

(12) INNOVATION PATENT
(19) AUSTRALIAN PATENT OFFICE

(11) Application No. **AU 2021100320 A4**

(54) Title
Development of solar driven photocatalyst and its application in degradation of organic pollutants

(51) International Patent Classification(s)
B01J 35/00 (2006.01) **C01G 19/02** (2006.01)
B01J 13/04 (2006.01) **C02F 1/30** (2006.01)
B01J 23/14 (2006.01) **C02F 1/72** (2006.01)
B01J 27/04 (2006.01) **C02F 101/30** (2006.01)
B01J 35/08 (2006.01)

(21) Application No: **2021100320** (22) Date of Filing: **2021.01.19**

(45) Publication Date: **2021.04.29**

(45) Publication Journal Date: **2021.04.29**

(45) Granted Journal Date: **2021.04.29**

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Development of solar driven photocatalyst and its application in degradation of organic pollutants

Abstract

In this project, core-shell CdS@SnO₂ particles have been prepared by Successive Ion Layer Adsorption and Reaction (SILAR) method. CdS is a well known low band gap semiconductor (of band gap ~ 2.4eV) and can thus harvest visible light of wavelength up to 520nm of the solar radiation. In our present work, we have implemented SILAR method with slight modification to coat thin CdS layer over fine SnO₂ particles to obtain core-shell CdS@SnO₂ particles. The SILAR method, which is usually used for the deposition of binary semiconducting thin films, has some advantage over other preparative methods, for example, this is a facile, less expensive and less time consuming technique, and it provides the provision to control the thickness of the film by adjusting the number of cycle of coating. In the present synthetic approach, fine SnO₂ powder has been prepared by hydrothermal method initially. The synthesized SnO₂ powder has been used as a substrate over which the CdS layer has been coated to obtain powder photocatalyst. SnO₂ is a large band gap semiconductor and has no impact on visible light absorption. The synthesized core-shell type CdS@SnO₂ composite photocatalyst has been characterized with FTIR technique. The activity of the synthesized photocatalyst has been investigated under visible light towards the photooxidative degradation of Rhodamine B (RhB), which is a toxic organic contaminant.

Development of solar driven photo catalyst and its application in degradation of organic pollutants

Abstract

In this project, core-shell CdS@SnO₂ particles have been prepared by Successive Ion Layer Adsorption and Reaction (SILAR) method. CdS is a well-known low band gap semiconductor (of band gap ~ 2.4eV) and can thus harvest visible light of wavelength up to 520nm of the solar radiation. In our present work, we have implemented SILAR method with slight modification to coat thin CdS layer over fine SnO₂ particles to obtain core-shell CdS@SnO₂ particles. The SILAR method, which is usually used for the deposition of binary semiconducting thin films, has some advantage over other preparative methods, for example, this is a facile, less expensive and less time consuming technique, and it provides the provision to control the thickness of the film by adjusting the number of cycle of coating. In the present synthetic approach, fine SnO₂ powder has been prepared by hydrothermal method initially. The synthesized SnO₂ powder has been used as a substrate over which the CdS layer has been coated to obtain powder photo catalyst. SnO₂ is a large band gap semiconductor and has no impact on visible light absorption. The synthesized core-shell type CdS@SnO₂ composite photo catalyst has been characterized with FTIR technique. The activity of the synthesized photo catalyst has been investigated under visible light towards the photo oxidative degradation of Rhodamine B (RhB), which is a toxic organic contaminant.

Introduction

The treatment and removal of pollutants from wastewater have become a crucial problem of environment and health. Development of semiconductor photo catalyst for the photo degradation of organics and dyes from wastewater has drawn immense attention in the past few years. A dye is a coloured compound that has an affinity to the substrate to which it is being applied. However, all coloured compounds are not dyes. To be as useful as a dye, a compound must show fastness to light, washing, heat and bleaching⁽¹⁾. Some common organic dyes are

Dyes are the main source of coloured organics generated as a waste from the textile dyeing process. Due to the high concentration of dyes in the effluents and the higher stability of modern synthetic dyes, the conventional biological treatment methods are not effective for removing the colour and degrading the dyes.

