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Magnetically separable, visible light improved, Photocatalytic activity of $TiO_2/CoFe_2O_4/SiO_2$ Nanocomposite

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Abstract: A magnetically separable, visible light improved TiO_2 nanophotocatalyst was successfully synthesized with TiO_2 as a shell, SiO_2 as an intermediate coating and permanent magnet $CoFe_2O_4$ as a core material. The characterization was carried out with the XRD, FESEM, VSM, UV-Vis. The band gap energy calculated by Tauc plot approach for $TiO_2/CoFe_2O_4/SiO_2$ nanophotocatalyst was 2.72 eV. The photocatalytic activity was studied with the hydrogenation of nitrobenzene under irradiation of an 8W UV-lamp with peak wavelength of 253.4 nm. In the photodegradation process almost complete nitrobenzene degradation observed after 105min. Further the TiO_2 nanophotocatalyst recovered under external magnetic field has shown better degradation efficiency.
Keywords: $TiO_2/CoFe_2O_4/SiO_2$; Visible light; Magnetically separable; Nitrobenzene.

Introduction:

In the present work, $CoFe_2O_4/SiO_2$ was synthesized by sol-gel auto combustion and then $TiO_2/CoFe_2O_4/SiO_2$ photocatalytic composite prepared by sol-gel hydrolysis process to achieve the desired magnetically separable and visible light improved photocatalyst. The photocatalytic efficiency of synthesized nanophotocatalyst has been evaluated by the degradation of a Nitrobenzene dye.

Experimental:

Preparation of $CoFe_2O_4/SiO_2$:

The $CoFe_2O_4/SiO_2$ nanoparticles were prepared by using sol-gel auto-combustion method.
The preparation includes two steps. TEOS was used as a source for Silicon dioxide. First, solution A was prepared by mixing 1.2 mL, 4.8 mL, 8.4 mL of TEOS, ethanol and water respectively. The TEOS was taken in 20 wt% of Cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$) and Ferric nitrate ($Fe(NO_3)_2 \cdot 9H_2O$). Acetic acid was added to keep pH 2. Then solution was stirred continuously for 2 h at 60 °C. Solution B was prepared by dissolving 1.5 g, 1.5 g of cobalt nitrate, ferric nitrate in DI water. 3 g of citric acid was dissolve in water and added to nitrates solution under stirring. Ammonia was added to keep pH 7. The solution A and B were mixed to prepare a homogeneous transparent solution and evaporated at 80 °C for 3 h with continuous stirring. The solution was heated at 100 °C for 24 h to form dry gel. Consequently by increasing the gel temperature to 250 °C in muffle

furnace auto-combustion takes place in self propagation manner. Finally, $CoFe_2O_4/SiO_2$ nanoparticles were formed.

Preparation of $TiO_2/CoFe_2O_4/SiO_2$:

The $TiO_2/CoFe_2O_4/SiO_2$ nanophotocatalyst was prepared by sol gel hydrolysis method. For that 200 mg of prepared $CoFe_2O_4/SiO_2$ nanoparticles was taken in 1:10 ratio of water and ethanol mixture. 3 M HCl was added to keep pH 6. The total suspension was sonicated for 30 min and stirred for 1 h at room temperature. Then mixture of 10 ml titanium isopropoxide and 30 mL ethanol were added drop wise added to the above suspension. The complete solution was stirred for minimum 8 h to make sure the covering of TiO_2 on $CoFe_2O_4/SiO_2$. The formed grey coloured precipitate was separated by centrifugation many times in ethanol. The prepared precipitate was dried and calcinated at 450 °C for 5 h.

Photocatalytic Activity Experiment:

The photocatalyst solution was prepared by adding 0.05 g of composite in a 50 mL of nitrobenzene (60 mg/litre) aqueous solution. The mixture was stirred for 50 min in dark to reach adsorption equilibrium. After stirring, the mixture was kept in photoreactor (Heber, HML-COMPACT-LP-MP-812) having UV light source of 8W lamp of 253.7 nm peak wavelength and at a certain time interval 4 mL suspension taken out. Filtered using filter paper and analyzed by UV-visible spectrometer.

