivity and high operating temperature, which needs to be overcome for further advancement of the MOS based gas sensors. Therefore, syntheses of highly sensitive and selective gas sensing materials have received much attention from the researchers worldwide. Many approaches have been started for the enhancement of gas sensing performance in

terms of sensitivity and selectivity, by aliovalent doping, functionalization of sensing materials with noble metals or creating metal oxide based heterostructures. Recently, noble metal nanoparticles (NPs) such as Au, Pd and Ag have been widely used in gas sensing applications due to their catalytic properties (Li, 2015). Among different ways, one of the ways to utilize these noble metal NPs in gas sensor is the design of core-shell hybrid structures, where the noble metal in contact with the oxide semiconductor plays a great role to enhance the sensor performance in terms of sensitivity and selectivity. In the core-shell structure, the core is isolated from the shell, and prevents it from aggregation during sintering. (Majhi, 2015). It is known that the structure and morphology of sensing material affects the sensor performances. However, it is also known that the shape and size of noble metal NPs also tailor the properties of a catalyst. Hence, the optimization of size of noble metal NPs along with the structure and morphology of metal core-oxide shell is very important in gas sensing field. (Rai, 2013) Among different noble metal NPs, Pd is an important catalyst used in various applications such as photocatalysis, alcohol

oxidation reaction, CO oxidation, including gas sensing such as alcohol, acetaldehyde and H<sub>2</sub>. Zinc oxide (ZnO) with a band gap of 3.37 eV, high excitation binding energy of 60 mV, high mobility of conduction electron (200 cm<sup>2</sup>/ (V s)), has exhibited promising role in many potential applications including gas sensors. (Majhi, 2015) Here in, we report a facile synthesis of Pd@ZnO core-shell NPs with two different sizes by using two different size of Pd metal NPs (15 and 50 nm) as core material for gas sensing application. It is known that Pd metal can be easily oxidised to PdO. Therefore, in this work we want to investigate the oxidation behaviour of Pd metal core of Pd@ZnO core-shell NPs. The gas sensing study for acetaldehyde gas will be carried out for two different sizes of PdO@ZnO core-shell NPs. The details of the synthesis procedure, gas sensing properties and mechanism will be discussed in this report.

## 2 EXPERIMENTAL

### 2.1 Synthesis of 15 nm Sized Pd NPs

To synthesize Pd nanoparticles (NPs), initially 2.5 ml of H<sub>2</sub>PdCl<sub>4</sub> (10 mM) was added to 50 mL of CTAB aqueous solution (12.5 mM) and heated at 100°C with rapid stirring. Then, 400 µL of freshly prepared AA (0.1 M) was quickly added to the above solution and the stirring continued for about 5 min to produce ~ 15 nm Pd NPs.

### 2.2 Synthesis of 50 nm Sized Pd NPs

Initially 12 ml of 0.001 M H<sub>2</sub>PdCl<sub>4</sub> was taken in a beaker. To this 3ml of 0.01M Tri-sodium citrate dihydrate was dropped and stirred for three minute. To the above solution 3 ml of 0.01M ascorbic acid (AA) was dropped with stirring. The reaction was further continued for 30 min for complete reduction.

### 2.3 Synthesis of Pd<sub>15</sub>@ZnO and Pd<sub>50</sub>@ZnO Core-shell NPs

Both the core-shell NPs were carried out in separate vessels using two different sizes of Pd NPs. Typically, a certain amount of CTAB were added into 60mL of DI water and kept at 60 °C in oven for five minutes for proper dissolving. After that, a certain amount of AA was added with stirring. To the above solution, calculated amounts of ZnNO<sub>3</sub> and HMTA were added and stirred well. Then, 3 mL

of both 15 and 50 nm sized Pd NPs were dropped to the above solution with stirring. Finally, the above solution was transferred and heated in oven at 85°C for 8h without stirring. After the reaction completed, the products were centrifuged, washed carefully for several times and then dried at 60°C in oven. The final products of Pd@ZnO core-shell NPs obtained were calcined at 500°C for 2 h. The synthesis of pure ZnO NPs was also carried out using similar method except adding of Pd NPs.

## 2.4 Characterizations

The as prepared products were analyzed by TEM (Hitachi-H7650), selected area electron diffraction (SAED) pattern, high-angle annular dark-field scanning TEM (HAADF-STEM), high resolution real-time line scan mapping and HRTEM (HRTEM, Zeiss EM-912, Omega). The powder XRD for as prepared products was analyzed by D/Max-2005, Rigaku, X-ray diffractometer (Cu K<sub>α</sub>, λ =1.54178 Å).