Filtration, coagulation, adsorption by activated carbon and treatment with ozone are some of the commonly used methods for dye degradation or removal. However, all these methods suffer from some drawbacks. For example, the use of charcoal is technically easy but is costly⁽²⁾; in filtration, low molecular mass dyes can easily pass through the filter system; coagulation using alum, ferric salts or lime is a low cost process but the disposal of toxic sludge is a severe drawback; the ozone treatment does not require disposal but suffers from high cost. Therefore, an alternative and more reliable method is photo catalysis⁽³⁾ in which, the photo catalyst can be reused after being used indicating the cost effectiveness of this method.

The main advantages of this method are:

1. Inherent destructive nature.
2. No mass transfer involved.
3. Can be carried out under ambient conditions and using atmospheric oxygen as the oxidant.
4. May lead to complete mineralisation of organic carbon into CO₂.

The use of semiconductor materials as photo catalysts has achieved great popularity over the past decade due to their ability to harness solar energy.

An efficient semiconductor must possess the following primary characteristics for photocatalytic reactions:

- Low band gap to utilize most part of the solar light.
- Low recombination of photo generated electrons and holes to maximize reactivity of the catalyst.
- Correct band-edge positions for redox reactions.
- Stability to chemicals and light.

Photo catalysis is the catalysis of a chemical reaction under light irradiation. It is the acceleration of a photoreaction in the presence of a photo catalyst⁽⁴⁾. As a photo catalyst, semiconductor materials can be used since they can harness light. For example, TiO₂ is a very common semiconductor which is used as a photo catalyst⁽⁵⁾. It is a stable and a non-toxic semiconductor. The band gap of TiO₂ (Titanium dioxide) is 3.05eV and thus it absorbs UV radiation because of which, it cannot harness much of the solar radiation as solar light comprises only 4% UV-radiation.

The mechanism of photo degradation of dyes using TiO_2 semiconductor photocatalytic has been well documented in literature⁽⁶⁾. The photo excited electron and hole pairs facilitate the oxidation and reduction reactions at the catalyst surface and generates hydroxyl free-radicals ($\text{OH}\cdot$) and superoxide ions (O_2^-). These species behave as strong oxidizer to degrade toxic organic pollutants in wastewater.

When a photo catalyst is irradiated with radiation of energy equal to or greater than the bandgap energy of the semiconductor photo catalysts, it absorbs energy and creates a positively charged hole in the valance band (VB) and negatively charged electron in the conduction band (CB) by exciting the electrons in the valance band to the conduction band.

Objective and scope of the present work

In the present project work, we have developed low band gap core-shell structure of cadmium sulphide coated tin oxide (CdS@SnO_2) semiconductor based photo catalyst using a simple, inexpensive, solution based chemical method namely, successive ion layer and adsorption reaction (SILAR) and hydrothermal techniques. We have chosen cadmium sulphide⁽⁷⁾ as it is a well-known low band gap semiconductor of band gap $\sim 2.4\text{eV}$. Therefore, it can absorb solar spectrum of wavelength $\sim 516\text{ nm}$ and thus can utilize a major portion of the sun's radiation. Solar light consists of 4% ultraviolet and 43% visible irradiations and thus the use of low bad gap semiconductor is realistic for harvesting the major portion of the solar light

In this project work we have used fine SnO_2 powder as a substrate, prepared by hydrothermal method, over which the CdS layer has been coated to obtain powder photo catalyst. SnO_2 is a large band gap semiconductor and plays no role in visible light absorption

Also, we have investigated the effectiveness of the developed photo catalyst towards the photo degradation of Rhodamine B under irradiation of visible light in the present project work.

