Preparation of Nanosized Palladium-Graphene Composites and Photocatalytic Degradation of Various Organic Dyes

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Abstract: Nanosized palladium particles were synthesized using palladium(II) chloride, trisodium citrate dihydrate, and sodium borohydride under stirring condition. Nanosized palladium-graphene composites were prepared from palladium nanoparticles, and graphene was enclosed with polyallylamine under stirring condition for 1 h followed by ultrasonication for 3 h. Nanosized palladium-graphene composites were heated in an electric furnace at 700 °C for 2 h and characterized by X-ray diffraction, scanning electron microscopy, and transmission electron microscopy. UV-vis spectrophotometry was used to evaluate the nanosized palladium-graphene composites as a catalyst in the photocatalytic degradation of various organic dyes such as methylene blue, methyl orange, rhodamine B, and brilliant green under ultraviolet light at 254 nm.

Keywords: nanosized palladium-graphene composites, photocatalytic degradation, X-ray diffraction, UV-vis spectrophotometry

Introduction

Palladium is a well-known metal with promising potential applications and high catalytic activity on account of its hydrogen adsorption properties.¹ Palladium-based catalysts have been used for cross-coupling reactions and powerful methods for the creation of new carbon-carbon bonds.²,³

Graphene is rising as a new type of carbon material that was first prepared by mechanical exfoliation from graphite in 2004, and as a new type of support substrates for functional nanosized materials.⁴-⁶ Graphene is a two-dimensional free-standing substance with a single-layer structure that has become one of the most popular topics in the fields of chemistry, biochemistry, nanotechnology, physics, and materials science.⁷ The combination of graphene with nanosized metal particles has been performed many times in research over the last decade owing to their novel optical, catalytic, mechanical, and electronic properties.⁶,⁸ Graphene has also attracted a lot of attention as a single layer of sp²-bonded carbon with zero band gap compacted into a two-dimensional honeycomb structure.⁹-¹¹ Among the nanosized composites, graphene can work as a high-performance supporting material because of its two-dimensional structure; therefore, it has various applications in fields like photocatalysis, sensing, and optics.⁵-⁷,⁹,¹¹-¹⁷

Nanosized metal particles can be dispersed homogeneously on the plane of graphene, and charge transfer at the interface of these hybrid materials can provide a synergistic effect inducing properties that are dissimilar from those of each individual component.¹³,¹⁸-²¹ Therefore, in this study, the photocatalytic activity of nanosized palladium-graphene composites was evaluated in the degradation of organic dyes methylene blue (MB), methyl orange (MO), rhodamine B (RhB), and brilliant green (BG) using a UV-vis spectrophotometer under ultraviolet light at 254 nm. The nanosized palladium-graphene composites were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The purpose of this study was to research the kinetics of photocatalytic degradation of organic dyes by nanosized palladium-graphene composites.

Experimental

1. Materials

Palladium(II) chloride (PdCl₂) was purchased from Kojima Chemicals Co., Ltd. Sodium borohydride (NaBH₄), sodium
chloride (NaCl), and ammonium hydroxide (NH₄OH) were obtained from Samchun Chemicals. Poly(allylamine hydrochloride) and organic dyes (MB, RhB, MO, and BG) were supplied by Sigma-Aldrich.

2. Graphene-polyallylamine hydrochloride (PAH)

To a beaker containing 50 mL of distilled water, 0.5 g of PAH and 0.5 mol of NaCl solution were added. The pH value of the solution was adjusted to 9.5 by adding a 0.5 M NH₄OH solution. To the PAH solution, 10 mg of graphene was added and then stirred for 1 h, followed by ultrasonication for 3 h. The graphene-PAH mixture in distilled water was prepared by stirring and ultrasonication.

3. Preparation of the nanosized palladium particles

In a beaker, 10 mL of 0.1 M trisodium citrate dihydrate (Na₃C₆H₅O₇·2H₂O) and 0.05 M PdCl₂ solutions were mixed. Subsequently, 0.015 mol of NaBH₄ was added to the solution with constant stirring. The mixture of Na₃C₆H₅O₇, PdCl₂, and NaBH₄ with a molar ratio of 2:1:0.3 in the solution was stirred for 10 min to provide nanosized palladium particles.

4. Preparation of the nanosized palladium-graphene composites

To 20 mL of the suspension of nanosized palladium particles, 20 mL of the graphene-PAH mixture was added. After leaving the mixture for 1 h, the suspension was centrifuged to separate the product from the solution as a precipitate. The precipitated product was dried at 60 °C. The synthesized nanocomposites were confirmed by XRD (Bruker, D8 Advance). The surface shape of the nanosized palladium-graphene composites was observed by SEM (JEOL Ltd., JSM-6510) at an accelerating voltage of 0.5 to 30 kV. The morphology and size of the crystal product were confirmed by TEM (JEOL Ltd., JEM-2010) at an acceleration voltage of 200 kV.

