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A Composite Photocatalyst for Methylene Blue Degradation Under Visible Light Irradiation

AHMED JALAL SAMED[1,*], M.A. HASNAT[1] and MASATO MACHIDA[2]

[1]Department of Chemistry, Graduate School of Physical Sciences, Shahajalal University of Science and Technology, Sylhet-3114, Bangladesh
[2]Department of Nano Science and Technology, Graduate School of Science and Technology, Kumamoto University, 2-39-1 Kurokami, Kumamoto 860-8555, Japan

*Corresponding author: Fax: +88 821 715752; Tel: +88 1712174049; E-mail: ajf75s@yahoo.com; ajf-che@sust.edu

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A new composite phocatalyst $Mn_{1-x}Cd_xS$ (x = 0.18) has been introduced, which can efficiently degrade methylene blue even under ordinary visible light. The order of reactivity, irrelevant to the nature of light, followed the order of $Mn_{1-x}Cd_xS$ (x = 0.18) > TiO_2 > ZnO > CdS at neutral pH. The lower band gap energy (2.1 eV) of the catalyst $Mn_{1-x}Cd_xS$ (x = 0.18) was identified as the reason of the higher reactivity.

Keywords: Composite catalyst, Degradation, Methylene blue, Mineralization, Rate constant.

INTRODUCTION

Dyes are organic colored materials used in textile, pharmaceutical, cosmetic and food industries for imparting different shades of attractive colors. The wastewater discharged from a large number of industries, associated with dye stuff activities, contains high concentration of reactive dyes which causes a serious environmental problem[1]. Some of these dyes have injurious health hazards[2]. Their discharge as wastewater in the ecosystem is a dramatic source of esthetic pollution, eutrophication and perturbations in aquatic life. Effluents discharged from textile and dyeing industries are characterized by low BOD, high COD and variation of pH in the range of 2-12[3-6]. These dyes in the strongly absorb sunlight, which decreases the intensity of light absorbed by water plants and phytoplankton, reducing photosynthesis and the oxygenation of water reservoirs[3,7-9]. The greatest number of the dyes are resistant to biodegradation and direct photolysis and many N-containing dyes such as methylene blue undergo natural reductive anaerobic degradation to yield carcinogenic aromatic amines[9].

There are various physico-chemical and biological methods for the treatment of reactive dyes in wastewater[2]. The conventional method of textile wastewater treatment comprises chemical coagulation and biological treatment followed by activated carbon adsorption. However these methods transfer dyes from the liquid to the solid phase which causes secondary pollution, requiring further treatment[10-13]. The presence of biologically high molecular weight dyestuffs in textile wastewater results in the low degradation efficiency of the biological treatment method[14].

The photocatalytic degradation of dyes is of growing interest for environmental remediation. Many organic and inorganic pollutants in air and water stream have been shown to be fully decomposed by means of photocatalysis[15]. A large number of studies have been reported in the past decades on the photodegradation of organic compounds using semiconductor particles as photocatalysts. Semiconductor photocatalysts, such as TiO_2 and ZnO are employed widely in the decomposition of organic pollutants due to their good long-term stability and perfect physical and chemical properties. The appropriate position of their conduction bands allows oxygen to act as acceptor of photogenerated electrons which is more important in their usage[16]. We investigated the photocatalytic degradation of several dyes using TiO_2 and ZnO dispersion under UV light reported and reported our findings previously[17,18].

The main problem of using oxide photocatalyst TiO_2 and ZnO for dye degradation is their less activity under visible light irradiation. Recently, we reported for the first time, hydrothermal synthesis of a series composite sulphide photo catalyst, $Mn_{1-x}Cd_xS$ (0 = x = 1) to generate hydrogen from water splitting[19]. Under this context, we assumed that such photocatalysts might be efficient for dye degradation too. Here we report the efficiency of $Mn_{1-x}Cd_xS$ (x = 0.18) in degrading an organic dye methylene blue under UV and visible light irradiation compare with oxide photocatalysts.