Results and Discussion:

XRD:

The fig. 1 represents the XRD patterns of the samples prepared by sol gel autocombustion and sol gel hydrolysis process. The fig. 1 (a) shows the XRD patterns of pure TiO_2 (Degussa, P25) according to the JCPDS # 21-1272. The peaks in the pure TiO_2 XRD pattern indicate the presence of both anatase and rutile phase. The fig.1 (b) shows the spinel phase of $CoFe_2O_4/SiO_2$ without calcination. The peaks are not detectable for SiO_2 as it is in amorphous form. The fig. 1(c) shows the XRD pattern of $TiO_2/CoFe_2O_4/SiO_2$ nanophotocatalyst. The patterns observed for $CoFe_2O_4/SiO_2$ supported TiO_2 implies fig. 1 (c) that there is formation of anatase crystal phase which is most active phase. The particle size calculated from the Schrerrer equation [2] using XRD peaks for TiO_2/CoFe2O4/SiO_2 was found to be approximately 47 nm.

UV-vis Spectrum:

Fig. 2 shows the UV-vis spectra of the samples. Compare to absorption spectrum of TiO_2 (Degussa, P25) the $TiO_2/CoFe_2O_4/SiO_2$ showed enhanced absorption efficiency in visible range. The sample was calcinated at 450 °C which has improved the visible range absorption intensiveness due to doping of the TiO_2 with the magnetic core of $CoFe_2O_4$. It is because of the electron on cobalt ion has diffused on the TiO_2 orbital that has improved the absorption in visible region. The band gap calculated from the Tauc plot graph approach of the $TiO_2/CoFe_2O_4/SiO_2$ was 2.72 eV fig. 2 (a) which was much lower than the TiO_2 (Degussa, P25) 3.2 eV[1]. This proves that magnetic core has decreased the band gap energy between the conduction band and valence band so that nanophotocatalyst can excite under very low photon energy that is under visible light irradiation.

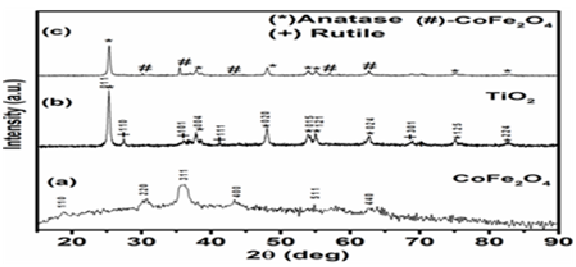

Fig. 1 XRD data: (a) $CoFe_2O_4/SiO_2$ (b) TiO_2 (c) $TiO_2/CoFe_2O_4/SiO_2$

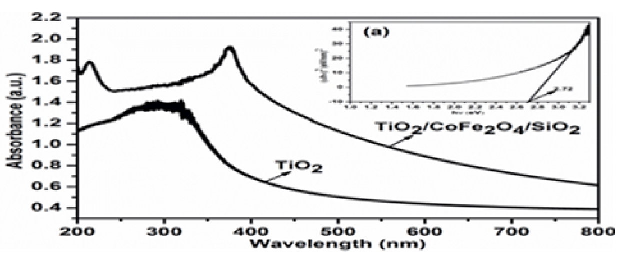

Fig. 2 UV-vis spectra of TiO_2, $TiO_2/CoFe_2O_4/SiO_2$. Inset graph (a) shows the Tauc plot for $TiO_2/CoFe_2O_4/SiO_2$

FESEM and EDX:

Fig. 3 (a) shows the FESEM images of the $TiO_2/CoFe_2O_4/SiO_2$ which has the average particle size of 47 nm same as calculated from XRD data. Further fig. 3 (a) shows the good clumping of $TiO_2/CoFe_2O_4/SiO_2$ nanophotocatalyst. The EDX data in fig. 3 (b) shows the presence of Ti, Co, Fe and Si in the nanophotocatalyst.