## 2.5 Gas Sensor Device Fabrication and Testing

About 10 mg of as prepared sensing materials were mixed and grounded evenly with  $\alpha$ -terpineol to make a paste, which was coated on the surface of alumina substrates (area:15 mm × 15 mm) and then dried at 60 °C. The as obtained sensor devices were heat-treated 500 °C for 2 h in air for stabilization and to remove the solvent, before the gas sensing test. Both the sensor devices were tested under a temperature-controlled environment. The test temperature was 350 °C and acetaldehyde was used as target gas. Nitrogen gas was used as background gas and the dry air was mixed to be 10.5% of oxygen. The change in resistance of the device due to the presence or absence of test gas was measured using a resistance meter (Agilent 34970A). The sensor response ( $R_s$ ) was calculated using ( $R_a/R_g$ ) where  $R_a$  is the resistance in air, and  $R_g$  is the resistance measured during the exposure of target gas.

### 3 RESULTS AND DISCUSSION

#### 3.1 Morphology and Structural Characterization of Pd<sub>15</sub>@ZnO Core-shell NPs

Figure 1a is the TEM image of CTAB assisted Pd NPs, which shows the formation of mixed type of shapes, such as semi-cubic and spherical. The size of Pd NPs was in the range of 5 to 15 nm. Figure 1b is the TEM image of as synthesized Pd<sub>15</sub>@ZnO core-shell NPs. The size of spherical shaped Pd<sub>15</sub>@ZnO core-shell NPs was in the range of 70-100 nm and each Pd@ZnO core-shell particles contains only one Pd NP in the centre of ZnO shell. Spherical shaped ZnO NPs in the range of 70-120 nm were formed in the absence of Pd NPs shows in Figure 1d. Generally, the gas sensor device fabricated requires heat-treatment at elevated temperature before gas sensing measurement and in our study the device was activated at 500°C. Therefore, the effect of heat-treatment on the morphology and phase of Pd<sub>15</sub>@ZnO core-shell was investigated. The phase and structural analysis of Pd<sub>15</sub>@ZnO core-shell NPs after the heat treatment was analyzed by XRD and shown in Figure 2. Since Pd metal can be oxidised to PdO at high temperatures in air, to know the oxidation behaviour of Pd metal, Pd@ZnO core-shell NPs were calcined at different temperatures starting from 100 to 500°C. Figure 2 shows the diffraction patterns of pure Pd NPs (15 nm sized) and Pd<sub>15</sub>@ZnO core-shell NPs calcined at different temperatures from 100 to 500°C-2 h. The diffraction pattern for Pd<sub>15</sub>@ZnO core-shell NPs can be index to wurtzite ZnO (JCPDS 36-1451). In case of Pd NPs the strongest three diffraction peaks corresponding to (111), (222) and (200) lattice planes of face centered cubic (FCC) metallic Pd.

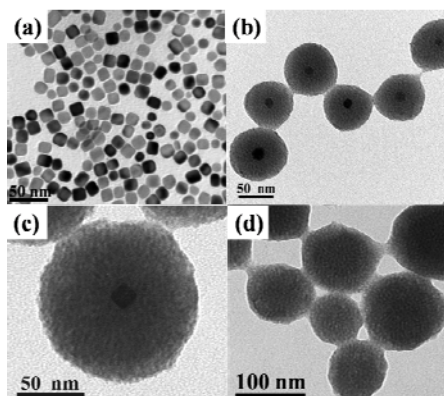


Figure 1: TEM images of the as synthesized (a) Pd NPs (b, c) Pd<sub>15</sub>@ZnO core-shell and (d) pure ZnO NPs.

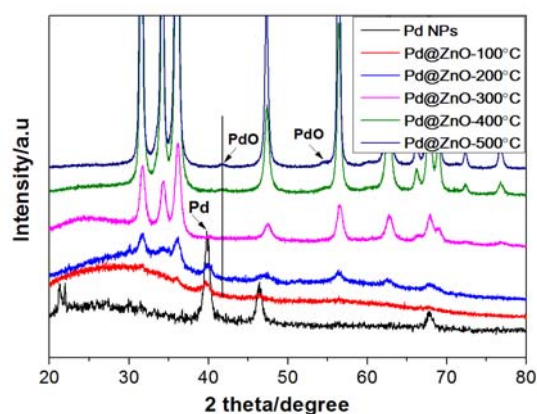


Figure 2: XRD patterns of the as synthesized Pd NPs, and Pd@ZnO core-shell NPs calcined at different temperatures from 100 to 500°C for 2 h.