EXPERIMENTAL

Titanium dioxide photocatalyst (P25, 90 % anatase, specific surface area 50 m^2 g^{-1}) ZnO and CdS were supplied by Walko Incorp. (Japan). The catalyst $Mn_{1-x}Cd_xS$ (x = 0.18) was hydrothermally synthesized. The detailed synthetic procedure has been reported in our previous paper[19]. The cationic dye methylene blue (Fig. 1) was obtained from Waldeck-Gmbh & Co. and was used as received. All other chemicals used in the experiments were reagent grade and were used without further purification. Double distilled and deionized water was used throughout the study.

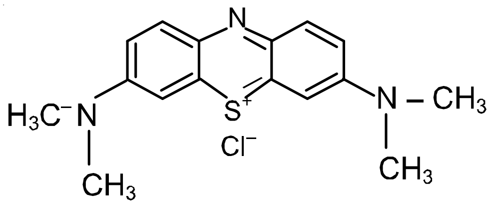

Fig. 1. Molecular structure of methylene blue

Reactor: Batch reactors were designed for the photodegradation study. For UV light induced degradation study three 10 W UV (Mercury) tube lights were placed parallel on the top inside of a wooden box, kept in a dark room. The walls, inside the box were covered with aluminum foil to ensure the maximum light to fall on the reaction vessel by reflection. Pyrex beaker (150 mL) was used as reaction vessel, which along with the reacting solution was placed about 15 cm below the tube light on a magnetic stirrer. Samples were taken at a regular interval by raising the lid of the box. For visible light induced degradation study a 500 W crown bulb, the visible light source, was hung with a holder and a stand over wooden stage in the dark room, about 15 cm apart from the surface of the solution. The thermostatic state was maintained using a cooling fan.

Method: Energy dispersive X-ray fluorescence (XRF, Horiba, MESA-500 W) analysis was used to determine chemical composition. The X-ray diffraction patterns (XRD) of the powder samples were measured at room temperature with a Rigaku powder diffractometer with CuK_α radiation. The nitrogen adsorption isotherm at 77 K was measured using a Belsorp Mini, Japan instrument.

The UV-visible spectrum of methylene blue was obtained for 10 μM solution in the range of 200-700 nm using a UV-visible spectrophotometer (UV-1650 PC, Shimadzu Corporation, Kyoto, Japan). The maximum absorbance was found at 664 nm (λ_{max} = 664 nm) and all photometric measurements were carried out at 664 nm. For UV light irradiation assisted temporal absorption spectrum changes study a mixture of methylene blue (15 μM, 200 mL) was prepared by taking 0.2 g photocatalyst at pH 7.5 . The as prepared mixture was stirred for 0.5 min in the dark to ensure its suspension behaviour and then was subjected to UV irradiation for 125 min. In order to monitor the concentration changes, 3 mL of aliquot portions were withdrawn at a regular time interval; centrifuged and UV-visible spectra were taken.

RESULTS AND DISCUSSION

As we already discussed[19] of the structure and photocatalytic properties of this catalyst for H_2 evolution, here we discuss only related to degradation of methylene blue by this catalyst. Fig. 2 shows the XRD pattern of the profiles of MnS (curve a) and CdS (curve b) along with composite material, prepared from the combination of γMnS and CdS (curve c) using hydrothermal method. From these profiles, it is clear that γMnS used in this study was a mixture cubic (R, rock salt structure) and hexagonal (γ, wurtzite structure) phases. However, the cubic phase of γMnS was vanished and at the same time signals due to cubic phase of CdS along with zinc blend type structure was noticed as soon as the component CdS was hydrothermally combined to the MnS system. The newly developed composite material having zinc blend type structure was designated as $Mn_{1-x}Cd_xS$, where the value of x using XRF technique was determined to be 0.18.