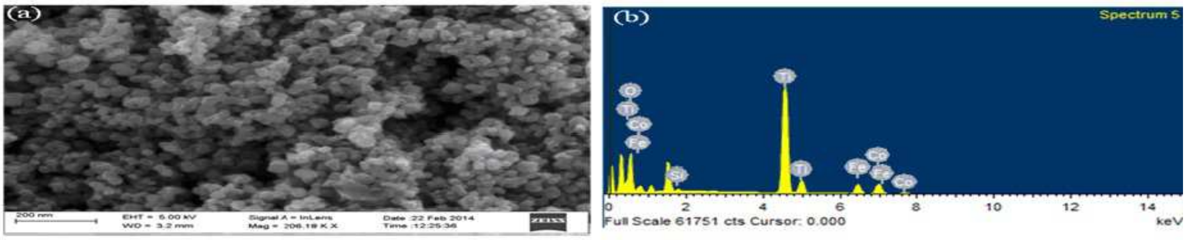

Fig. 3 (a) FESEM image and (b) EDAX spectrum of TiO2/CoFe2O4/SiO2.

VSM Analysis:

Fig. 4 (a) shows the change in the magnetization with the applied field at room temperature. Due to the coating of the TiO_2 on the $CoFe_2O_4/SiO_2$ the nanophotocatalyst has decreased magnetization compared to $CoFe_2O_4/SiO_2$. The SiO_2 covering on the surface of $CoFe_2O_4$ has avoided the effect of magnetization on photocatalytic activity of the TiO_2 and vice versa. The remanence magnetism on the removal of the external magnetic field tends to zero[3], which implies that these particles are able to separate from treated water by applying external magnetic field and can be reused many times with enhanced photocatalytic activity.

Photocatalytic Activity:

There is a presence of anatase TiO_2 so on irradiation of UV light the nanophotocatalyst is considered to undergo photoexcitation. The photodegradation occurs mainly due to the hole generation on semiconductor which oxidizes the adsorbed surface molecules and allows electron to flow. Also forms free radicals (OH^-) to oxidize organic molecules in the mixture solution. Fig. 4 (b) shows the light absorbance spectrum changes of aqueous nitrobenzene solution in the influence of $TiO_2/CoFe_2O_4/SiO_2$ under UV irradiation. Initially the adsorbance rate of photocatalyst was very high as the light absorbance of nitrobenzene at 268 nm falls very fast. As irradiation time increases the nitrobenzene degradation rate slowly decreases. Finally at 105 min almost all of the nitrobenzene has degraded from the aqueous solution. The nanocatalyst then seperated from solution via external magnetic fields and again tested for photodegradation which has the same degradation rate as that of the fresh nanoparticles.

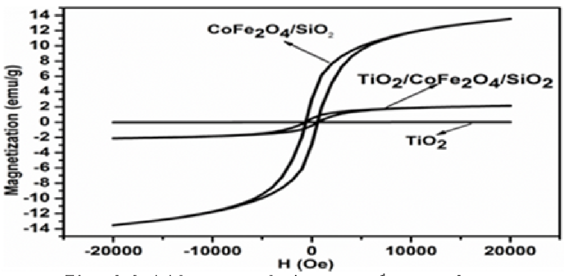

Fig. 4 (a) Hysteresis loops of samples.

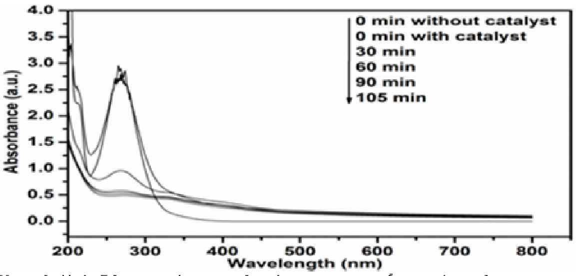

Fig. 4 (b) Photodegradation curve for nitrobenzene.

Conclusion:

We successfully prepared novel magnetically separable $TiO_2/CoFe_2O_4/SiO_2$ photocatalyst.

The nanophotocatalyst has degraded the pollutants very fast which proves that it has enhanced photocatalytic activity and separable under magnetic field. The nanocomposite has low band gap energy and hence it is visible light improved nanophotocatalyst

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