5. Evaluation of the photocatalytic activity of nanosized palladium-graphene composites

The nanosized palladium-graphene composites were used as a photocatalyst to test the degradation of organic dyes MB, MO, RhB, and BG. The nanosized palladium-graphene composites were placed in separated 10 mL vials containing 10 mL of the aqueous organic dye solutions. Each vial was irradiated under light at a wavelength of 254 nm by a UV lamp. The degradation of the organic dyes by the photocatalyst was analyzed by a UV-vis spectrophotometer (Shimadzu UV-1691PC).

6. Kinetics study for the photocatalytic degradation of organic dyes

Kinetics data for the photocatalytic degradation of organic dyes MB, MO, RhB, and BG with nanosized palladium-graphene composites were measured, and then the regression analysis of the kinetics data was performed using the software package Microsoft Excel (version 2010).

Results and Discussion

1. SEM and TEM analysis

Figure 1 presents a typical SEM image of the nanosized palladium-graphene composites. The image reveals salt-like particles with a hexahedral shape. The TEM image shows that the nanosized palladium-graphene composites are spherical with a mean diameter of 50 nm (Figure 2).

2. XRD analysis

The nanosized palladium-graphene composites were analyzed by XRD (Figure 3). Samples of the as-prepared nanosized palladium-graphene composites were calcined at 700 °C.
The nanosized palladium-graphene composites showed a 2θ value of 26.7° and were assigned to the (002) owing to the nanosized graphene particles. Five diffraction peaks at 2θ of 40.12°, 47.56°, 68.48°, 82.59°, and 87.68° in Figure 3 were indexed to the (111), (200), (220), (311), and (222) crystallographic planes of the nanosized palladium particles, respectively (JCPDS44-1159).

3. UV-vis spectroscopy analysis of the nanosized palladium-graphene composites as a photocatalyst

Figure 4 shows the photocatalytic performance of nanosized palladium-graphene composites. In the present study, the UV-vis spectra were used to examine the photocatalytic degradation of (a) MB, (b) MO, (c) RhB, and (d) BG with nanosized palladium-graphene composites under ultraviolet irradiation at 254 nm for 10 min.

4. Evaluation of kinetics for photocatalytic degradation of various organic dyes

Figure 5 reveals that the degradation curves of organic dyes in the presence of nanosized palladium-graphene composites followed a pseudo-first-order reaction rate law. This meant that the rate of degradation was substantially constant. The order of the kinetics of the photocatalytic degradation of the organic dyes was BG > MB > RhB > MO.

Conclusion

Nanosized palladium-graphene composites were synthe-
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The nanosized palladium-graphene composites were dehydrated in a drying oven at 60 °C. XRD data confirmed the product to be nanosized palladium-graphene composites. SEM showed that the nanosized palladium-graphene composites were in the form of salt-like particles with a hexa-

Figure 4. UV-vis spectra of photocatalytic degradation (a) methylene blue, (b) methyl orange, (c) rhodamine B and (d) brilliant green using nanosize palladium-graphene composites.
hedral shape. TEM showed that the nanosized palladium-graphene composites had a spherical shape with a mean size of 50-70 nm. In addition, the nanosized palladium-graphene composites were synthesized to be used as a photocatalyst for the degradation of MB, MO, RhB, and BG under UV light at 254 nm. Kinetics analysis indicated a first-order kinetics equation for the photocatalytic degradation of MB, MO, RhB, and BG. The order of the kinetics of the photocatalytic
degradation of the organic dyes was BG > MB > RhB > MO.

