

## Palladium Doped Graphene Nanocomposites Synthesized with Microwave-Assisted Method and their Application for Hydrogen Evolution†

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This study reports the deposition of palladium nanoparticles on the surface of graphene nanosheet by a simple approach, using a microwave-assisted method. The surface structure, crystal phase and elemental identification of these composites were characterized X-ray diffraction, energy dispersive X-ray analysis and transmission electron microscopy. The photocatalytic activity has been investigated for hydrogen evolution. Especially, the hydrogen evolutions were attributed to the cooperation between graphene and Pd element, due to the high photoelectron transport properties from graphene and the Pd nanoparticles attached on the surface of graphene sheet, which act as reaction centers for H<sub>2</sub> evolution. This work highlights the potential application of graphene-based materials in the field of energy conversion.

**Keywords:** Microwave, Palladium, Graphene, Transmission electron microscopy, Hydrogen evolution.

### INTRODUCTION

The homogeneous palladium catalyst is known as one of the most efficient catalytic systems for carbon-carbon and carbon-heteroatom bond formations. Properly designed Pd/ligand systems have shown fast reaction rates, high turnover frequency, good selectivity and high production yields in various C-C and C-X coupling reactions<sup>1</sup>.

Graphene, a two-dimensional material, has been shown to have excellent electrical and mechanical properties and is well known as a potential support in accepting and transferring electrons at molecular level<sup>2,3</sup>. Due to functional groups on the surfaces of graphene oxide (GO), it can be used as anchoring sites for metal nanoparticles<sup>4</sup>, so it is possible to use them as a support to produce graphene hybrids.

In this paper, we report the preparation of Pd/graphene nanocomposite by fast and facile microwave assisted method. The application of Pd/graphene nanocomposite as a photocatalyst for hydrogen evolution was investigated. The hydrogen evolution took place in aqueous solution containing Na<sub>2</sub>S/Na<sub>2</sub>SO<sub>3</sub> and methanol as sacrificial reagent. The hydrogen evolution rate was found to be markedly high, as compared to other reports. The research reveals that methanol behaves as a hole scavenger, graphene as a light absorber and electron acceptor and transferor and Pd nanoparticles provide a reaction center for hydrogen evolution.

In this study, we deposit Pd nanoparticles on a graphene sheet to design an effective catalyst. To improve the catalysis activity, three samples as composites were prepared by the microwave process. The prepared catalysts were characterized by XRD, EDX and TEM techniques. The catalytic efficiency of the Pd/graphene composites was evaluated by hydrogen evolution.

### EXPERIMENTAL

**Preparation of photocatalyst:** Graphene oxides were prepared by further ultrasonication of graphite oxide. In the typical synthesis, graphene oxide (100 mg) and PdCl<sub>2</sub> (0.5 mmol) were dispersed in ethylene glycol (EG) solution (20 mL) under vigorous stirring, to form a stable suspension. After mixing together by being stirred for several minutes, the solution was then transferred into a 120 mL reaction vessel and placed in a conventional microwave oven. The solution was then irradiated with microwave at full power for 5 s on and 5 s off for 300 s and cooled at room temperature, washed several times with hot water and transferred into a dry oven for 6 h. The weight ratios of PdCl<sub>2</sub> to graphene oxide were 10 %, 20 %, 25 % and the obtained samples were labeled as Pd/GO1, Pd/GO2 and Pd/GO3, respectively.

**Characterization:** The crystal structures and phases of the samples were obtained by XRD (Shimata XD-D1, Japan) with Cu K<sub>α</sub> radiation ( $\lambda = 1.54056$ ) in the range of  $2\theta$  from 10

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to 80°, at a scan speed of 1.20 m<sup>-1</sup>. The decomposition kinetics for the photocatalytic activity was measured in the range between 300 and 700 nm, by spectrometer (Optizen POP, Mecasys, Korea). The morphology of the samples was studied by energy dispersive X-ray spectroscopy (EDX) was also employed for elemental analysis. Transmission electron microscopy (TEM, JEOL, JEM-2010, Japan) was used to observe the surface state and structure of the photocatalyst composites at an acceleration voltage of 200 kV. TEM was also used to examine the size and distribution of the Pd particles deposited on the graphene sheet.

**Photocatalytic reaction and mechanism study:** The photocatalytic reaction was carried out at room temperature. The photocatalyst powder 50 mg Pd/graphene were dispersed by magnetic stirrer, in 150 mL aqueous solution containing 0.1 mol L<sup>-1</sup> Na<sub>2</sub>S and 0.04 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>3</sub> and 20 % methanol as a sacrificial reagent. UV light source having 356 nm in wavelength was used at a distance of 20 cm from the glass reactor. The amount of hydrogen gas evolved was detected by Minimax (X13010683) XP H<sub>2</sub> sensor.