However, in case of Pd<sub>15</sub>@ZnO core-shell NPs, PdO peaks are found from 300°C calcination temperature. With the increasing the calcination temperature of Pd<sub>15</sub>@ZnO core-shell NPs the intensity of PdO peaks increases. Figure 3a and b depicts the TEM images of pure ZnO and Pd<sub>15</sub>@ZnO core-shell NPs after calcined at 500°C for 2 h. The spherical shape and size was maintained after the heat treatment at 500°C for 2 h. However, the ZnO shell becomes more crystalline after the calcination.

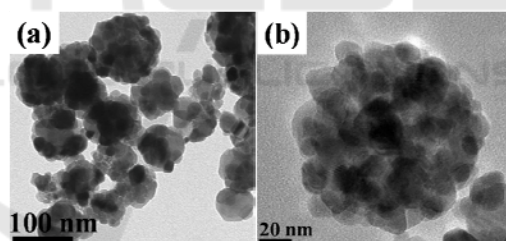


Figure 3: TEM images of (a) ZnO NPs and (b) PdO<sub>15</sub>@ZnO core-shell NPs after calcined at 500°C.

#### 3.2 Morphology and Structural Characterization of Pd<sub>50</sub>@ZnO Core-shell NPs

To prepare the different sizes of Pd@ZnO core-shell NPs, about 50 nm sized Pd NPs were synthesized by sodium citrate method and then used to prepare Pd<sub>50</sub>@ZnO core-shell NPs which was shown in Figure 4. Figure 4a shows the sodium citrated method synthesized around 50 nm sized Pd NPs, which are nearly spherical in size. Figure 4b shows the TEM image of Pd<sub>50</sub>@ZnO core-shell NPs and the total size are around 110-120 nm. Figure 4c is the TEM image of Pd<sub>50</sub>@ZnO core-shell NPs after

calcined at 500°C for 2 h. The spherical shape and size also maintained as like as Pd<sub>15</sub>@ZnO core-shell NPs. The phase structure was analyzed by XRD which is shown in Figure 5. The XRD patterns indicates that after calcined at 500°C for 2 h, the 50 nm sized Pd metal core in Pd<sub>50</sub>@ZnO core-shell NPs also was oxidized to PdO.

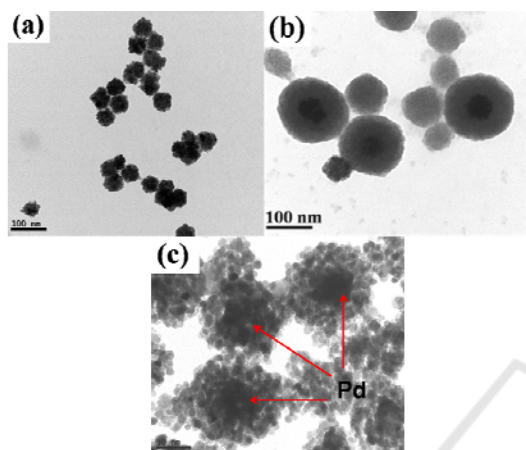


Figure 4: TEM images of the as synthesized (a) 50 nm sized Pd NPs, (b) Pd<sub>50</sub>@ZnO core-shell and (c) PdO<sub>50</sub>@ZnO core-shell NPs calcined at 500°C for 2 h.

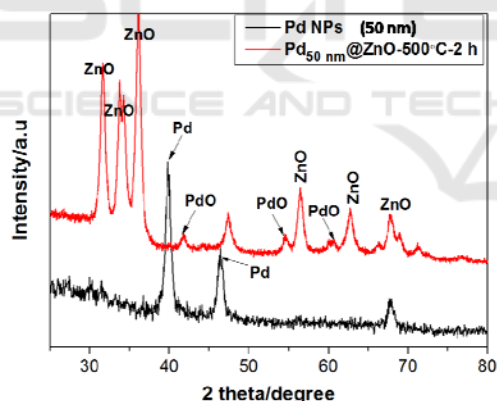


Figure 5: XRD patterns of 50 nm sized Pd NPs and PdO<sub>50</sub>@ZnO core-shell NPs after calcined at 500°C.

### 3.3 Gas Sensing Properties

To know the gas sensing performance, all the three sensor devices such as pure ZnO, PdO<sub>15</sub>@ZnO and PdO<sub>50</sub>@ZnO NPs were investigated for acetaldehyde gas. Figure 6 shows the dynamic response of all the three sensors when orderly exposed to acetaldehyde from 2 to 100 ppm. Since the Pd metal core was oxidised to PdO from 300°C calcination temperature, in this study the gas sensing

testing temperature was kept at 350°C. It can be seen that the corresponding responses of sensors were dependent on the concentration of acetaldehyde. With increasing the acetaldehyde concentration the response increases. It can be seen that all the three sensors show the typical n-type semiconducting behaviour that is after the expose of target gas the resistance decreases. The responses of all the three sensors tested at 350°C for 100 ppm of acetaldehyde is shown in Figure 7. The maximum response of PdO<sub>15</sub>@ZnO core-shell NPs for 100 ppm acetaldehyde was 75 whereas the maximum response of PdO<sub>50</sub>@ZnO core-shell NPs was 28 as compared to the pure ZnO (Rs=18).

