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Enhanced Photocatalytic Activity of Pd-MWCNT/TiO_2 Catalysts Synthesized by Ultrasound-Assisted Method and their Application for Hydrogen Evolution†

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Multi-walled carbon nanotubes (MWCNT) modified using TiO_2 nanoparticles (MWCNT/TiO_2) were prepared. Then, Pd-MWCNT/TiO_2 catalysts were prepared by a ultrasound-assisted method for hydrogen evolution. The physico-chemical properties of the catalysts were characterized by TEM, XRD and EDX spectroscopy, respectively. The hydrogen evolutions were attributed to the Pd element and TiO_2 nanoparticles attached on the surface of multi-walled carbon nanotubes, which act as reaction centers for H_2 evolution.

Keywords: Ultrasound, Palladium, TEM, Multi-walled carbon nanotubes, H_2 evolution.

INTRODUCTION

Titanium dioxide has excellent photocatalytic properties with applications in medicine, buildings and environmental remediation[1]. Titanium dioxide has been studied intensively as a photocatalyst for the complete degradation of organic pollutants[2] because it is easily available, nontoxic, inexpensive and chemically stable. However, TiO_2 has some shortcomings preventing its widespread applications. Titanium dioxide is difficult to separate from aqueous phase and has relatively low quantum yield due to the rapid recombination of electron/hole pairs and can only used under ultraviolet (UV) light. To develop more efficient photocatalysts, considerable effort has been made to modify TiO_2 to develop multifunctional materials and enhance the photocatalytic performance. These efforts include doping with other elements, sensitizing with dyes and coating the surface with noble metals or other semiconductors[3]. The high degree of recombination between the photogenerated electrons and holes in semiconductor particles is a major limiting factor in the photodegradation process[4]. To induce visible light activity in TiO_2, the band gap must be shifted to lower values. The visible light activity can be induced by doping TiO_2 with various metal atoms such as Pt, Ag, Pd, Ru and Cu[5].

In this study, we combined Pd nanoparticles on an MWCNT matrix to design an effective catalyst. To improve the catalysis activity, TiO_2, MWCNT/TiO_2 and Pd-MWCNT/TiO_2 as composites were prepared by the ultrasonic process. The prepared catalysts were characterized by XRD, EDX and SEM techniques. The catalytic efficiency of the Pd-MWCNT/TiO_2 composite was evaluated by H_2 evolution.

EXPERIMENTAL

Synthesis of MWCNT/TiO_2 composite: Multi-walled carbon nanotubes are very stable, they need to be treated with strong acids to introduce active functional groups on their surface. In this experiment, 6.0 g MCPBA was suspended in 200 mL of benzene as a solvent. Then 3 g of MWCNTs powder was put into the solution and the mixture was treated by magnetic stirring for 6 h at 455 K. The resultant solution was filtered and continuously washed with deionized water and ethanol 5 times. The sample was dried at 493 K and fully milled in agate mortar. One beaker containing 20 mL of ethanol (95.0 %) was prepared; 2 mL of TNB was then added to the solution, followed by magnetic stirring for 5 min; 10 mL distilled water was added drop-wise to the solution with constant stirring. Then we add 0.5 g as-prepared oxidized MWCNTs and 50 mL benzene into the solution with constant stirring and ultrasonicated (using 750 W, Ultrasonic Processor VCX 750, Korea) for 4 h. After completion, the black solution was filtered, washed 3 times with deionized water and ethanol and then dried at 873 K. Finally, the sample was heated at 873 K for 1 h. This photocatalyst was named MWCNT/TiO_2.

Synthesis of Pd-MWCNT/TiO_2 composites: From the above, after addition 10 mL distilled water into the TNB (2 mL) and ethanol (20 mL) solution, 50 mL volume fraction of 5 % hydrochloric acid solution; 0.5 g as-prepared oxidized

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MWCNT powder and 0.5 g $PdCl_2$ yellow powder were added into the solution respectively with constant stirring and ultrasonicated (using 750 W, Ultrasonic Processor VCX 750, Korea) for 4 h. After that, use the same process to wash the black solution 5 times as above, dried at 473 K. Then heat treated at 873 K in a hermetic oven for 1 h. This sample was named Pd-MWCNT/TiO_2.

RESULTS AND DISCUSSION

SEM and EDX analysis: The X-ray diffraction (XRD) patterns of anatase TiO_2, MWCNT/TiO_2 and Pd-MWCNT/TiO_2 composites are shown in Fig. 1. It could be confirmed that the TiO_2 in the as-prepared photocatalysts is anatase phase. For these three samples (101), (004), (200), (105), (211) and (204) crystal planes are originated from the anatase TiO_2 phase while (111), (112), (121), (103), (031), (200), (213) and (134) crystal planes are originated from the Pd elemental phase[6]. After refinement, the cell constants are calculated to a = 4.2261 Å, b = 6.9238 Å, c = 7.8547 Å (JCPDS card no. 14-0072). No impurity phase is detected. The broadening of these diffraction peaks indicates that the sample is nanosized. The crystalline size of the sample is estimated to be 15 nm from the Scherrer equation.

