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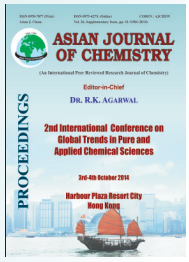

Photodegradation of Nitrobenzene Using Cobalt Modified Zinc Oxide Particles

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This paper reports the synthesis and modification of zinc oxide, ZnO nanoparticles from zinc nitrate hexahydrate, citric acid and cobalt nitrate hexahydrate, using polyethylene glycol as a surfactant *via* a combination of hydrothermal and sol-gel methods. The sample was calcined at 500 °C for 2 h. The characterization of the nanoparticles was done using XRD, TEM, FESEM and BET surface area measurement analysis. The photodegradation study was run for 2 h in an improvised photoreactor using an 18 W visible light source. The extent of photodegradation and mineralization was conducted using UV-visible spectroscopy, COD and TOC measurements. The band gap energy was measured using UV-visible spectroscopy and it was found to be 3.22 eV. The XRD results confirmed the ZnO nanoparticles of being hexagonal with Wurtzite structure. The morphology as revealed by TEM and FESEM showed the samples to be spherical in shape and with particle size less than 100 nm. The surface area of the catalyst as measured *via* BET is 17.566 m^2/g. After 2 h of degradation 80.39 % of nitrobenzene was removed. The COD and TOC results removal reach 79 and 66 %, respectively. From the results it could be understood that ZnO synthesized and modified using cobalt nitrate could be an effective candidate for wastewater treatment.

Keywords: Cobalt, Hydrothermal, Nitrobenzene, Photodegradation, Sol-gel, ZnO.

INTRODUCTION

The relationship between industrial activity and environmental pollution is an extensively documented reality of recent decades[1-4]. Many efforts have been devoted to develop technologies that are able to minimize the hazardous effects caused by industrial activities[5,6]. Among many options, the development of processes to transform the toxic and hazardous pollutants into harmless compounds is one of the most effective solutions. Photochemical processes are important, mainly due to their capacity to degrade toxic and hazardous pollutants into environment friendly compounds in short reaction times. The oxidation process which, include advanced oxidative process previously used for wastewater treatment for municipal supply and/or some agricultural activities has been widely used in many countries. However, the process has not been without a problem because of the inability of the process to convert the non-biodegradable compounds into harmless products. The coming up of semiconductor photocatalysis has indeed helped greatly towards remedying the enormous dangers pollutants caused to our environments, particularly water and air environment. However, difficulty in the recovery of the semiconductor after the photodegradation is posing a great problem. Recent studies have confirmed the improvement in the efficiency of some semiconductor photocatalysts when doped using some elements/compounds. Some studies have also shown that selection of appropriate method of synthesis can allow the use of photocatalysts under different irradiation conditions with much improved photoactivity, in which light several methods were used[7-20].

From the various synthesis methods, sol-gel and hydrothermal methods are among the best techniques used due to the fact that, sol-gel is capable of synthesizing nanosized semiconductor with high purity state and hydrothermal method enable synthesis with more uniform distribution in particle size. The combination of the two methods brings together the two advantages of high purity and more uniform distribution in particle size, there by producing the catalyst with lower band gap energy and controlled particle size (15-20 nm) than sol-gel and hydrothermal methods[16].

Tsay *et al.*[22] prepared, characterized and studied the photocatalytic activity of Co-doped ZnO powders with the result showing great improvement in the photocatalytic properties of Co-doped ZnO over un-doped ZnO using methyl orange as substrate. Hong *et al.*[23] studied the effect of dopant concentration and annealing temperature of ferromagnetism properties

of Co-doped ZnO thin films. Cobalt doping has been shown to possessed high photocatalytic activity than other metals like iron, chromium, manganese, zirconium *etc*., due to shifting of the wavelength of maximum absorption towards visible region as well as smaller particle size[21]. The rate of photocatalytic removal of methylene blue and chromium metal complex was reported by Shrivastava[24] and showed that the removal increases with increase in contact time.

Nitrobenzene is a nitro aromatic hydrocarbon used to produced aniline and it was nominated by the National Institute of Environmental Health Sciences for listing in the Report on Carcinogens based on the conclusions of an International Agency for Research on Cancer (IARC) working group that there is sufficient evidence of its carcinogenicity in experimental animals and that it is possibly carcinogenic to humans[25]. Minero *et al*.[26] reported that degradation of nitrophenols is slightly faster than that of nitrobenzene and also reported that TiO_2 showed better efficiency on the degradation of nitrobenzene than ZnO. Nitrobenzene is considered to be highly toxic aromatic compound which is widely used in explosives, pesticides, prepharmo, dye production, *etc.*[27-29].

