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Synthesis of Hybrid Fullerene Oxide[$C_{60}(O)_n$, (n≥1)] – Silver Nanoparticle Composites and Their Catalytic Activity for Reduction of 2-, 3-, 4-Nitroaniline

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Abstract: Fullerene oxide[$C_{60}(O)_n$, (n ≥ 1)] was synthesized by dissolving fullerene[C_{60}] and 3-chloroperoxybenzoic acid in toluene under refluxing condition for 5 h. Hybrid fullerene oxide–silver nanoparticle composites were synthesized by dissolving fullerene oxide and silver nitrate[$AgNO_3$] in diethylene glycol under ultrasonic irradiation for 3 h. The synthesized hybrid nanocomposites were characterized by X-ray diffraction, scanning electron microscopy, and ultraviolet-visible[UV-vis] spectroscopy. The catalytic activity for the reduction of various nitroanilines[NAs] was identified by UV-vis spectrophotometer. The efficiency of the catalytic reduction by the synthesized hybrid nanocomposites has an order of 4-NA > 2-NA > 3-NA.

Keywords: Fullerene oxide[$C_{60}(O)_n$, (n≥1)], Silver nanoparticle, Ultrasonic irradiation, Catalytic activity, Nitroanilines

Introduction

Fullerene (C_{60}) is the shape of a soccer ball with pentagonal and hexagonal structure of carbon atoms, and the fullerene molecule with sixty carbon atoms was first made by Kroto and Smally.[1] Fullerene (C_{60}) is a carbon allotrope such as diamond and graphite, which has a stable structure that can withstand high heat and pressure, as results, has less reactivity and exhibits unique properties that absorb light and electricity well.[2] Fullerenes are used in various fields[3] and exhibit sensitive reactions owing to their fine structures. Therefore, they can be used as new fibers, catalysts, and sensors.[4] Fullerene derivatives have received considerable attention, and various novel fullerene-based molecules have been reported.[2] One of the simplest among them is the fullerene oxide [$C_{60}(O)_n$, (n≥1)]. In this molecule, the attached oxygen atom breaks the icosahedral symmetry of the C_{60} molecule and hence it affects to the properties and both the intra- and inter-molecular dynamics.[5] The orientation and motion of the oxygen atoms in this molecule are of particular interest.[6,7] Metal nanoparticles (NPs) act as excellent catalysts for reduction in the presence of $NaBH_4$.[8] The catalytic activity of silver metal particles depends significantly on their particle size. When particle size become smaller, not only their surface area of catalyst but also catalytic activity are increased.[9] Over the past few years, silver nanoparticles as catalyst have gained immense attention since the activity of metal nanoparticles is extremely effective as heterogeneous catalysts.[10,11] Ag NPs are less expensive than other reported metal nanoparticles and have similar catalyst efficiency.[12] Generally, *p*-nitroaniline (NA) is primarily chosen industrially as a precursor to *p*-phenylenediamine, an important dye component. Nitroanilines (NAs) can cause long-term damage to the environment, especially if discharged into waterbodies.[13] NAs are harmful for human health and the environment. Therefore, it is imperative to transform them into less toxic materials before discharging them into the environment.[14] Reduction of nitroaromatic compounds using noble metal nanoparticle is an important method for conversion of toxic compound into environmental friendly meterials.[15] In this research, ultrasonic irradiation was used for anchoring of Ag nanoparticles on fullerene oxide. Ultrasonic irradiation is an efficient method to obtain catalyst that holds uniform loading of silver nanoparticles. The effects of ultrasound irra-

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diation is due to the acoustic cavitation phenomenon. When a liquid is irradiated with ultrasound, bubbles are created, these bubbles then grow and subsequent collapse, thus releasing the accumulated ultrasonic energy within a very short time.[16-18]

Experimental

1. Materials

Fullerene[C_{60}] (TCI), *m*-chloroperoxybenzoic acid (Sigma-Aldrich), toluene (Samchun), silver nitrate[$AgNO_3$] (Duksan), 2,3,4-nitroaniline (Sigma-Aldrich), sodium borohydride[$NaBH_4$] (Sigma-Aldrich), and diethylene glycol[DEG] (TCI) were used in this experiment.