Our Approach

SILAR stands for Successive Ion Layer Adsorption and Reaction. This method is usually used for film deposition. The SILAR method which is usually used for the deposition of binary semiconducting thin films has some advantages over other. The relative simplicity of the successive ion layer adsorption and reaction (SILAR) method, its potential application for layer area deposition, the requirement of relatively lower temperature, less expensive, less time consuming and the provision to control the thickness of the film by adjusting the number of cycle

of coating makes this method very attractive. Most of the common methods for the preparation of CdS nanomaterial usually includes high temperature, inert atmosphere supported by argon, nitrogen, etc., the use of expensive chemicals like trioctyl phosphine oxide, trioctyl phosphine, etc., and the product formed usually suffers from unavoidable agglomeration⁽⁸⁾. Therefore, based on the advantages of SILAR method described above, we have chosen this method for the preparation of CdS@SnO₂ photocatalyst. However, this method has been used for the first time to make CdS coated SnO₂ for the photo degradation of RhB. In this project work, we have used tin oxide (SnO₂) as a substrate (support) on the surface of which we have coated CdS. (Fig. 1)

Experimental

1. *Hydrothermal synthesis of SnO₂ powder:*

In the present approach, fine SnO₂ powder has been synthesized by hydrothermal method. Hydrothermal synthesis refers to the synthesis by chemical reactions of substances in a sealed heated solution above ambient pressure and boiling point. The hydrothermal synthesis of SnO₂ was done by following the below given procedure:

Firstly, 1.72 g of sodium dodecyl sulphate [SDS:CH₃(CH₂)₁₁SO₄Na⁺] was dissolved in 12 mL of distilled water. SDS is an anionic surfactant, frequently used as a template/capping agent to control the nucleation and subsequent growth of the particles in the synthesis of mesostructures of the material. This aqueous solution of SDS was acidified with 10 mL conc. HCl. Then 4.5 g stannous chloride (SnCl₂.2H₂O.) was dissolved to this acidic solution and 6.2 mL 30% hydrogen peroxide (H₂O₂) was added drop wise in that solution under continuous stirring condition. Next, the precipitation of metal (hydrous) oxide was carried out by adding ammonium hydroxide (NH₄OH) drop wise to the resulting solution in stirring condition. The solution was then autoclaved at 120°C for 24 h. After the reaction, the sealed bottle was allowed to cool down naturally to room temperature. The resulting precipitate was centrifuged, washed with distilled water for a number of times to remove ions remained in the final product and dried in an oven at 100°C for 2 h. Finally, as-synthesized product was calcined at 500°C for 2 h in air using a furnace to remove the organic surfactant remained in the product. (Scheme 1) (Fig. 2)

2. *Synthesis of CdS coated SnO₂ powder by SILAR method:*

2 g of the prepared SnO₂ powder was taken in a centrifuge tube and 25 mL of 100mM cadmium acetate (CdAc) solution in ethanol was added to it. It was then stirred to ensure SnO₂ dispersion. This was then centrifuged to separate solid SnO₂. It was then washed with ethanol (EtOH) to remove

excess cadmium acetate and centrifuged. After that, same volume of 100mM sodium sulphide (Na_2S) solution in ethanol was added to cadmium acetate coated SnO_2 , stirred, centrifuged. This was again washed with ethanol to remove excess Na_2S . This whole process was repeated to complete 5 cycles. The resulting solid was then dried in an oven at 80°C for half-an-hour in a covered vial thus to get the product i.e., CdS coated SnO_2 . (Scheme 2) (Fig. 3).

The bands at 650cm^{-1} and 730cm^{-1} correspond to Cd-S stretching band. The bands at 1620 and 3550cm^{-1} are attributed to bending vibration of water. The band at around 3401.5cm^{-1} may correspond to the stretching vibration of O-H bond. This band is due to the OH groups and the adsorbed water bound at the SnO_2 surface. The peak at 447cm^{-1} might be due the stretching vibration of the terminal Sn-OH, while the peak at 613cm^{-1} may correspond to the stretching modes of Sn-O-Sn. Although FTIR data does not actually confirm the formation of metal oxides, though we can obtain some data like: The bands at 650cm^{-1} and 730cm^{-1} correspond to Cd-S stretching band. (Fig. 4)

Photodegradation of Rhodamine B (RhB) using the developed photocatalyst

Photocatalytic activity of the synthesized core-shell composite CdS@SnO_2 was evaluated by investigating the degradation of Rhodamine B (RhB) dye in water. 200 mg of the developed CdS@SnO_2 was taken and dispersed in 0.01 mM 50 mL solution of RhB. The suspension was exposed to visible light irradiation provided by three 200 W tungsten filament bulb (each produces light in the range of 420 nm to 800 nm) under constant stirring condition. 4.5 mL of the aqueous solution was taken out before the irradiation and after 2 h of irradiation and was centrifuged to remove any solid particles for analysing the degradation.

