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Synthesis of NiO/ZnO Nanoparticles: Application for Photodegradation of Methylene Blue

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Abstract— NiO/ZnO nanocomposites synthesized by sol-gel method with zinc chloride and nickel nitrate hexahydrate in ethanol used as solvent. Material was characterized by Particle size analyzer, UV-Vis, FTIR, TGA and DSC. NiO/ZnO nanoparticles investigated as a suitable photocatalytic material for the methylene blue degradation i.e. an organic dye under visible light irradiation. The UV–vis absorption spectra of the NiO/ZnO nanoparticles shown peaks in the UV region, corresponding to the band gap of the NiO/ZnO nanoparticles. The band gap of NiO/ZnO nanoparticles is calculated 3.55 eV by Tauc's plot method. Then UV visible data showed the methylene blue degradation with NiO/ZnO nanoparticles, behaving as active catalyst.

Keywords: ***Catalysis, Ethanol, Methylene Blue, NiO/ZnO Nanoparticles, Sol-gel method***

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I. INTRODUCTION

Semiconductor metal oxides have many properties such as chemical stability, nontoxic nature and low cost. Because of these properties these are used as photocatalyst in environmental remediation (1-3). Nowadays, increasing population is affecting the quality of water. Researchers are attracted towards proficient treatments of wastewaters to resolve the water pollution issues. Preferably, method for wastewater treatment must be cost-effective and viable for large-scale applications. A huge amount of water could be saved after being treated, treated water might be useful in many applications such as textile industry, agriculture or factory. Semiconductor oxide nanomaterials are effective in the treatment of wastewater (4).

NiO is a notable metal oxide that has many applications. NiO metal oxide used in supercapacitor as cathode material (5). NiO has most important feature that it has magnetic properties and NiO nanoparticles showed ferromagnetic as well as superparamagnetic behavior (6). NiO is a p-type semiconductor with band gap of 3.5 eV and rock salt or cubic structure. NiO has applications in numerous field (7) such as catalyst (8), battery (9), gas sensors (10), electrochromic films (11). Nickel oxide (NiO) mainly studied because of its electronic structure, strongly affected by Ni 3d electrons which are localized in space but spread out over a wide energy range because of strong coulomb repulsion between them (7, 12).

Another metal oxide is ZnO. Which is n-type semiconductor and has bandgap of 3.2 eV. ZnO is cheaper and active relative to TiO2, but Zn^{2+} ions release in solution and Zn $(OH)_2$ is formed at the surface which is commonly known as photo-corrosion. it leads to the deactivation with time and that's why it's restricted for commercial use (13,14). Hence, photocatalytic activity of ZnO must be increased to use it as a catalyst. For ZnO to achieve its commercial equivalency the shortcoming of photo-corrosion that leads to the release of Zn^{2+} ions in solution must be addressed by the transfer of photogenerated electrons from the metal atoms to oxygen (14). Hence, numerous methods have been developed in order to quench the photogenerated electrons to decrease photo-corrosion range and to suppress the electron hole (undesired) recombination rate of ZnO with enhanced activity (15-17).

Two methods can be used to achieve surface modification, first one is doping with metals or non-metals and second one is formation of composites, both methods are effective because these involve mutual transfer of charge carriers from the one semiconductor to the other which help for suppressing unwanted charge carrier recombination process.

In the last two decades, with the development of nanotechnology, the major efforts in the field of photocatalysis are dedicated to the adapting of the existing photocatalysts to enhance the efficiency and performance. It described nanocomposites can be synthesized with better performance after the coupling of different nanostructured materials in order to form coupled structures (18-20). It is reported that crystallite size, specific surface area, morphologies and textures are responsible for ZnO photocatalytic activity (21-25).

In this study we synthesized NiO–ZnO nanocomposites through sol-gel method using ethanol solvent. Then these nanocomposites were used for the degradation of organic dye i.e. methylene blue.

II. MATERIAL AND METHODS

A. CHEMICALS

Zinc chloride ($ZnCl_2$) with molecular weight 136.29 g/mol obtained from Riedel-de Haen. Nickle chloride hexahydrate ($NiCl_2.6H_2O$) with molecular weight 237.69g/mol, sodium hydroxide (NaOH) with molecular weight 40 g/mol and methylene blue dye (99.9 % pure) purchased from Sigma Aldrich. Ethanol (C_2H_5OH) with molecular weight 108.14 g/mol bought from Labscan. Deionized water used for the experiment. All chemicals used without purification.

