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Fabrication of graphene aerosol hybridized coordination polymer derived CdO/SnO_2 heteronanostructure with improved visible light photocatalytic performance

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ABSTRACT

A new graphene aerosol hybridized CdO/SnO_2 (CdO/SnO_2/GA) heterostructure is fabricated for visible photocatalytic degradation of organic pollutants. Firstly, CdO/SnO_2 heteronanostructure is prepared by solid-state conversion of a nano coordination polymer. Then, the prepared CdO/SnO_2 material is hybridized with graphene oxide under hydrothermal condition to get the CdO/SnO_2/GA hybrid. The CdO/SnO_2/GA hybrid is successfully characterized by powdered X-ray diffraction, Fourier transform infrared spectroscopy, transmission electron microscopy, scanning electron microscopy, energy dispersive X-ray, X-ray photoelectron spectroscopy, photoluminescence spectroscopy and UV–Visible diffuse reflectance spectroscopy. It is observed that CdO/SnO_2/GA exhibits improvement in visible light photocatalytic activity towards degradation of dyes compared to pure CdO/SnO_2, GA or earlier reported SnO_2/graphene based hybrids. The enhanced photocatalytic activity can be ascribed by synergistic effect of CdO, SnO_2 and graphene, and also for higher surface area and porous nature of the graphene aerosol and effective charge separation in the CdO/SnO_2/GA. Importantly, graphene and dye are also acting as the co-photosensitizer with CdO/SnO_2 absorbing more visible light and enhancing charge separations. Furthermore, the CdO/SnO_2/GA hybrid exhibits high photo-stability up to five cycles without any photo-corrosion implying its potential applications for environmental remediation.

1. Introduction

Semiconductor photocatalysis has widely attracted the researchers because of its potential for solar energy conversion, hydrogen generation and pollutant degradation [1–5]. Among the semiconductors, TiO_2 and ZnO have been extensively applied in photocatalysis for the degradation of organic pollutants. However, the utilization of ultraviolet light (UV) for activating the photocatalysts limits the practical applications because of lower content of UV light (only about 2–3%) in the solar spectrum. Hence, various efforts have been made for exploiting new photocatalysts, which are active under visible light. In dye sensitized photocatalysis [6], modified semiconductors can be sensitized by organic dyes under visible light irradiation, in which the dye is excited and transfer an electron from the excited state to the conduction band of the semiconductor, and the electron is then utilized by surface adsorbed oxygen to form various reactive oxygen species responsible for the mineralization of the dye. Hence, most of the sunlight can be utilized by this process, which makes it more superior to that of the UV light assisted photocatalysis. It is established that coupling of different semiconductor metal oxides or hybrids can reduce the electron–hole pair combination under irradiation and consequently, higher photocatalytic activity is achieved. The hybrid semiconductor materials with having two different energy-level systems can play an important role in increasing charge separation. Hence, various heterostructures such as NiO/SnO_2, SnO_2/CdS, ZnO/SnO_2 and TiO_2/SnO_2, etc. have been successfully fabricated for different attractive properties [7–10]. Among various metal oxides, CdO and SnO_2 are important semiconductors with band gap of 2.2 and 3.6 eV, and have been recognized as versatile materials for opto-electronic application, dye sensitized solar cells, sensors and Li-ion batteries because of its excellent gas sensitivity, photoelectrical properties and chemical stability [11–16]. Now-a-days, SnO_2 has been exploited as promising photocatalytic material for environmental cleanup [17]. However, the CdO or CdO-based semiconductor heterostructure is to be investigated as photocatalyst, since they have the potential for the visible light photocatalytic application [16,18,19]. Hence, it is anticipated that the combination of CdO and SnO_2 will exhibit new interesting properties and will also be expected to enhance the absorption of visible light.

In recent years, graphene-inorganic semiconductor hybrid materials have got much attention in the area of solar energy conversion. Graphene, a

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zero band gap two-dimensional (2D) sp^2-hybridized carbon atoms has very high charge carrier mobility, specific surface area, excellent optical properties as well as good thermal and chemical stability [20]. The giant 2-D structure of the graphene sheet helps to avoid particle aggregation, and the special π-conjugation structure helps for the adsorption of organic contaminants. Furthermore, the Fermi level difference of graphene and semiconductor produces a strong heterojunction electric field, which enhances the separation of photogenerated carriers. Hence, integrating the grapheme with any wide band gap semiconductor such as, TiO_2, ZnO, SnO_2, etc. would be promising to utilize efficient visible light photocatalytic activity [17,21,22]. However, most of the SnO_2-graphene hybrids reported earlier have been extensively applied for Li-ion battery, gas sensor and supercapacitor applications [23–25]. There are very few literatures that report the photocatalytic performance of the SnO_2-graphene hybrid for environmental cleanup [17], however, to the best of our knowledge, there is no literature reporting the photocatalysis of the ternary CdO/SnO_2/graphene based hybrids. Moreover, the mechanism of visible-light-driven photocatalysis in presence of dye photosensitizer has not been thoroughly investigated yet as well, which is crucial for developing visible-light assisted semiconductor-graphene hybrid photocatalysts. Hence, it is expected that the synergistic combination of CdO and SnO_2 with graphene and also using dye as the co-photosensitizer will give effective photocatalytic degradation of dyes as well as additional insight into the visible light photocatalytic mechanism.