2. Synthesis of fullerene oxide[$C_{60}(O)_n$, n≥1]

Initially, 40 mg of fullerene[C_{60}] was dissolved in 100 ml of toluene, 196 mg of *m*-chloroperoxybenzoic acid was added to former solution. The mixture so obtained was refluxed for 5 h and then, toluene in the resulting solution was evaporated. The remaining solid material was washed with methanol to remove excess 3-chloroperoxybenzoic acid and dried in a vacuum oven for overnight.

3. Synthesis of hybrid fullerene oxide[$C_{60}(O)_n$, (n≥1)] – silver nanoparticle composites

15 mg of fullerene oxide[$C_{60}(O)_n$, (n≥1)] was dissolved into 22.5 ml of DEG, added 0.075 g of $AgNO_3$ and 2.5 ml of distilled water. The resulting mixture solution was stirred for 30 min to ensure absorption of Ag nanoparticles on the surface of fullerene oxide[$C_{60}(O)_n$, (n≥1)].[17] Ultrasonic irradiation was performed to mixed solution for 3 h (amplitude 70%) and was washed five times with distilled water by centrifugation. Then, the product was dried at 100°C for overnight.

4. Catalytic reduction of various nitroanilines

Nitroaniline was reduced by the Ag nanoparticles which were anchored on the fullerene oxide[$C_{60}(O)_n$, (n≥1)]. 10 mg of $NaBH_4$ was added to 50 mL of 0.25 mM 2-,3-,4-NA aqueous solutions with continuous stirring. And then, 3 mg of hybrid fullerene oxide[$C_{60}(O)_n$, (n≥1)] – silver nanoparticle composites as catalyst were added to various nitroanilines solution. The reduction of 2-,3-,4-nitroaniline was examined by obtaining the absorbance spectra of the solutions after every 5 min by UV-vis spectrophotometer, respectively.

5. Instrumental Analysis

The crystalline structure of hybrid fullerene oxide [$C_{60}(O)_n$, n≥1] – silver nanoparticle composites were examined by X-ray diffraction (XRD, D8-Advance, Bruker) equipped with Cu Kα radiation over 2θ range of −10° to 60°. Scanning electron microscopy (SEM, JEOL, JSM-7600F, Japan) was used to identify the surface morphology of the synthesized composite. The optical absorption spectra of samples were recorded using an UV-vis spectrophotometer (1601 PC, Shimadzu, Japan).

Results and Discussion

1. XRD study

2 mg of fullerene oxide[$C_{60}(O)_n$, (n≥1)] – silver nanoparticle composites were examined for the XRD analysis and XRD patterns were shown in Figure 1. From the Figure 1, the diffraction peaks of fullerene oxide[$C_{60}(O)_n$, (n≥1)] – silver nanoparticle composites were observed at 2θ = 38.11°, 44.30°, and 64.44° as 2θ due to silver nanoparticles. This confirms the anchoring of Ag nanoparticles on the surface of the fullerene oxide[$C_{60}(O)_n$, (n≥1)] during the synthesis of the hybrid nanoparticle composites. The peak of 10.67°, 17.57°,

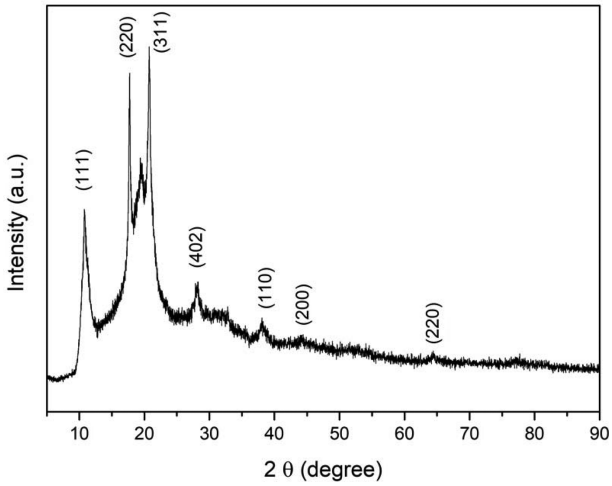

Figure 1. XRD pattern of the hybrid fullerene oxide[$C_{60}(O)_n$, n≥1] – silver nanoparticle composites.