B. PREPARATION OF NiO/ZnO NANOPARTICLES

0.01 M solution of pH 1 prepared by dissolving 0.013g zinc chloride and 0.024g of nickel chloride hexahydrate in 10 ml ethanol. Solution was homogenized by stirring it at room temperature for 5 minutes. 0.043 M solution of sodium hydroxide prepared by dissolving 0.034 g NaOH in 20 ml distilled water. 0.01 M solution of salts stirred at room temperature and 0.043 M sodium hydroxide added at rate of 0.3 ml per 5 minutes until pH 9 obtained. The above solution first centrifuged and then washed by using distilled water at 12500 rpm for 2 minutes. Precipitates dried in oven overnight and calcined at 450 °C for 2 hours in order to convert hydroxides into oxides. Green precipitates of NiO/ZnO nanoparticles obtained.

C. PHOTOCATALYTIC DEGRADATION OF METHYLENE BLUE

Photocatalytic activity of NiO/ZnO nanoparticles determined by the degradation of methylene blue dye under continuous visible radiations. Methylene blue solution (20 ppm) prepared by using deionized water. Firstly, blank solution run through UV-Vis spectrophotometer (UV-1700 Shimadzu), to measure Λ_{max} that was observed 659 nm after correction of baseline. 20 mL of methylene blue solution pipetted out from stock solution in a separate beaker and 10 mg of NiO/ZnO nanoparticles added into 20 mL of methylene blue solution. Then sample solution run through UV-Vis spectrophotometer at 659nm to measure the absorbance after every 20 minutes. Then data used to assess the photocatalytic activity of synthesized nanoparticles.

III. RESULTS AND DISCUSSION

Fourier-transform infrared spectroscopy (FTIR) results in Figure 1. shows a common peak in the range of 2800 to 3500 cm^{-1} corresponds to the O–H stretching bond. Next band around 2900 cm^{-1} represents the symmetric and asymmetric C-H stretching bond for ZnO, NiO and NiO/ZnO (26). The absorption band in region 600-700 cm^{-1} is attributed to Ni-O stretching vibration bond (27). The band around 708 cm^{-1} attributed to deformation vibration of Zn-O (28).

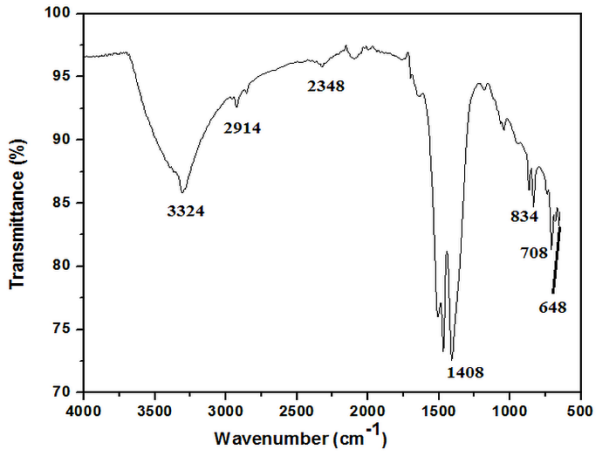

Figure 1. FTIR of NiO/ZnO nanoparticles

Optical properties and band gap of NiO/ZnO nanoparticles has been studied by using UV-Visible spectrum, employed in diffuse reflectance spectra (DRS) mode. Optical band gap was calculated by using the equation 1:

$$(h\nu\alpha)^n = A\left(h\nu - E_g\right) \quad (1)$$

Where, hν is the photo energy, α is the absorption coefficient, n is either 1/2 for an indirect transition or 2 for a direct transition, A is a constant relative to the material, and E_g.represents band gap. Figure 2. shows $(\alpha h\nu)^2$ versus hν and band gap for NiO/ZnO nanoparticles calculated 3.55 eV.