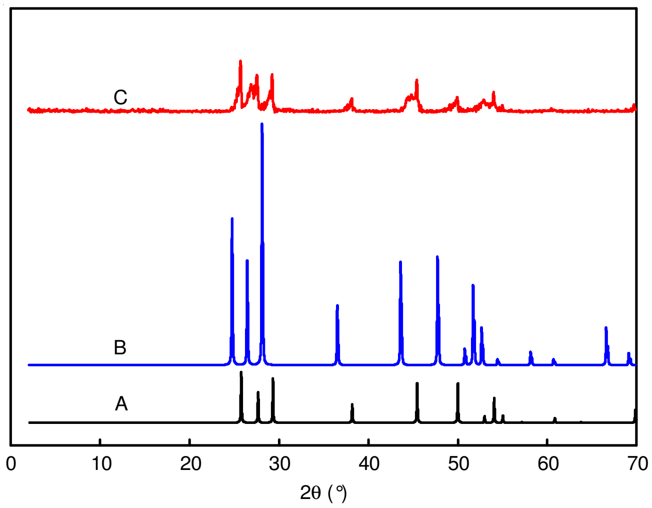

Fig. 2. XRD patterns of (A) γ MnS (B) CdS and (C) $Mn_{1-x}Cd_xS$ (x = 0.18)

Using the as prepared material, photocatalytic degradation experiments of methylene blue have been performed both under UV and visible light irradiation. Fig. 3 shows the spectral changes of methylene blue molecules recorded at 25 min regular intervals under visible light condition. The absorption spectrum of methylene blue shows two major peaks, one at 664 nm due to substitution of $>N(CH_3)_2$ group to heteroaromatic ring (responsible for color) and another at 292 nm associated with localized bands of the unsaturated heteroaromatic system[7]. These peaks were decreased markedly in intensity and were almost completely disappeared after 125 min irradiation. The disappearance of the peak at 664 nm indicates decolorization (either due to functional groups removal or due to mineralization or due to both reasons). Meanwhile, the disappearance of the peak at 292 nm indicates the mineralization of methylene blue molecules. Since the intensity of the peaks was decreased exponentially, we estimated the relative photocatalytic performances by evaluating first order rate constant (k) at both 664 and 292 nm. The linear form of the first order decolorization has been shown in Fig. 4 measured at 664 nm both in presence of visible and UV light. It has been found that the value of k at 664 was 15.1×10^{-3} min^{-1}, slightly higher than 13.3×10^{-3} min^{-1} which was observed at 292 nm. This results indicate that mineralization of methylene blue molecules took place followed by decolorization probably due to N-de-ethylation as was also observed by other researchers using oxide photocatalysts[20-23]. In order to confirm the mineralization TOC

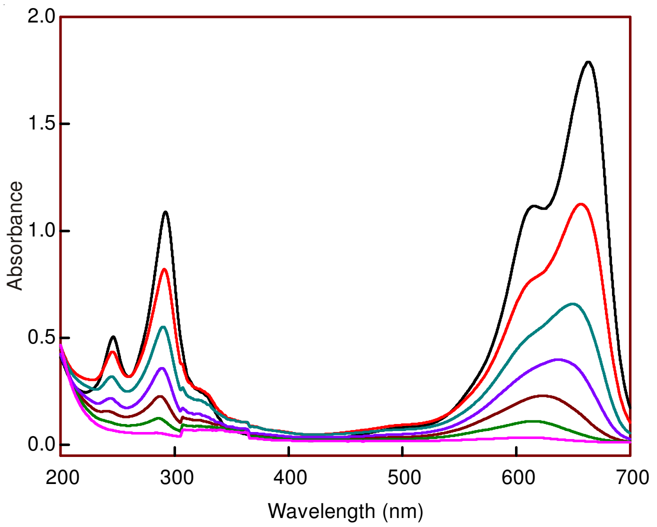

Fig. 3. The temporal absorption spectrum changes of methylene blue taking place under visible light irradiation. The lines indicate the change of decolorization/degradation every 25 min intervals. Initial concentration of methylene blue: 15 µM (200 mL), $Mn_{1-x}Cd_xS$ ($x = 0.18$); 0.2 g, pH: 7.5