and 20.64° as 2θ was corresponded to the (1 1 1) (2 2 0) and (3 1 1) plans of the fullerene oxide[$C_{60}(O)_n$, (n≥1)].

2. UV-vis spectral analysis

UV-vis spectroscopy was used to investigate the optical properties of fullerene oxide[$C_{60}(O)_n$, (n≥1)] – silver nanoparticle composites. The absorption spectra of the catalyst was recorded in the range from 200 to 800 nm. The peaks related to fullerene oxide[$C_{60}(O)_n$, (n≥1)] and Ag NPs were observed. As it is known, the absorption band corresponding to the Ag NPs was observed at 380-430 nm, while that corresponding to fullerene oxide[$C_{60}(O)_n$, (n≥1)] was observed at 330-336 nm because of the surface plasmon vibrations of the conducting electrons.[18] As shown in Figure 2, the absorption peak at 432 nm can be attributed to the Ag NPs, while that at 332 nm corresponds to the fullerene oxide[$C_{60}(O)_n$, (n≥1)].

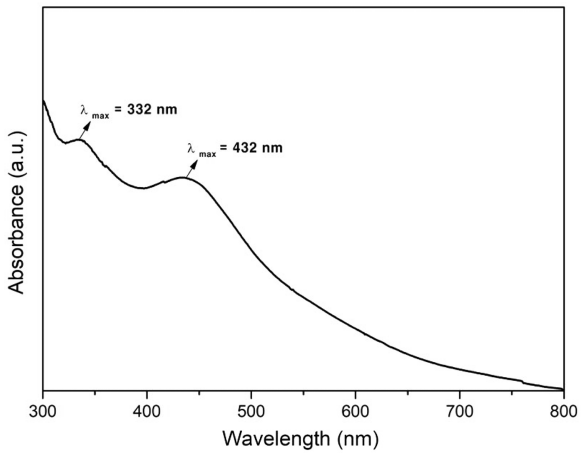

Figure 2. UV-vis spectra of the hybrid fullerene oxide[$C_{60}(O)_n$, n ≥1] – silver nanoparticle composites.

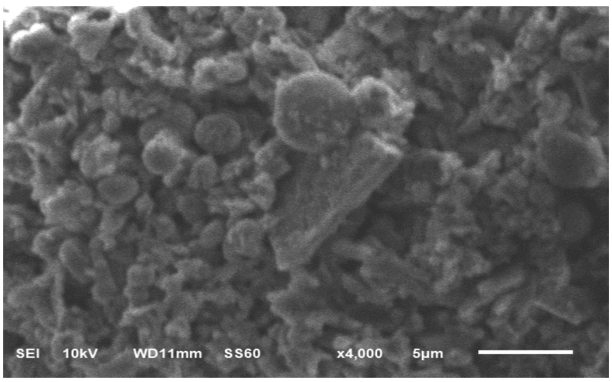

Figure 3. SEM image of the hybrid fullerene oxide[$C_{60}(O)_n$, n≥ 1] – silver nanoparticle composites.