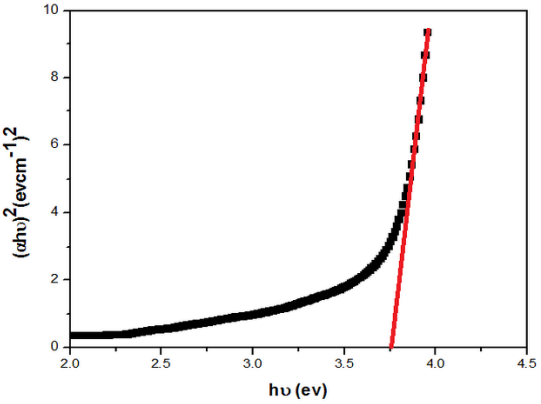

Figure 2. Band Gap of NiO/ZnO Nanoparticles

Thermogravimetric analysis (TGA) has been observed at different temperatures to study weight changes (29). The TGA curve of NiO/ZnO nanoparticles synthesized by sol-

gel method showed in Figure 3. The curve goes down until it became flat and horizontal at 500 ºC. The TG traces show first weight loss (9%) during the heating from 90 ºC to 100 ºC. This weight loss attributed to the loss of physically adsorbed water (30). The weight loss (6%) has been observed during the heating from 135 ºC to 230 ºC, may be corresponding the decomposition of chemically bonded solvents and residues (ash) (31). Another weight loss (18%) during temperature from 250 ºC to 330 ºC has been attributed to the conversion of hydroxides to oxides, confirmed from literature that Ni $(OH)_2$ converts to NiO at temperature of 270 ºC and Zn $(OH)_2$ converts to ZnO till 300 ºC (33). After 550 ºC, no further weight loss has been observed up to 1200 ºC, indicated the formation of NiO/ZnO nanoparticles (inorganic particles) (34).

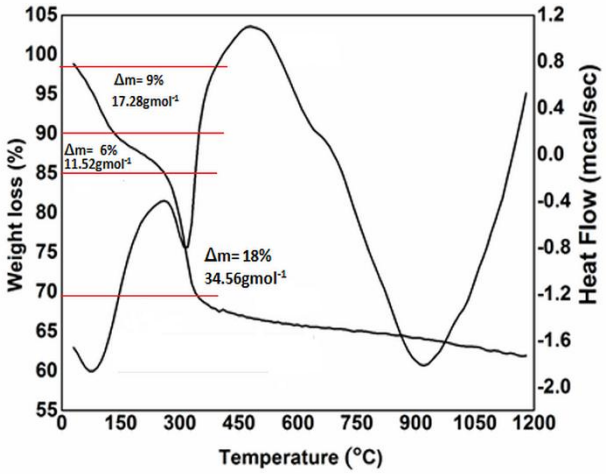

Figure 3. TGA of uncalcined NiO/ZnO nanoparticles

In Differential Scanning Calorimetry (DSC) curve showed two peaks between 250 ºC to 330 ºC as shown in Figure 4. First endothermic peak observed at 270 ºC, might represent the dehydration of Ni $(OH)_2$. Second exothermic peak observed at 320 ºC, confirmed Zn $(OH)_2$ dehydration.

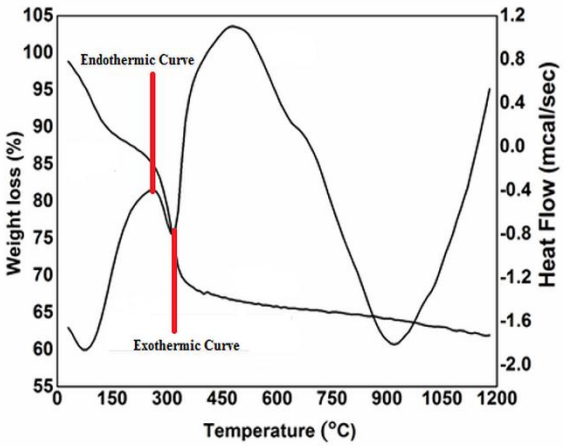

Figure 4. DSC curve of NiO/ZnO nanoparticles

Particle size analyzer (PSA) determined the particle size of the sample. Particle size of sample was analyzed by after every hour as reaction duration was for 4 hours. 173nm particle size with 13.66 m^2/g specific surface area observed after one hour. 140nm particle size with 17.24 m^2/g specific surface area observed after two hours. After three hours particle size observed was 96.8nm with 23.74 m^2/g specific surface area. After four hours 64.4nm particle size with specific surface area 31.68 m^2/g was observed. There was an inverse relation observed between particle size and surface area. 64.4 nm particle size with 31.68 m^2/g specific surface area of the NiO/ZnO nanoparticles (uncalined) was observed as shown in Figure 5.