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References

1. M. Rezaei, S. H. Tabaian, and D. F. Haghshenas, “Electrochemical nucleation of palladium on graphene: A kinetic study with an emphasis on hydrogen co-reduction”, Electrochim. Acta, 87, 381 (2013).
2. X. F. Wu, P. Anbarasan, H. Neumann, and M. Beller, “From noble metal to nobel prize: palladium-catalyzed coupling reactions as key methods in organic synthesis”, Angew. Chem. Int. Ed., 49, 9047 (2010).
3. E. I. Negishi, “Palladium–or nickel-catalyzed cross coupling. A new selective method for carbon-carbon bond formation”, Acc. Chem. Res., 15, 340 (1982).
4. G. Wang, Jintao Bai, Y. Wang, Z. Ren, and Jinbo Bai, “Preparation and electrochemical performance of a cerium oxide-graphene nanocomposite as the anode material of a lithium ion battery”, Scripta Mater., 65, 339 (2011).
5. K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonons, I. V. Grigorieva, and A. A. Firson, “Electric field effect in atomically thin carbon films”, Science, 306, 666 (2004).
6. H. Gao, F. Xiao, C. B. Ching, and H. Duan, “One-step electrochemical synthesis of PtNi nanoparticle-graphene nanocomposites for nonenzymatic amperometric glucose detection”, Appl. Mater. Interfaces, 3, 3049 (2011).
7. M. Zhu, P. Chen, and M. Liu, “Graphene oxide enwrapped Ag/AgX (X=Br, Cl) nanocomposite as a highly efficient visible-light plasmonic photocatalyst”, ACS Nano, 5, 4529 (2011).
8. W. Lu, R. Ning, X. Qin, Y. Zhang, G. Chang, and S. Liu, “Synthesis of Au nanoparticles decorated graphene oxide nanosheets: nanocovalent functionalization by tween 20 in situ reduction of aqueous chloroaurate ions for hydrazine detection and catalytic reduction of 4-nitrophenol”, J. Hazard. Mater., 197, 320 (2011).
9. Y. Li, Y. Yu, J. G. Wang, J. Song, Q. Li, M. Dong, and C. Liu, “CO oxidation over graphene supported palladium catalyst”, Appl. Catal. B-Environ., 125, 189 (2012).
10. X. Zhou, X. Huang, X. Qi, S. Wu, C. Xue, F. Y. C. Boey, Q. Yan, P. Chen, and H. Zhang, “In situ chemical synthesis of SnO2-graphene nanocomposite as anode materials for lithium-ion batteries”, J. Phys. Chem. C., 113, 10842 (2009).
11. F. Y. Kong, X. R. Li, W. W. Zhao, J. J. Xu, and H. Y. Chen,
“Graphene oxide-thionine-Au nanostructure composites: preparation and applications in non-enzymatic glucose sensing”, *Electrochem. Commun.*, **14**, 59 (2012).

12. C. G. Navarro, R. T. Weitz, A. M. Bittner, M. Scolari, A. Mews, M. Burghard, and K. Kern, “Electronic transport properties of individual chemically reduced graphene oxide sheets”, *Nano Lett.*, **7**, 3499 (2007).

13. L. Jiang, M. Yao, B. Liu, Q. Li, R. Liu, H. Lv, S. Lu, C. Gong, B. Zou, T. Cui, and B. Liu, “Controlled synthesis of CeO2/graphene nanocomposites with highly enhanced optical and catalytic properties”, *J. Phys. Chem. C.*, **116**, 11741 (2012).

14. N. R. Wilson, P. A. Pandey, R. Bleanland, R. G. Young, I. A. Kinloch, L. Gong, K. Suenag, J. P. Rourke, and J. Sloan, “Graphene oxide: structural analysis and application as a highly transparent support for electron microscopy”, *ACS Nano*, **3**, 2547 (2009).

15. C. N. R. Rao, A. K. Sood, K. S. Subrahmanyam, and A. Govindaraj, “Graphene: The New Two-Dimensional Nanomaterial”, *Angew. Chem., Int. Ed.*, **48**, 7752 (2009).

16. Akhavan, “Photocatalytic reduction of graphene oxides hybridized by ZnO nanoparticles in ethanol”, *Carbon*, **49**, 11 (2011).

17. M. G. Chung, D. H. Kim, D. K. Seo, T. W. Kim, H. U. Im, H. M. Lee, J. B. Yoo, S. H. Hong, T. J. Kang, and Y. H. Kim, “Flexible hydrogen sensors using graphene with palladium nanoparticle decoration”, *Sensors Actuat. B-Chem.*, **169**, 387 (2012).

18. J. Du, X. Lai, N. Yang, J. Zhai, D. Kisailus, F. Su, D. Wang, and L. Jiang, “Hierarchically Ordered Macro-Mesoporous TiO2–Graphene Composite Films: Improved Mass Transfer, Reduced Charge Recombination, and Their Enhanced Photocatalytic Activities”, *ACS Nano*, **5**, 590 (2011).

19. Y. Y. Liang, Y. G. Li, H. L. Wang, J. G. Zhou, J. Wang, and T. Regier, “Co3O4 nanocrystals on graphene as a synergistic catalyst for oxygen reduction reaction”, *Nat. Mater.*, **10**, 780 (2011).

20. Z. S. Wu, W. Ren, D. W. Wang, F. Li, B. Liu, and H. M. Cheng, “High-energy MnO2 nanowire/graphene and graphene asymmetric electrochemical capacitors”, *ACS Nano*, **10**, 5835 (2010).

21. M. D. Dios, V. Salgueirino, M. P. Lorenzo, and M. A. C. Duarte, “Synthesis of carbon nanotube-inorganic hybrid nanocomposites: an instructional experiment in nanomaterials chemistry”, *J. Chem. Educ.*, **89**, 280 (2012).