EXPERIMENTAL

Nitrobenzene, (98 % purity) was purchased from British Drug House; UK. The capacity of the visible light lamp is 18 W (Philips). ZnO (99 % purity) obtained from Merck was used wherever commercial zinc oxide is mentioned in all the experiments. For the synthesis, zinc nitrate hexahydrate, $Zn(NO_3)_2{\cdot}6H_2O$ (98 % purity) obtained from Bendosen; cobalt nitrate hexahydrate, $Co(NO_3)_2{\cdot}6H_2O$ (98 %) obtained from Aldrich; citric acid, $C_6H_8O_7{\cdot}H_2O$ (99.83 % purity) purchased from Fisher scientific; polyethylene glycol, (PEG2000) obtained from R&M Chemicals and NH_4OH (30 % purity) purchased from R&M Chemicals were used.

Synthesis of ZnO *via* sol-gel and hydrothermal methods: ZnO was synthesized *via* the combination of sol-gel and hydrothermal methods by dissolving 8.9253 g of zinc nitrate hexahydrate and 6.3042 g of citric acid in a mixture of 100 cm^3 of deionized water and 10 cm^3 of 1 % PEG2000. The solution was magnetically stirred for few minutes to allow for complete dissolution. The pH of the solution was adjusted to pH 7 using few cm^3 of conc. ammonium solution. The solution was then warmed in a steam bath at 80 °C for 4 h after which it was aged at room temperature for another 4 h and then magnetically stirred at 85 °C for 15 h. After the gel is formed, the gel solution is transferred into a Teflon-line stainless steel vessel and taken into hydrothermal oven operated at 80 °C for 18 h. The precipitate formed is filtered, washed using deionized water and finally dried in the oven at 100 °C for 12 h. The sample was then grinded and calcined at 500 °C for 2 h, in a carbolite furnace with a heating rate of 10 °C/min.

Modification of ZnO using cobalt nitrate: The modification of the ZnO was done in order to produce a sample with a better efficiency. The procedure was the same as in the case of the synthesis *via* sol-gel and hydrothermal methods, with the addition of 0.50 % (0.1012 g) of cobalt nitrate hexahydrate, $Co(NO_3)_2{\cdot}6H_2O$ at the initial stage.

General photocatalytic procedure: A 1 L nitrobenzene prepared solution is placed inside the glass vessel and the vessel is placed on the speed controlled magnetic stirrer set at 190 rpm. Air is pumped through rubber tubing and an appropriate mass of the catalyst (commercial ZnO or synthesized ZnO) was added. Where necessary, pH adjustment is made using drops of conc. NH_4OH or HCl. The solution is agitated for 30 min before light (visible lamp) is irradiated. The experiment runs for 120 min after the 30 min of adsorption time. About 10 cm^3 of the test solution is withdrawn from the reactor using a clean pipette at a regular interval of 15 min. The withdrawn solution is immediately filtered into pre-labeled sample vial using a cellulose nitrate filter and kept for analysis. The concentration of the test solution is determined using Perkin Elmer (P.E.) Lambda 35 UV-visible spectrometer.

Optimization studies: In order to determine the optimum condition for the application of the synthetic ZnO on nitrobenzene, commercial ZnO was used. In the optimization study, substrate concentration and catalyst mass loading were the main consideration. In terms of substrate concentration, 10, 15, 20, 25 and 30 ppm of nitrobenzene were taken while for the catalyst mass loading, 0.25, 0.50, 0.75 and 1.00 g of commercial, synthesized and Co-modified ZnO were considered.

RESULTS AND DISCUSSION

The optimization study conducted using commercial ZnO has shown that, the best operating conditions for the intended study was 20 ppm pollutant concentration and 0.75 g catalyst loading. A slight modification of Vijayan *et al.*[11] combined sol-gel and hydrothermal method has produced ZnO nanoparticle with good photoactivity against nitrobenzene.

Modification of the synthesized ZnO with cobalt has shown an improvement in its photoactivity. The characterization studies conducted show that, XRD patterns (Fig. 1) of the modified ZnO nanoparticles depicts perfectly with the hexagonal wurtzite structure of ZnO (JCPDS No: 98-003-1345). The TEM and FESEM analyses (Figs. 2 and 3) confirms the shape of the particles to be spherical and having sizes less than 100 nm. Particle sizes measured using TEM is close to the crystallite size calculated using Scherer's formula. The band gap energies were estimated from the plots of $(ahv)^2$ *versus* photon energy (hv) and were found to be 3.18, 3.20 and 3.22 eV for SP3, SP2 and SP1, respectively. The linear dependence of the $(ahv)^2$ on photon energy showed that the synthesized ZnO nanoparticles are direct band semiconductors[30]. Similarly,