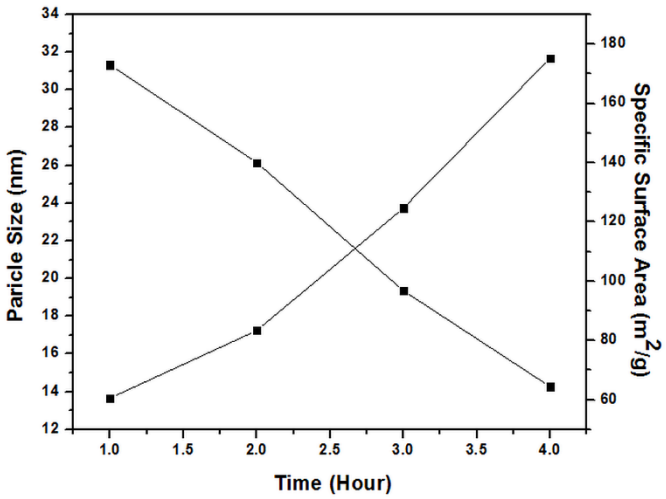

Figure 5. Relationship between Particle size and Specific surface

NiO/ZnO nanoparticles were used as catalyst for the degradation of methylene blue. The data collected from the degradation clearly showed a gradual decrease in peak intensity with an increase in irradiation time.

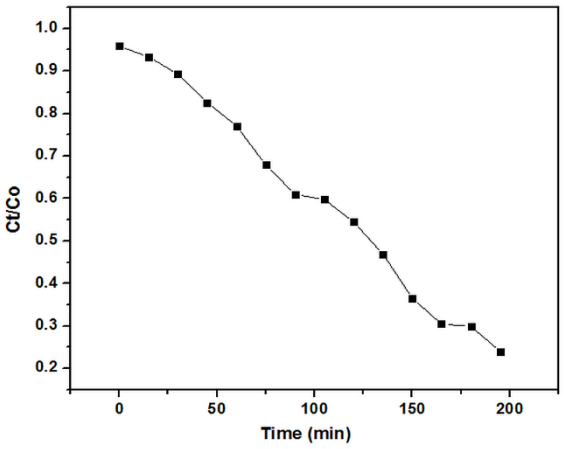

Figure 6. Degradation of methylene blue dye as a function of UV light irradiation time

Figure 6 showed linear relationship of C/C_o versus irradiation times. Degradation efficiency of methylene blue against irradiation time using ZnO nanoparticles has been shown in Figure 7. The synthesized ZnO nanoparticles has the potential to degrade the methylene blue dye up to 76% in the given condition. The changes in solution color from

deep blue to colorless can be visually seen owing to the degradation of methylene blue dye under UV light irradiation.

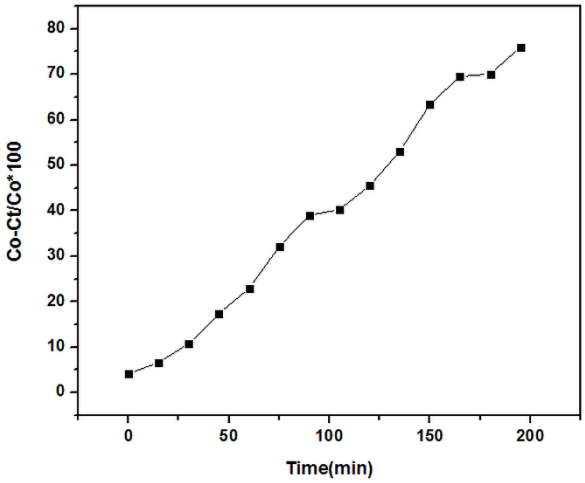

Figure 7. Methylene blue degradation efficiency of ZnO NPs

IV. CONCLUSION

NiO/ZnO nanoparticles synthesized by sol-gel method. Nickle chloride hexahydrate and zinc oxide as precursors, used for NiO/ZnO nanoparticles synthesis. NiO/ZnO nanoparticles formation, confirmed using different techniques such as Fourier Transform Infrared Spectroscopy (FT-IR), UV/Visible, Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetery (DSC). The particle size of NiO/ZnO nanoparticles (uncalcined) observed 64.4nm. NiO/ZnO nanoparticles synthesized by this method found to be active catalyst because they help in the degradation of methylene blue up to 76%.

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