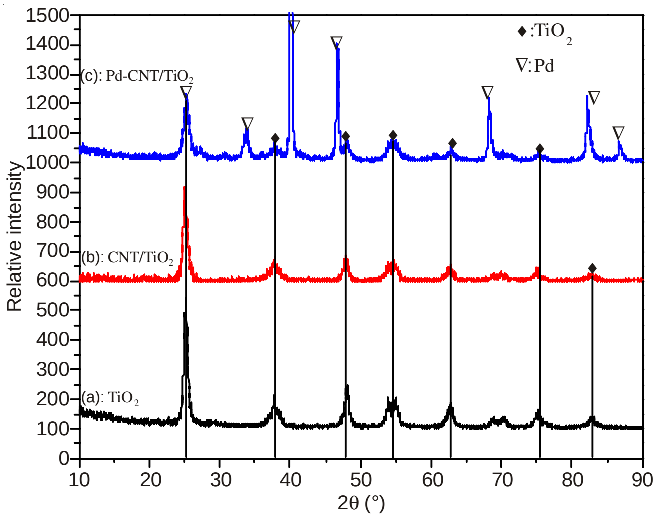

Fig.1. XRD patterns of pure anatase TiO_2 (a), MWCNT/TiO_2 (b) and Pd-MWCNT/TiO_2 (c).

It can be indicated that the Pd-MWCNT/TiO_2composite with high purity has been successfully synthesized in this study. The elemental contents of MWCNT/$TiO_2$and Pd-MWCNT/TiO_2composite photocatalysts were listed in Table-1.

TABLE-1
EDX ELEMENTAL MICROANALYSIS (wt %) OF MWCNT/TiO_2 AND Pd-MWCNT/TiO_2 COMPOSITES

Sample	Elements (wt %)				Impurity
	C	O	Ti	Pd	
MWCNT/TiO_2	5.44	42.72	49.63	0	2.21
Pd-MWCNT/TiO_2	5.67	41.33	26.34	22.33	4.33

TEM analysis: The TEM images of the MWCNT/TiO_2 and Pd-MWCNT/TiO_2 composites are shown in Fig. 2. From Fig. 2 (a) and 2(b), it could be observed that the TiO_2 particles were well dispersed on the surface of MWCNT with a few TiO_2 particles agglomerated together due to the formation of large grains. The difference in the particle size distribution between the images in Fig. 2(c) and 2(d) was clearly observed. A few regular black dots were observed, which correspond to Pd particles. The mean size of the Pd nanoparticles was approximately 8-10 nm, as obtained from the TEM image. In other words, the Pd particles with a small size were attached uniformly to the surface of the MWCNT. The size of the TiO_2 particles was approximately 10-20 nm and they were distributed uniformly on the surface of the MWCNT. A generally precipitate-free and smooth interface was observed among the Pd, TiO_2 and the MWCNT matrix.

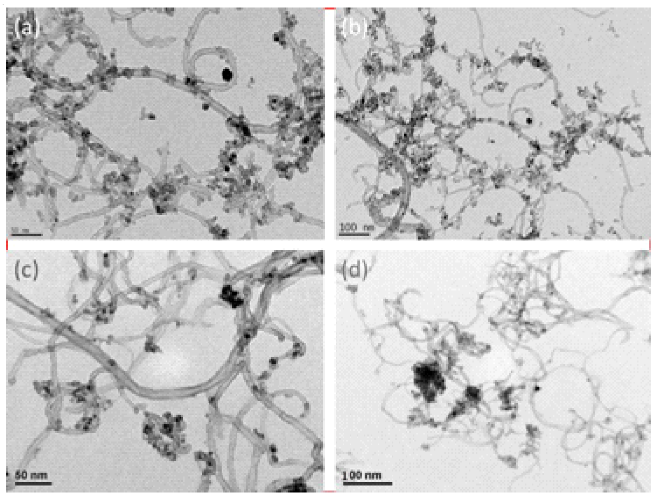

Fig. 2. TEM images of composite photocataysts: (a)&(b) MWCNT/TiO_2, (c)&(d) Pd-MWCNT/TiO_2

Photochemical production of hydrogen: The as-prepared samples were well dispersed in an aqueous solution containing Na_2S/Na_2SO_3 as sacrificial reagent. The Pd nanoparticles on the MWCNT surface act as H_2 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:

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

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

where, n_p is the amount of incident photon, t is the irradiation time, s is the irradiation area in m^2 and Q is the photon flux of the incident light. The quantum yield was calculated from the ratio of the number of reacted electrons during hydrogen evolution, to the number of incident photons according to eqn. b, where n_H is the amount of the photo generated H_2[7].