The photodegradation of organic dyes, like RhB, by semiconductors had been studied extensively by various groups. However, design of some novel effective semiconductor hybrid system suitable to work under the visible light is always in demand. Herein, we report the fabrication of highly efficient novel CdO/SnO_2/GA ternary nanohybrid for the degradation of organic pollutants like RhB and 2,4-D in aqueous medium under visible light. It is found that our designed semiconductor systems exhibits much faster degradation of RhB and 2,4-D under visible light compared to many recent reports [17,26–38] even better than standard Degussa P25 with respect to catalytic dose, dye concentration, light intensity and duration of process [27], and hence, indicating its potential under solar or visible light condition. Our prepared catalyst is not only superior in term of high catalytic activity, but also stand unique in terms of stability, facile preparation and cost effectiveness. The CdO/SnO_2 heteronanostructure is firstly prepared by facile solid state transformation of a nano coordination polymer, and then by anchoring graphene aerosol into the CdO/SnO_2 heteronanostructure under hydrothermal condition as shown in Scheme 1. The as prepared CdO/SnO_2/GA nanohybrid is characterized and applied as a visible light photocatalyst for elimination of organic pollutants.

2. Experimental

2.1. Reagents and materials

Tin (II) acetate and Cadmium (II) acetate dihydrate were obtained from Sigma-Aldrich and SISCO Research Laboratories Pvt. Ltd. (India), respectively. Terephthalic acid (1,4-H_2BDC) was obtained from Central Drug House (P) Ltd. (India). The dye RhB was obtained from S.D. Fine chemical Ltd. (India). All other chemicals (solvents) were analytical grade (99.9%), and the solutions were prepared in Millipore water (Milli-Q system).

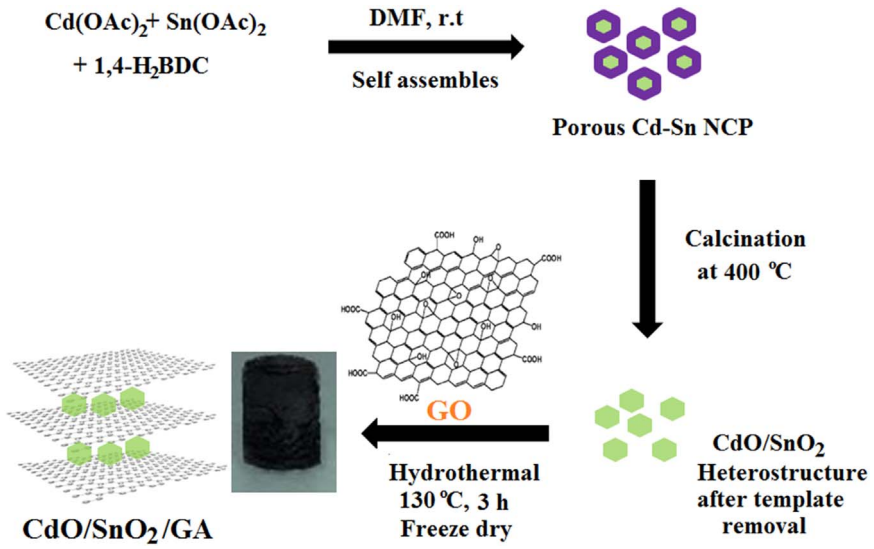
2.2. Preparation of CdO-SnO_2 heteronanostructures from nano coordination polymer (NCP) route

The CdO-SnO_2 heteronanostructures was first prepared by facile nano coordination polymer route discussed in our previous report with modifications of salt and ligand [39,40]. A solution of $Cd(OAc)_2{\cdot}2H_2O$ (0.042 mmol) and $Sn(OAc)_2{\cdot}2H_2O$ (0.007 mmol) was dissolved in a 6: 1 ratio in a minimum amount of DMF, and 4 mL DMF solution of 1,4-benzene di-carboxylic acid (1,4-H_2BDC) (0.035 mmol) was added to the above prepared solution. NCPs began to form very fast. Products were centrifuged and then washed with acetonitrile several times. The mixed-metal Cd-Sn NCPs were then dried at open air (yield ~55%).

Finally, the as-synthesized mixed-metal Cd-Sn NCPs were then heated in a furnace at 400 °C for 75 min. The CdO/SnO_2 heteronanostructure was generated, and it was cooled at room temperature. The percentage (%) weight loss from polymer to metal oxides was ~40%. The as-prepared Cd-Sn NCP was characterized by FT-IR, PXRD, TGA, and TEM analysis (Figs. S1–2).

2.3. Preparation of CdO/SnO_2/GA hybrid

The graphene oxide was synthesized from natural graphite by Hummer's method [41]. The CdO/SnO_2/GA was obtained by simple self-assembly of GO and CdO/SnO_2 under hydrothermal condition. In a typical synthesis, 1 mg/mL GO was added into 50 mL of deionized water under magnetic stirring for 30 min to produce of GO suspension. The GO solution (5% and 10%, wt%) was then mixed with the prepared CdO/SnO_2 powder. After that, the mixtures were sonicated for 1 h and magnetically stirred for 30 min. Then the mixtures were sealed in 90 mL of Teflon lined autoclaves and hydrothermally treated 130 °C for 3 h. After cooling the autoclaves at room temperature, a black cylindrical 3D CdO/SnO_2/graphene hydrogel, (CdO/SnO_2/GH) was obtained. The as-obtained CdO/SnO_2/GH sample was freeze-dried



Scheme 1. Schematic representation for the formation of CdO/SnO_2/GA hybrid.