## RESULTS AND DISCUSSION

**Growth and characterization of Pd/Graphene nanocomposites:** Fig. 1 shows the XRD patterns for Pd/GO1, Pd/GO2 and Pd/GO3 samples. In this figure, the (002) diffraction peak of graphene shifts to higher angle ( $2\theta = 26.2^\circ$ ). During microwave radiation, graphene oxide is partially converted to graphene and its crystalline structure is restacked. The XRD pattern of Pd/graphene nanocomposites describes strong diffraction peaks at 39.7, 46.0, 67.4, 80.1, 85.0, which are in good agreement with the (111), (112), (121), (103), (031), (200), (213) crystal planes of pure Pd with face-centered-cubic (fcc) phase<sup>5</sup>. From the XRD spectra, the position of the 002 diffraction peak at 26.2° indicates that graphene oxide is further converted to the crystalline graphene and the conjugated graphene network (*sp*<sup>2</sup> carbon) has been reestablished<sup>6</sup>.

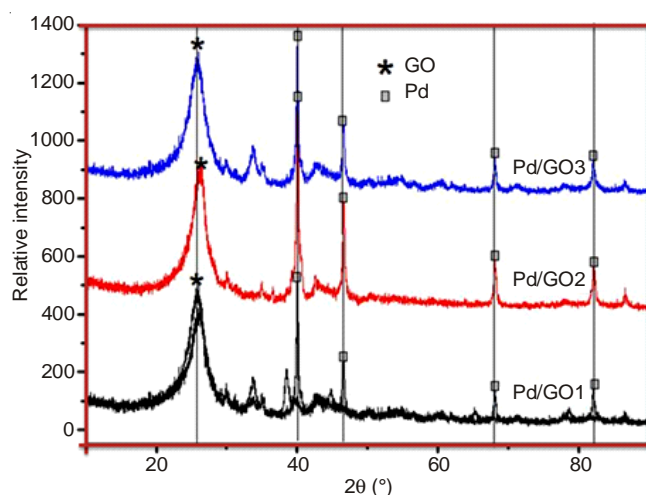


Fig. 1. XRD pattern of Pd/graphene nanocomposites

The EDX analysis of the Pd/graphene nanocomposites indicates that the nanocomposites were synthesized successfully. The elemental contents of Pd/GO1, Pd/GO2 and Pd/GO3 nanocomposite were listed in Table-1.

TABLE-1  
EDX ELEMENTAL MICROANALYSIS (wt %) OF  
Pd/GO1, Pd/GO2 AND Pd/GO3 NANOCOMPOSITES

Sample	Elements (wt %)			Impurity
	C	O	Pd	
Pd/GO1	75.32	16.26	5.44	2.98
Pd/GO2	71.18	17.48	5.81	5.53
Pd/GO3	63.34	18.86	9.31	7.89

For the nanoscale confirmation, the Pd nanoparticles on the surface of graphene sheet (TEM images) were observed. Typical TEM images of the Pd/graphene nanocomposite are shown in Fig. 2. The TEM images of Pd decorated graphene clearly demonstrate that Pd nanoparticles are uniformly dispersed with particle size of 3-9 nm, throughout the surface of transparent graphene sheets. This uniform distribution of Pd nanoparticles on graphene sheet has advantages in catalytic activity and sensor sensitivity<sup>7</sup>.