Results and discussions:

The absorbance spectra of an aqueous solution of RhB exposed to visible light irradiation and extracted from the reaction medium is displayed in fig.6. From fig.5 it can quite clearly be seen that the dark pink colour of RhB solution has become very faint pink after 2 h of irradiation indicating the degradation of RhB. This has further been proved by the data provided by the UV-VIS spectrophotometer. (Fig. 5, 6)

The absorption peak at $\lambda=553\text{ nm}$ was found to diminish under the visible light irradiation, indicating the photocatalytic activity of the synthesized material in the degradation of RhB dye. The absorption peak at $\lambda=553\text{ nm}$ diminished after about 2 hours. The shift of the major

absorption band of RhB dye to shorter wavelengths (hypsochromic shift) was, in accordance to literature (Zhao et al. *J. Mater. Chem.*, 2007, 17, 2526 *J. Phys. Chem. B*, 2002, 106, 5022) due to the removal of ethyl groups, indicating the photo degradation of RhB dye.

Plausible reaction mechanism is mentioned in Fig. 7.

Conclusion

The approach to use SILAR method has been quite successful to coat the particle i.e., CdS coated SnO₂. From the experimental data, as shown in fig., 5, and the UV-VIS data, as shown in fig., 6, it can be concluded that the test for the application of the developed photo catalyst for the photo degradation of Rhodamine B has become quite successful. Further improvements can be made by comparing the results which we can get by using more than five or less than five cycles in the preparation of the photo catalyst CdS@SnO₂ by SILAR method. Also, the use of XRD data for the confirmation of the prepared photo catalyst instead of FTIR is more preferred. Nevertheless, the results have come to be very good with the photocatalyst CdS@SnO₂ prepared by using 5 cycles.

Therefore, SILAR method can be employed to develop an effective semiconductor photo catalyst.

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Claim:

- In this invention, core-shell CdS@SnO₂ particles have been prepared by Successive Ion Layer Adsorption and Reaction (SILAR) method. CdS is a well known low band gap semiconductor (of band gap ~ 2.4eV) and can thus harvest visible light of wavelength up to 520nm of the solar radiation.
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- The application of the developed photocatalyst for the photodegradation of Rhodamine B has become quite successful