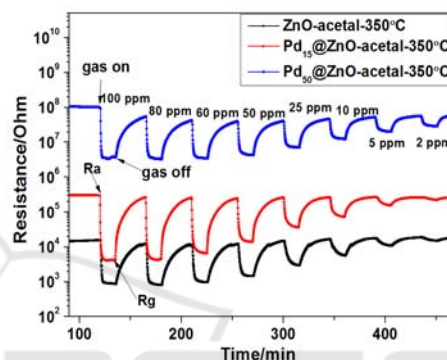


Figure 6: Response transient of all three sensors such as pure ZnO, PdO<sub>15</sub>@ZnO and PdO<sub>50</sub>@ZnO core-shell NPs tested at 350°C for acetaldehyde (2-100 ppm).

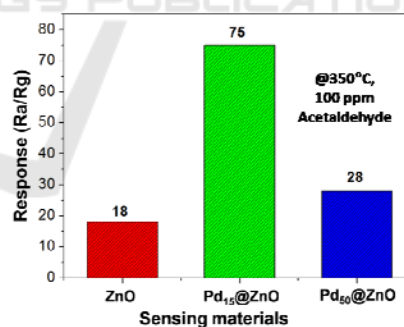


Figure 7: Response of all three sensing materials tested for 100 ppm of acetaldehyde at 350°C.

### 3.4 Gas Sensing Mechanism

Figure 8 shows the gas sensing mechanism of pure ZnO NPs and PdO@ZnO core-shell NPs in air and acetaldehyde medium. The response of PdO@ZnO core-shell NPs shows higher than bare ZnO NPs, which is due to the more depletion layer formation in PdO@ZnO core-shell NPs, which increases the resistance of the core-shell NPs when exposed in air.

After the acetaldehyde gas was exposed, the gas molecules react with oxygen ion species and releases more number of electrons to the conduction band of PdO@ZnO core-shell than pure ZnO. Hence the response of PdO@ZnO core-shell NPs shows higher than pure ZnO NPs. However, the high response of PdO<sub>15</sub>@ZnO core-shell NPs than PdO<sub>50</sub>@ZnO core-shell NPs is due to the smaller size of PdO core, which has more catalytic activities than 50 nm sized PdO core (Ma, 2015).

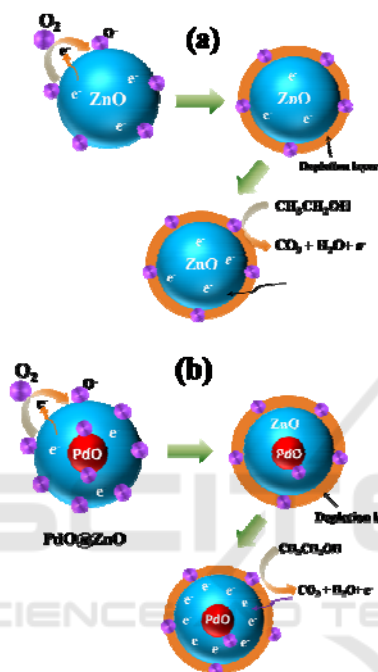


Figure 8: Gas sensing mechanism of (a) pure ZnO NPs and (b) PdO@ZnO NPs in air and acetaldehyde gas medium.

## 4 CONCLUSIONS

In summary, two different sizes of Pd@ZnO core-shell NPs were successfully synthesized by a facile and lower temperature approach, where two different sizes of Pd core such as 15 and 50 nm were used. The overall particles size of Pd<sub>15</sub>@ZnO core-shell NPs was about 80-100 nm, whereas the total size of Pd<sub>50</sub>@ZnO core-shell was 100-120 nm. The spherical shape and structure of as prepared two Pd@ZnO core-shell NPs were maintained after calcined at 500°C for 2 h. The Pd metal core was oxidized to PdO from 300°C calcination temperature. The maximum response of PdO<sub>15</sub>@ZnO core-shell NPs for 100 ppm of acetaldehyde at 350°C was 75, whereas the maximum response of PdO<sub>50</sub>@ZnO

core-shell NPs was 28 as compared to pure ZnO ( $R_s=18$ ). The response of PdO<sub>15</sub>@ZnO core-shell NPs is higher than PdO<sub>50</sub>@ZnO core-shell NPs. The possible reason is due to the smaller size of Pd core, which has more catalytic activity than 50 nm sized Pd core.

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