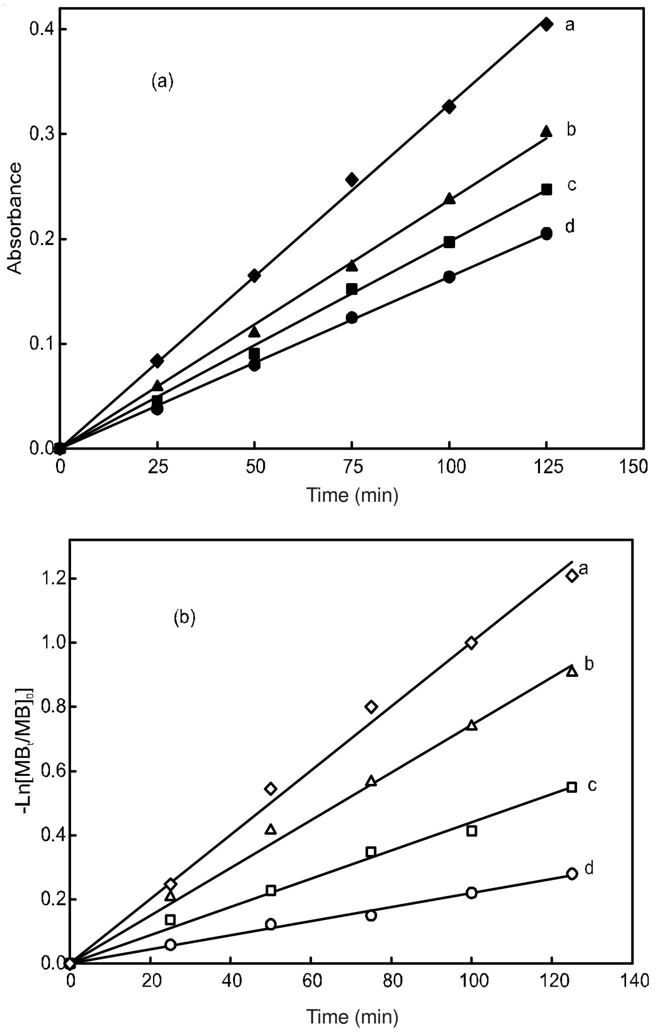

Fig. 4. Linear form of first order decolorization at 664 nm of methylene blue (200 mL, 15 µM) in presence of (a) visible light irradiation and in presence of (b) UV light irradiation. The lines a, b, c and d indicate the presence of 0.2 g $Mn_{1-x}Cd_xS$ ($x = 0.18$), TiO_2, ZnO and CdS photocatalysts, respectively

was determined as below detection limit (< 0.1 %) after 150 min irradiation. The main interesting feature to point out is the relative activity of the as prepared catalyst under visible light irradiation. The most familiar semiconductor photocatalysts are TiO_2 and ZnO. In order to compare the relative activities, experiments were performed under same condition using TiO_2, ZnO, CdS and as prepared $Mn_{1-x}Cd_xS$ catalyst.

Though the catalysts TiO_2 and ZnO were relatively active under UV-light irradiation but they are deemed under visible light condition as is reported in Table-1. The activity of the as prepared $Mn_{1-x}Cd_xS$ under visible light irradiation was almost closer to that observed for TiO_2 even under UV-irradiation. In case of both peaks decolorization/mineralization followed the order of $Mn_{1-x}Cd_xS > TiO_2 > ZnO > CdS$ irrespective to light used for photolysis. The reasons of such high activity of the as prepared $Mn_{1-x}Cd_xS$ catalyst might be because either due to its larger surface area and or due to reasonable smaller band gap energy. We therefore investigated the surface area and band gap energy of the catalyst.

TABLE-1
TEMPORAL ABSORPTION SPECTRUM CHANGE KINETIC RESULTS OF METHYLENE BLUE UNDER UV AND VISIBLE LIGHT IRRADIATION

Catalyst	Rate constant at UV-light		Rate constant at visible light	
	$k_{664\,nm}$ ($10^{-3}min^{-1}$)	$k_{292\,nm}$ ($10^{-3}min^{-1}$)	$k_{664\,nm}$ ($10^{-3}min^{-1}$)	$k_{292\,nm}$ ($10^{-3}min^{-1}$)
TiO_2	19.2	18.1	7.8	6.5
ZnO	10.9	8.2	2.1	1.9
CdS	4.1	2.3	1.6	1.0
$Mn_{1-x}Cd_xS$ ($x = 0.18$)	22.3	19.1	15.1	13.3