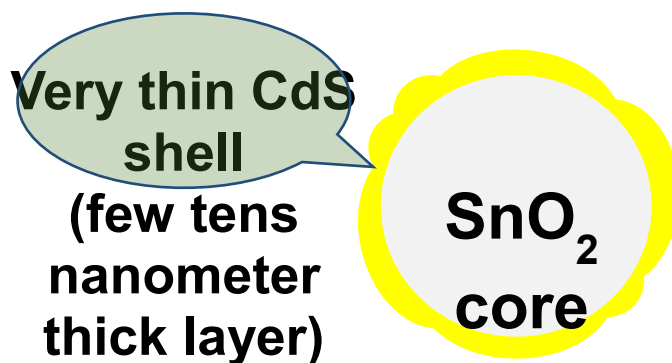
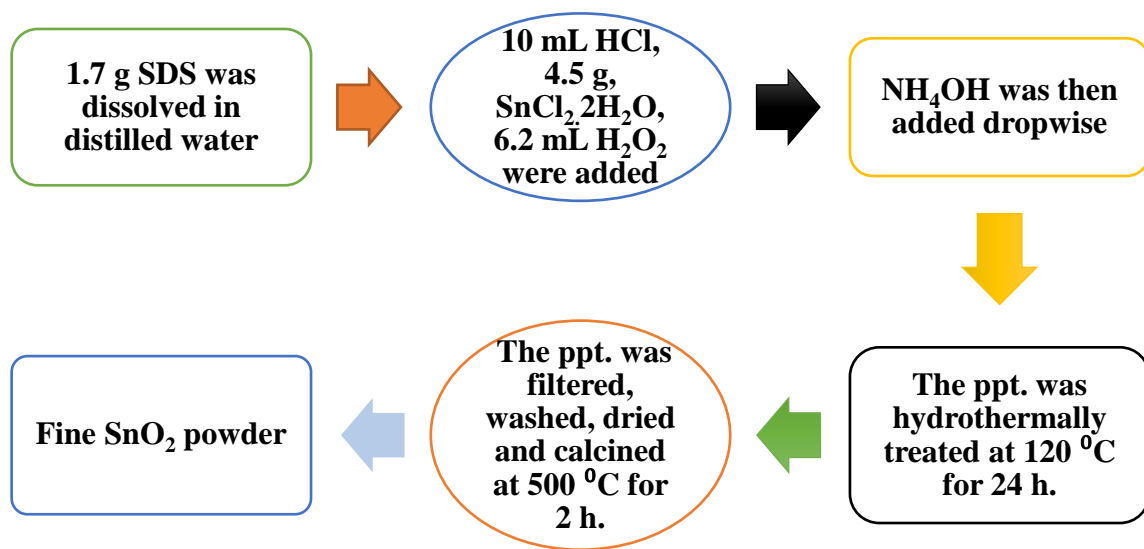


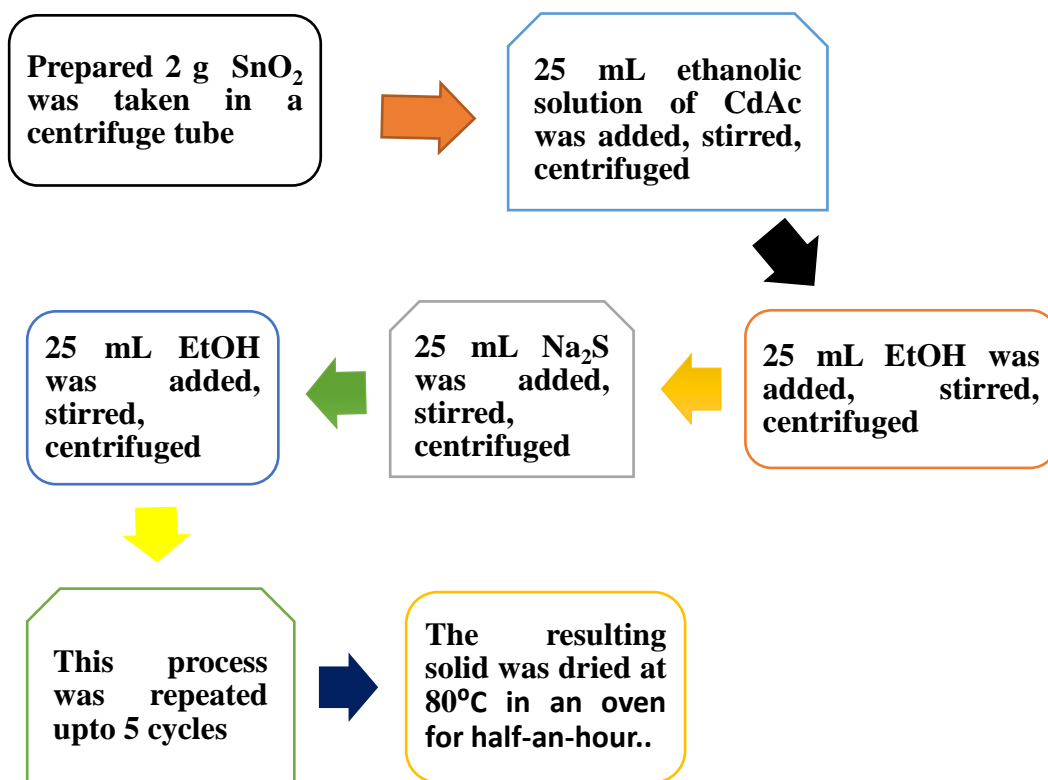
Fig.1 Core-shell structure of CdS coated SnO₂(CdS@SnO₂) photocatalyst by SILAR and hydrothermal method.