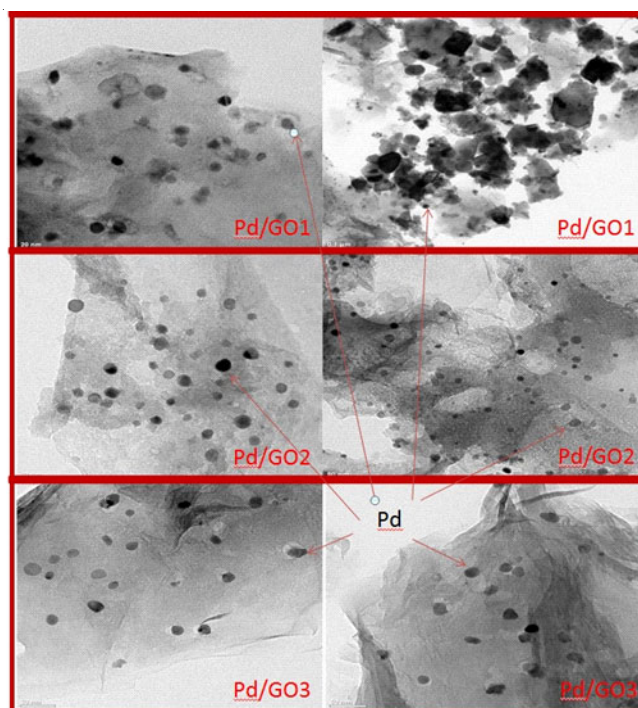


Fig. 2. TEM images of Pd/graphene nanocomposite

**Photochemical production of hydrogen:** The Pd/graphene nanocomposites were well dispersed in an aqueous solution containing Na<sub>2</sub>S/Na<sub>2</sub>SO<sub>3</sub> as sacrificial reagent. The Pd nanoparticles on the graphene surface act as H<sub>2</sub> evolution centers, decorated *via* microwave-assisted method. Light source having wavelength 356 nm was adjusted, such that the maximum area of the sealed container would be exposed. The quantum yield were observed using the equation

$$n_p = t \times S \times Q \quad (3)$$

$$\text{Quantum yield (\%)} = n_H/n_p \times 100 \quad (4)$$

where,  $n_p$  is the amount of incident photon,  $t$  is the irradiation time,  $s$  is the irradiation area in m<sup>2</sup> and  $Q$  is the photon flux of the incident light. The  $Q$  (Y) was calculated from the ratio of the number of reacted electrons during hydrogen evolution, to the number of incident photons according to eqn. 4, where  $n_H$  is the amount of the photogenerated H<sub>2</sub><sup>8</sup>.

The photocatalytic H<sub>2</sub> evolution and the quantum yield efficiency for Pd/graphene nanocomposites and P-25 are shown in Figs. 3 and 4, respectively. The quantum yields of individual Pd/graphene nanocomposites are 5.5, 6.2 and 6.7 %, using Na<sub>2</sub>S/Na<sub>2</sub>SO<sub>3</sub> as reagent. On the other hand the H<sub>2</sub> evolution and the quantum yield efficiency for P-25 were found to be smaller than the Pd/graphene nanocomposites under the same conditions. The reduced H<sub>2</sub> evolution and corresponding quantum yields efficiency may attributed to the fast recombination rate of the excited electron and hole pair in TiO<sub>2</sub>. These results also highlight the importance of graphene which is absent in the P-25. The sacrificial reagent providing electrons to consume the photogenerated holes and Pd can act as a reaction center for the production of H<sub>2</sub> from water. The H<sub>2</sub> evolution plot for 20 % methanol solution having Pd/graphene and P-25 as a photocatalyst are shown in Fig. 5. A relatively lesser amount of H<sub>2</sub> evolution was reported, as compared to Na<sub>2</sub>S/Na<sub>2</sub>SO<sub>3</sub> aqueous solution, the plot for the quantum yields being shown in Fig. 6. The corresponding value for the H<sub>2</sub> evolution and quantum yields efficiency for P-25 were found to be 369 μmol/9 h and 5.5 % respectively. This also confirms that graphene exhibited a significant influence on the photocatalytic activity and alter the corresponding value for H<sub>2</sub> evolution. For the Pd/GO1 sample, a relatively low photocatalytic H<sub>2</sub>-production rate (349 μmol/9 h) was observed, which is attributed to the rapid recombination of electrons and holes<sup>9</sup>. This value significantly increased, with the increasing amount of wt % PdCl<sub>2</sub> in the composites. In order to further demonstrate the photo-stability and cyclic performance of the Pd/graphene composite photocatalyst, cyclic experiments were carried out for the photocatalytic hydrogen evolution. As shown in Fig. 6, the photocatalysts exhibit of photocatalytic activity for hydrogen evolution under the same condition after three runs. Indicating the photocatalytic stability of the nanocomposites. The reused catalyst does not show any noticeable change in the quantum yields efficiency which emphasizes the excellent chemical stability of the catalysts that is beneficial for practical application.

**Photo-degradation mechanism:** It has been reported that graphene sheet does not have band opening. The stabilized band gap in our composites reflects that some of the oxygen functional groups still remain in the photocatalytic reaction, to sustain the band gap width. In this work graphene is photo-

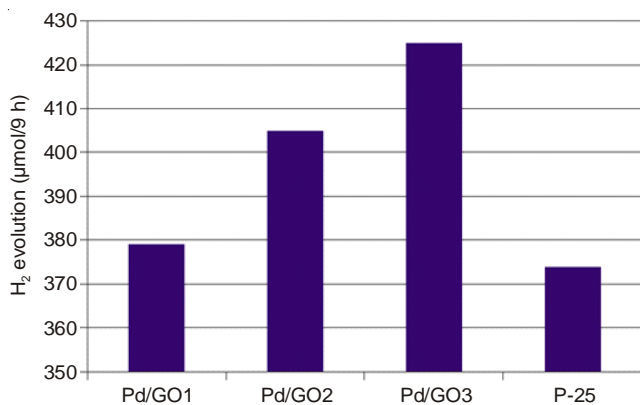


Fig. 3. Photocatalytic H<sub>2</sub> evolution of Pd/graphene and P-25 using Na<sub>2</sub>S/Na<sub>2</sub>SO<sub>3</sub> as sacrificial reagent