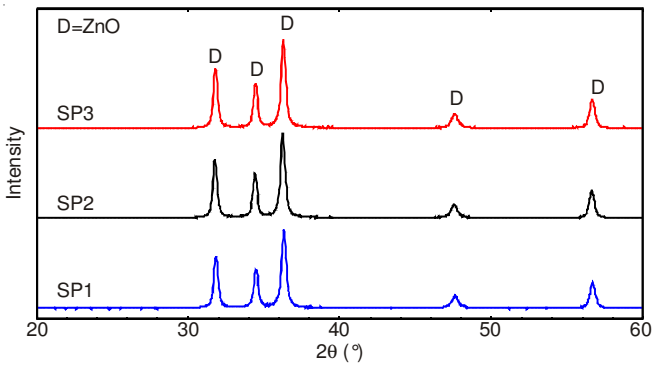

Fig. 1. XRD patterns for modified ZnO under different dopant concentration

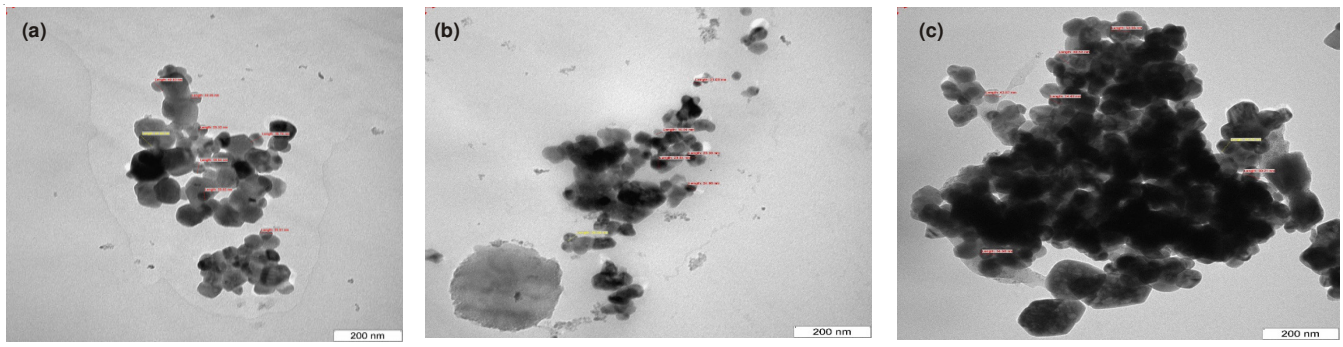

Fig. 2. (a) TEM image for SP1; (b) TEM image for SP2; (c) TEM image for SP3

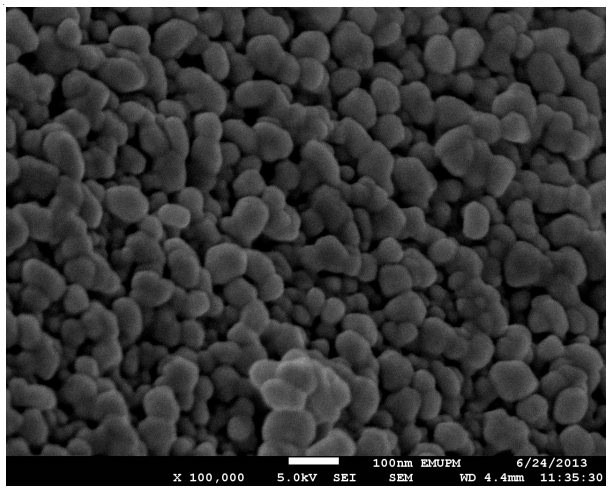

Fig. 3. FESEM image for SP3

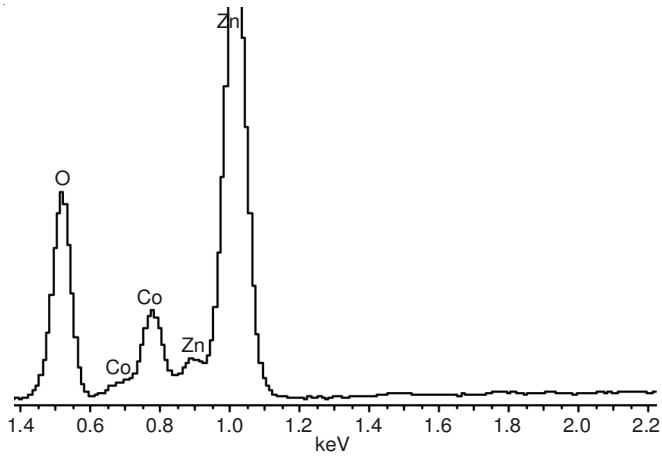

Fig. 4. EDX spectrum for SP3

surface area plays a vital role in the catalytic activity of a catalyst and hence, BET technique was employed to determine the specific surface area of the synthesized nanoparticles. The result is as shown on Table-1 and revealed (to a lesser extent) the dependence of photoactivity on the surface area. The reason for this variance may be attributed to other factors that came to play, such as band gap energy, crystallinity and particle size. In terms of adsorption-desorption isotherms, it is of type IV for both particles and reflects the characteristics of typical mesoperous materials[31].