Scheme 1 Flowchart synthesis of fine SnO₂ powder.



Fig. 2 Fine SnO₂ powder prepared via hydrothermal synthesis.



Scheme 2. Flowchart synthesis of CdS@SnO₂.



Fig: 3 Photograph of CdS@SnO₂

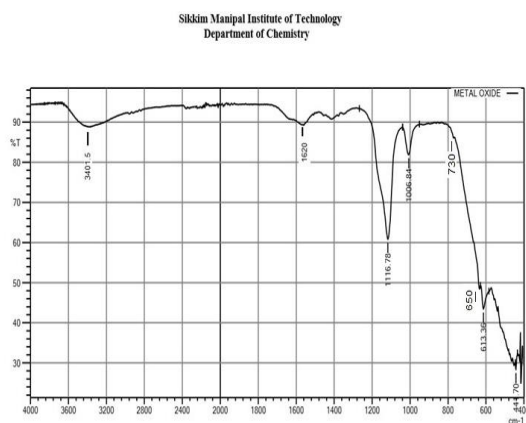


Fig. 4 FTIR data of the synthesized CdS@SnO₂ photocatalyst



Fig.5 Photograph of RhB before the irradiation and after 2 h.

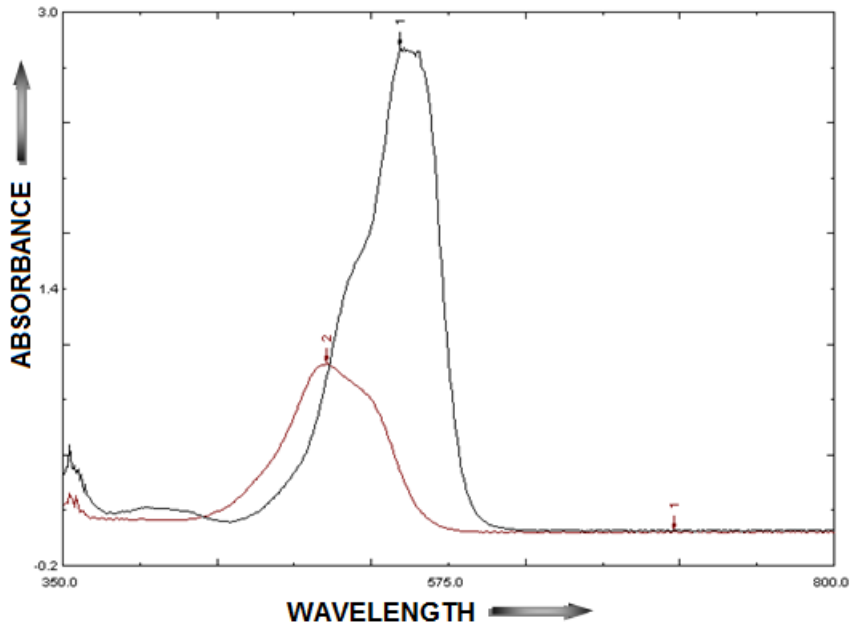


Fig. 6 UV-VIS data.

Mechanism

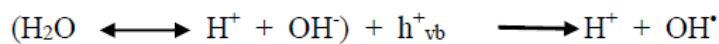
1. Absorption of photons by CdS and the production of photo-holes and electron pairs.



2. Oxygen ionosorption.



3. Neutralisation of OH^- by photo-holes.



4. Reaction of an organic pollutant (dye like RhB) with hydroxyl radical or directly with the holes to produce the degraded products (CO_2 and H_2O).

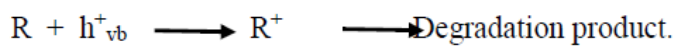
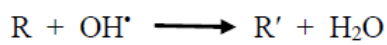


Fig. 7 (Reaction mechanism)