3. Scanning electron microscopy

The structural morphology of the fullerene oxide[$C_{60}(O)_n$, (n≥1)] – silver nanoparticle composites was characterized

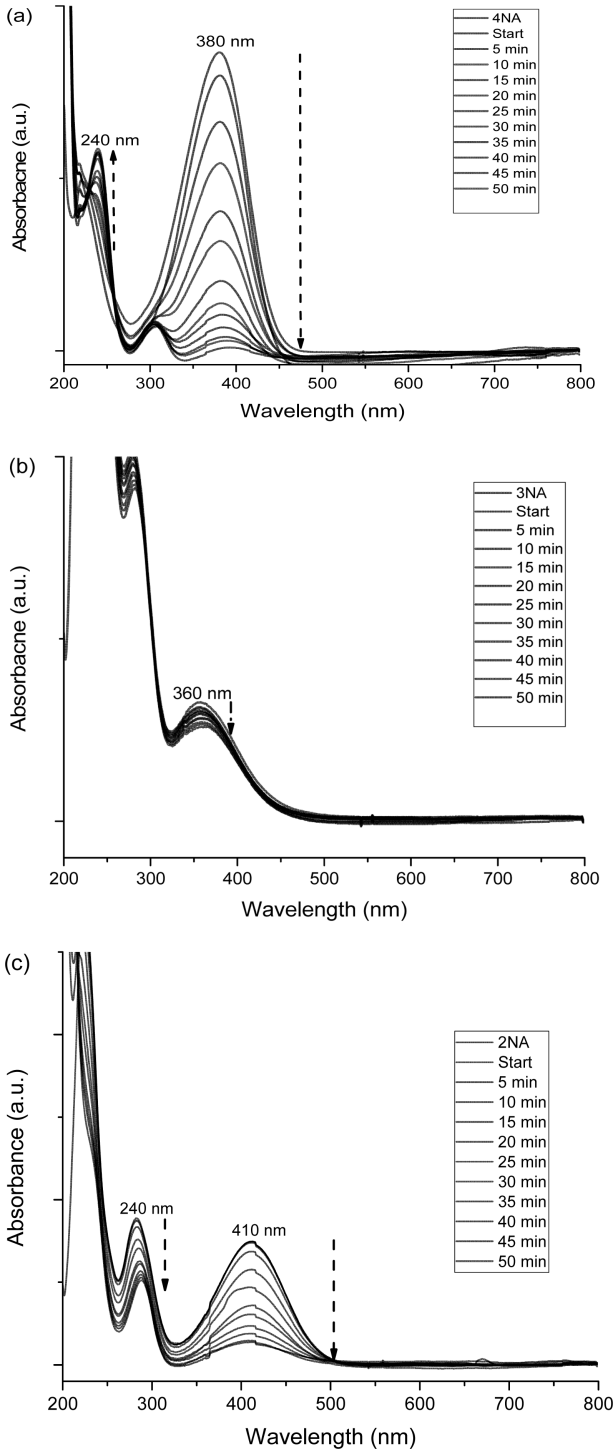

Figure 4. UV-vis spectra of the catalytic activity for the reduction of (a) 4-nitroaniline, (b) 3-nitroaniline, (c) 2-nitroaniline in the presence of fullerene oxide[$C_{60}(O)_n$, n≥1] – silver nanoparticle composites catalyst with $NaBH_4$.

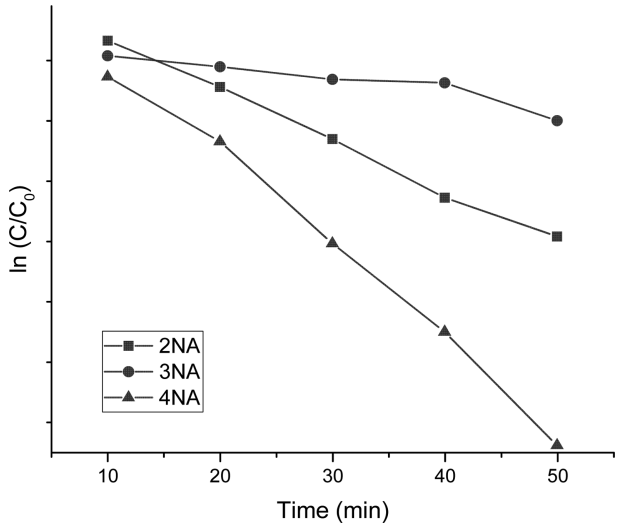

Figure 5. Kinetics study for the reduction of the nitroanilines using the hybrid nanocomposites as the catalyst in the presence of $NaBH_4$.

using scanning electron microscopy as shown in Figure 3.