Fig. 5 shows the N_2 adsorption isotherm for $Mn_{1-x}Cd_xS$ ($x = 0.18$). This is similar to type II isotherm defined in the IUPAC classification, indicating relatively strong interaction between sample surface and adsorbate. Adsoprtion isotherm is typical for non porous material. It starts up taking N_2 homogeneously from relative pressure (p/p^o) zero then decreases apparently at higher pressure until at relative pressure 0.4. This signifies that adsorption in this nonporous material is generally accompanied by the formation of a monolayer followed by a multilayer and thereby lacking of capillary condensation. The specific surface area was determined using BET method and found 31 m^2g^{-1} with high correlation coefficient of the BET straight line, which is quite low compared to TiO_2 (50 m^2/g) and ZnO (100 m^2/g)[18]. However, the composite $Mn_{1-x}Cd_xS$ catalyst having this surface area exhibited excellent activity to degrade methylene blue.

Finally, we estimated the band gap energy by measuring the reflectance spectra of the composite catalyst. The diffused reflectance spectrum of the composite material $Mn_{1-x}Cd_xS$ ($x = 0.18$) is shown in Fig. 6. The band gap energy of the catalyst $Mn_{1-x}Cd_xS$ ($x = 0.18$) estimated from this spectrum was estimated to be 2.2 eV. This value is significantly smaller than oxide photocatalysts anatase TiO_2 (3.2 eV) and ZnO (3.4 eV)[18]. Therefore lower band gap energy of the composite catalyst $Mn_{1-x}Cd_xS$ ($x = 0.18$) might be the reason of the activated photocatalytic performance for the degradation of methylene blue molecules even under visible light condition.

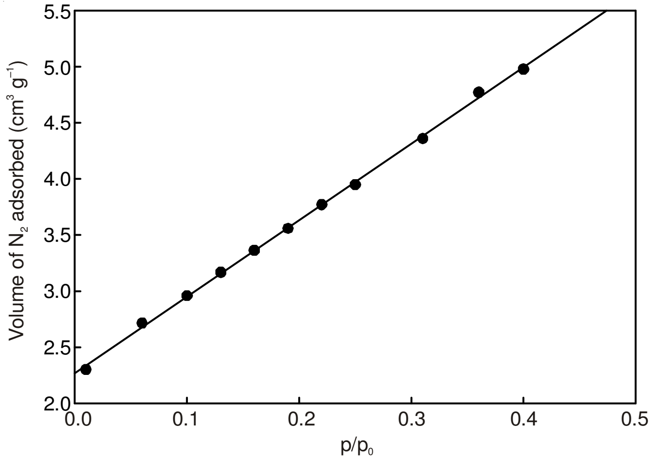

Fig. 5. BET isotherm of as prepared $Mn_{1-x}Cd_xS$ (x = 0.18) catalyst

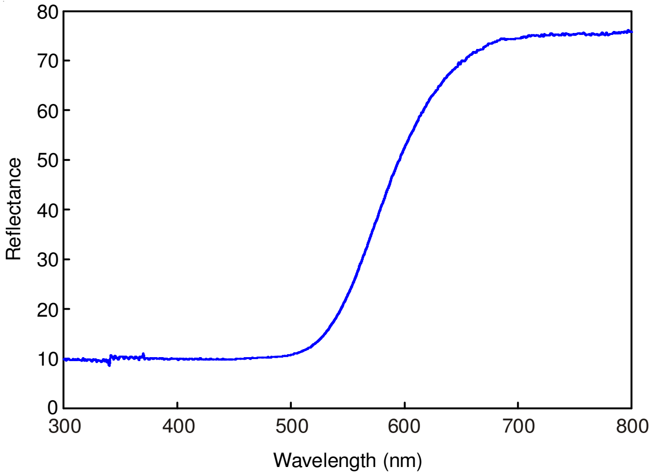

Fig. 6. Reflectance spectra of the as prepared $Mn_{1-x}Cd_xS$ (x = 0.18)

Conclusion

The newly developed catalyst efficiently degraded methylene blue molecules, comparable with widely used TiO_2 photocatalyst. At acidic pH dissolution of the catalyst was occurred, whereas in the basic pH (9) coagulation of the catalyst particles were observed. This catalyst exhibited the best activity at neutral pH, which is considered promising for the environmental pollution control point of view. For this reason, this new generation photocatalyst has the potential enough to be used for the degradation of methylene blue only under the irradiation of visible light.

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