The photocatalytic H_2 evolution and the quantum yield efficiency (QYs) for Pd/graphene nanocomposites and P-25 are shown in Figs. 3 and 4, respectively. In order to further demonstrate the photo-stability and cyclic performance of the Pd-MWCNT/TiO_2 composite photocatalyst, cyclic experiments were carried out for the photocatalytic hydrogen evolution. As shown in Fig. 5, the photocatalysts exhibit of photocatalytic activity for hydrogen evolution under the same condition after three runs indicating the photocatalytic stability

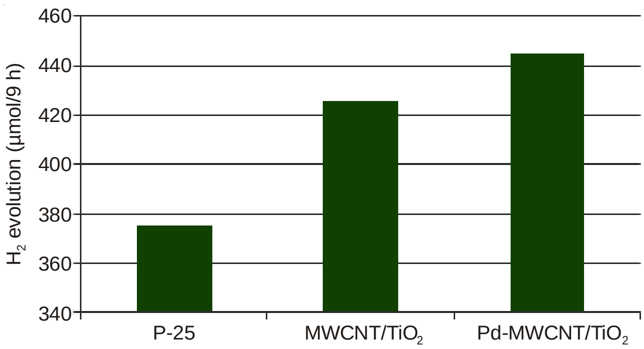

Fig.3. Photocatalytic H_2 evolution of as-prepared samples and P-25 using Na_2S/Na_2SO_3 as sacrificial reagent

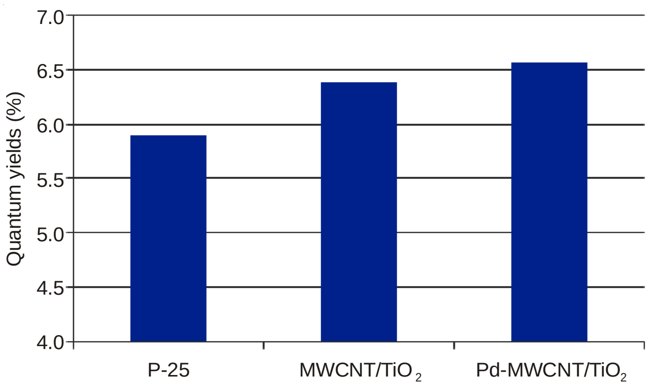

Fig. 4. Quantum yields for hydrogen evolution by as-prepared samples and P-25 with Na_2S/Na_2SO_3 aqueous solution

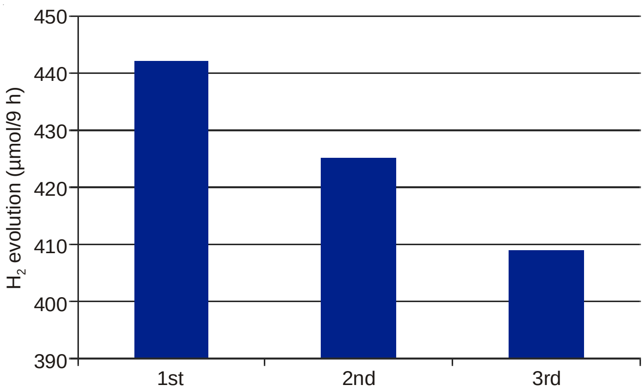

Fig. 5. Cyclic test of Pd-MWCNT/TiO_2nanocomposite using Na_2S/Na_2SO_3 as sacrificial reagent under UV light irradiation

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.

Conclusion

MWCNT/TiO_2 and Pd-MWCNT/TiO_2 composites were synthesized by ultrasonic method. EDX analysis showed that the elemental contents of Pd-MWCNT/TiO_2 were mainly C, O, Ti and Pd. The Pd and TiO_2 particles were uniformly loaded on the wall of the MWCNT in the form of small spots. We observed that Pd-MWCNT/TiO_2 composite gives more enhanced hydrogen evolution, than other composites in our samples. After the third time recycling, the sample still remains relative stable hydrogen evolution efficiency. So, it is suggested that as-prepared Pd-MWCNT/TiO_2 sample have a good effect on recycling hydrogen evolution.

REFERENCES

1. W.-C. Oh, K. Ullah, L. Zhu, Z.-D. Meng, S. Ye and S. Sarkar, *Mater. Sci. Semicond. Process.*, **25**, 34 (2014).
2. T. Ghosh, K. Ullah, V. Nikam, C.-Y. Park, Z.-D. Meng and W.-C. Oh, *Ultrason. Sonochem.*, **20**, 768 (2013).
3. L. Zhu, Z.D. Meng and W.C. Oh, *Chin. J. Catal.*, **32**, 926 (2011).
4. L. Zhu, Z.D. Meng and W.C. Oh, *J. Nanomater.*, Article ID 586526 (2012).
5. Q. Zhang and C.D. Vecitis, *J. Membr. Sci.*, **459**, 143 (2014).
6. M.B. Suwarnkar, R.S. Dhabbe, A.N. Kadam and K.M. Garadkar, *Ceram. Int.*, **40**, 5489 (2014).
7. Y. Koo, G. Littlejohn, B. Collins, Y. Yun, V.N. Shanov, M. Schulz, D. Pai and J. Sankar, *Composites Part B*, **57**, 105 (2014).
8. L. Zhu, S.B. Jo, S. Ye, K. Ullah, Z.D. Meng and W.C. Oh, *J. Ind. Eng. Chem.*, **22**, 264 (2015).