SEM images exhibited that these nanoparticle composites has two shapes of surface morphology. The fullerene oxide [$C_{60}(O)_n$, (n≥1)] showed multiple square shaped layers, while the Ag NPs existed as small spherical agglomerates. These results indicate that Ag NPs were successfully anchored on the fullerene oxide[$C_{60}(O)_n$, (n≥1)] as supporting material.

4. Catalytic activity

In order to investigate the catalytic activity of the hybrid nanocomposites, three isomers of nitroaniline (*o*-NA, *m*-NA and *p*-NA) were reduced to *o*-PDA, *m*-PDA and *p*-PDA, respectively, using the hybrid nanocomposites as the catalyst according to the procedures discussed in the previous sections.[19,20] The effect of the Ag nanoparticles on the reduction of the nitroanilines was also investigated.[19,20]

Figure 4 shows the variation of UV-vis spectra of *o*-NA, *m*-NA, and *p*-NA with time, which were reduced in the presence of the catalyst. The absorption peaks of *o*-NA to *o*-PDA were shown at 410 nm and 240 nm. The absorption peaks of *m*-NA to *m*-PDA were shown at 360 nm and 300 nm. The absorption peaks of *p*-NA to *p*-PDA were shown at 380 nm and 240 nm. As shown in Figure 5, the kinetics study for catalytic reduction of various nitroanilines was followed at a slope of pseudo-first order reaction rate, which is expressed by a simple equation of $\ln (C/C_0) = -k_{app} \cdot t$, where the k_{app} is an apparent rate constant, the C/C_0 is concentration ratio of different measuring state at time *t* and initial state. In the observation of catalytic activity, the efficiency of nitroaniline reductions has an order of 4-NA > 2-NA > 3-NA.

Conclusions

In summary, we successfully synthesized hybrid nanoparticle composites which Ag NPs were located on the surface of fullerene oxide[$C_{60}(O)_n$, (n≥1)] by ultrasonic irradiation. XRD, UV-vis spectrophotometer and SEM were used to characterize the hybrid nanoparticle composites which were synthesized. The hybrid nanocomposites were used as catalyst to reduce 2-,3-,4-nitroaniline to 2-,3-,4-phenylenediamine and exhibited excellent catalytic activity.

Acknowledgements

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References

1. W. C. Oh, A. R. Jung, and W. B. Ko, "The preparation and characterization of a silver-containing fullerenes", *J. J. Ceram. Process Res.*, **9**, 19 (2008).
2. A. Hirsch, "The era of carbon allotropes", *Nat. Mater.,* **9**, 868 (2010).
3. M. Sathish and K. Miyazawa, "Size-tunable hexagonal fullerene (C_{60}) nanosheets at the liquid-liquid interface", *J. Am. Chem. Soc.*, **129**, 13816 (2007).
4. O. V. Kharissova, C. M. O. González, and B. I. Kharisov, "Solubilization and dispersion of carbon allotropes in water and non-aqueous solvents", *Ind. Eng. Chem. Res.*, **57**, 12624 (2018).
5. M. P. Barrow, N. J. Tower, R. Taylorb, and T. Drewello, "Matrix-assisted laser-induced gas-phase aggregation of C_{60} oxides", *Chem. Phy. Lett.*, **293**, 302 (2008).
6. C. Y. Zo, Z. D. Meng, W. C. Ji, S. Q. Liu, Z. Shen, Y. Zhang, and N. S. Jiang, "Preparation of a fullerene[60] iron oxide complex for the photo fenton degradation of organic contaminants under visible light irradiation", *Chin. J. of Cat.*, **39**, 1051 (2018).
7. R. M. Nikonova, M. A. Merzlyakova, V. I. Lad'yanov, and V. V. Aksenova, "X-ray diffraction and UV/Vis spectroscopic study on thermal stability of fullerenes/fullerites", *Inorg. Mater. Appl. Res.*, **3**, 44 (2012).
8. C. H. Prasad, K. Srinivasulu, and P. Venkateswarlu, "Catalytic reduction of 4-nitrophenol using biogenic silver nanoparticles