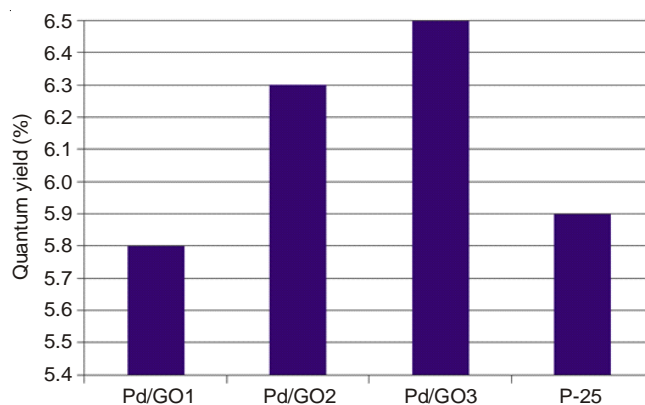


Fig. 4. Quantum yields for hydrogen evolution by Pd/graphene and P-25 with Na<sub>2</sub>S/Na<sub>2</sub>SO<sub>3</sub> aqueous solution

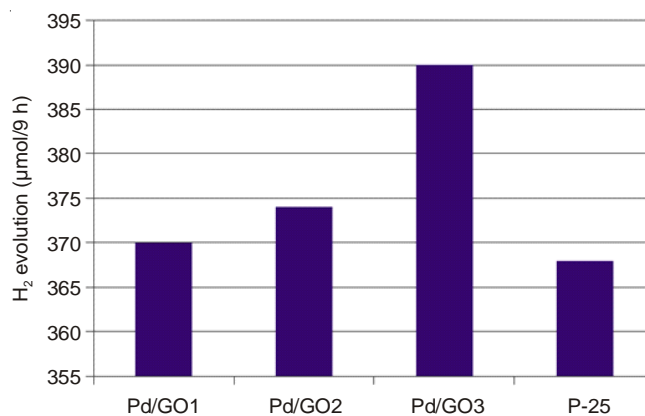


Fig. 5. Quantum yields for hydrogen evolution by Pd/graphene and P-25 with 20 % methanol

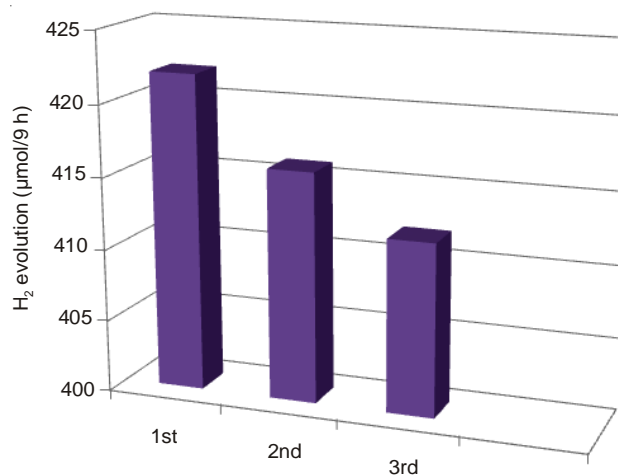


Fig. 6. Cyclic test of Pd/GO3 nanocomposite using Na<sub>2</sub>S/Na<sub>2</sub>SO<sub>3</sub> as sacrificial reagent under UV light irradiation

excited and accumulate the generated electrons on graphene sheet and also act as photo absorber to increase the light absorption<sup>10</sup>. Thus the utilization of visible light in future may further explore new ideas to improve the above proposed photocatalyst mechanism.

## Conclusion

In this work, we successfully employed Pd/graphene nanocomposites as an efficient electron transfer carrier, to develop a highly efficient photocatalytic H<sub>2</sub> evolution.

Graphene in the composite enhanced the crystallinity and the surface area. The loading effect has been examined, by varying weight ratios of graphene oxide as a starting material. We observed that Pd/GO3 composite gives more enhanced hydrogen evolution and dye degradation efficiency, than other composites in our samples. This is attributed to the large surface area, thus providing a large number of reaction centers for the H<sub>2</sub> evolution and hence enhancing the photocatalytic activity. This work not only verified the potential of graphene as a support for Pd nanoparticles in photocatalytic hydrogen production, but more generally, also highlights the potential application of graphene-based materials, in the field of energy conversion.

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