TABLE-1
BET MEASUREMENTS FOR SP1, SP2 AND SP3

Sample	BET surface area (m^2/g)	Pore volume (cc/g)	Pore radius (A)
SP1	14.672	0.091	77.914
SP2	17.565	0.119	30.530
SP3	16.070	0.107	43.947

From the photodegradation study performed using visible light irradiation, it was found out that, sample SP3 (0.50 % Co) gave the best performance in relation to ZC (commercial ZnO), SP1 (1.0 % Co) and SP2 (0.25 % Co) as reflected on Fig. 5. During the 2 h irradiation time SP3 sample brought about 82.84 % nitrobenzene removal in comparison to 78.71, 77.14 and 79.91 % removal by ZC, SP1 and SP2, respectively. In order to ensure that, the organic pollutant has been successfully degraded to environmentally friendly products, TOC and COD analyses were conducted. In TOC analysis, 66 %

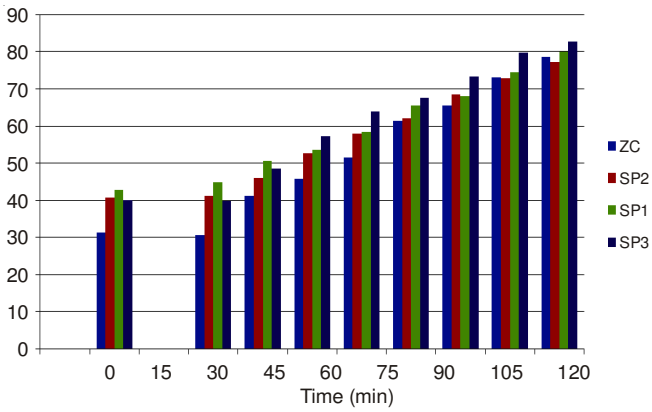

Fig. 5. Comparison of photodegradation of ZC, SP1, SP2, SP3 under visible light irradiation

TABLE-2
TOC MEASUREMENTS FOR THE PHOTODEGRADED SOLUTION USING SP3

Sample	TC	IC	TOC	TOC removal (%)
Blank	0.14730	0.3412	0.1939	-
Initial	0.05271	0.3940	0.3413	-
0 min	9.96100	0.4299	9.5310	0.00
15 min	8.30200	0.4977	7.8040	18.1200
30 min	8.91600	2.3250	5.8710	38.4000
45 min	7.65500	2.3670	5.2880	44.5100
60 min	7.10600	0.5350	6.5710	31.0500
75 min	6.66700	0.5787	6.0890	36.1100
90 min	6.05000	2.1160	3.9340	58.7200
105 min	5.42500	2.1350	3.2900	65.4800
120 min	5.23300	2.0140	3.2200	66.2200

TABLE-3
COD MEASUREMENT AND PERCENTAGE REMOVAL

Sample	COD (mg/L)	Removal (%)
0 min	40.00	0.00
15 min	28.00	11.63
30 min	32.00	25.58
45 min	11.00	30.23
60 min	28.00	34.88
75 min	24.00	44.19
90 min	16.00	62.79
105 min	19.00	67.44
120 min	09.00	79.09

TABLE-4
COMPARISON OF CRYSTALLITE SIZE CALCULATED USING SCHERER'S FORMULA WITH PARTICLE SIZE MEASURED USING TEM

Sample	XRD (nm)	Particle size from TEM (nm)
SP1	34.19	27 – 42
SP2	34.15	16 – 28
SP3	30.74	24 – 52

removal was achieved indicating that nitrobenzene was degraded in the reaction. Likewise, there was increased in IC in the first 45 min of irradiation suggesting that part of the organic carbon might have been converted to inorganic carbon compounds. The COD test served as an additional test to support the mineralization of the nitrobenzene. The COD results indicates 79 % removal in 2 h duration. This result could be adjudged as fairly okay when compared to 78, 85 and 94 % TOC removal in the photodegradation study conducted on *m*, *o* and *p*-cresols by Yadollah *et al.*[32-34] for a 6 h duration.

Conclusion

In conclusion, this study was able to successfully synthesized, modified, characterized and applied ZnO particles on the removal of nitrobenzene using visible light irradiation. The characterization study reveals good characteristics of the product suggesting probable relationship with the product photoactivity. The modified sample resulted in a better removal than the commercial ZnO. In a similar manner, COD and TOC measurements expresses opinion that the nitrobenzene was successfully mineralized to H_2O and CO_2. However, more researches need to be conducted in order to get better understanding of chemical processes taking place during the synthesis, on the surface of the photocatalysts and the end products in order to give a realistic relationship between synthesis method, characteristic and application of photocatalysts.

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