derived from papaya (carica papaya) peel extract", *Ind. Chem.*, **1**, 1000104 (2015).
9. S. Özkar, "Enhancement of catalytic activity by increasing surface area in heterogeneous catalysis", *Appl. Surf. Sci.*, **256**, 1272 (2009).
10. T. N. J. I. Edison, E. R. Baral, Y. R. Lee, and S. H. Kim, "Biogenic synthesis of silver nanoparticles using cnidium officinale extract and their catalytic reduction of 4-nitroaniline", *J. Clust. Sci.*, **27**, 285 (2016).
11. Z. Dong, X. Le, X. Li, W. Zhang, C. Dong, and J. Ma, "Silver nanoparticles immobilized on fibrous nano-silica as highly efficient and recyclable heterogeneous catalyst for reduction of 4-nitrophenol and 2-nitroaniline", *Appl. Catal. B-Environ.*, **158**, 129 (2014).
12. Z. H. Farooqi, R. Khalid, R. Begum, U. Farooq, and Q. Wu, "Facile synthesis of silver nanoparticles in crosslinked polymeric system by in-situ reduction method for catalytic reduction of 4-nitroaniline", *Environ. Technol.*, **40**, 2027 (2019).
13. P. Dauthal and M. Mukhopadhyay, "Agro-industrial waste-mediated synthesis and characterization of gold and silver nanoparticles and their catalytic activity for 4-nitroaniline hydrogenation", *Korean J. Chem. Eng.*, **32**, 837 (2015).
14. V. Arumugam, P. Sriram, T. Yen, G. G. Redhi, and R. M. Gengan, "Nano-material as an excellent catalyst for reducing a series of nitroanilines and dyes: triphosphonated ionic liquid-$CuFe_2O_4$-modified boron nitride", *Appl. Catal. B-Environ.*, **222**, 99 (2018).
15. M. Ismail, M. Khan, S. B. Khan, K. Akhtar, M. A. Khan, and A. M. Asiri, "Catalytic reduction of picric acid, nitrophenols and organic azo dyes via green synthesized plant supported Ag nanoparticles", *J. Mol. Liq.*, **268**, 87 (2018)
16. I. Hua and M. R. Hoffmann, "Optimization of ultrasonic irradiation as an advanced oxidation technology", *Environ. Sci. Technol.*, **31**, 2237 (1997).
17. Z. Mohammadi and M. H. Entezari, "Sono-synthesis approach in uniform loading of ultrafine Ag nanoparticles on reduced graphene oxide nanosheets: An efficient catalyst for the reduction of 4-nitrophenol", *Ultrason. Sonochem.*, **44**, 1 (2018).
18. T. Yamamoto and S. Komarov, "Investigation on acoustic streaming during ultrasonic irradiation in aluminum melts", by C. Chesonis(ed) pp 1527-1531, *Light Metals* 2019, The Minerals, Metals & Materials Series,Springer, Cham, 2019.
19. Q. Zhou, G. Qian, Y. Li, G. Zhao, Y. Chao, and Junwei Zheng, "Two-dimensional assembly of silver nanoparticles for catalytic reduction of 4-nitroaniline", *Thin Solid Films*, **516**, 953 (2008).
20. H. L. Lin, N. L. Sou, and G. G. Huang, "Single-step preparation of recyclable silver nanoparticle immobilized porous glass filters for the catalytic reduction of nitroarenes", *RSC Adv.*, **5**, 19248 (2015).