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Sol-gel assisted hydrothermal synthesis and characterization of hybrid ZnS-RGO nanocomposite for efficient photodegradation of dyes

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ABSTRACT

In the present work, assembly and fabrication of nano-sized Zinc Sulphide (ZnS) particles grown on Graphene Oxide (GO) by the facile sol-gel method treated with microwave irradiation and assisted by hydrothermal processing. The production of high quality and self-assembled ZnS-RGO hybrid nanocomposites without the use of any surfactants/templates are been reported. Synthesis, interaction, kinetics and mechanism of hybrid ZnS-RGO composite are been studied. The results show that the photodegradation efficiency of brilliant blue under UV light irradiation for hybrid nanocomposite was better than GO and ZnS are reported. The photocatalytic activity strongly depended on the coverage of ZnS nanoparticles on the surface of graphene oxide sheets and the synergic adsorptive interaction between ZnS and GO. The enhancements of photo-catalysts activity are attributed to high migration efficiency of photoinduced electrons and inhibited charge carrier's recombination due to electronic communication between ZnS and GO. The nanocomposite having large surface area and microporous in nature played a vital role in absorptive activity are confirmed by BET surface area measurement. In addition, photoluminescence spectra of nanohybrids of ZnS-RGO composites displayed the surface plasma resonance and fluorescence quenching property. XRD, FT-IR, Raman spectroscopy, UV–visible spectroscopy, SEM with EDS, XPS, TEM and HR-TEM confirmed the structure and morphology of nanocomposite.

1. Introduction

A semiconductor nanoparticle is an important topic of interest because of their unique optical and electronic properties owing to quantum confinement effect and large surface area [1,2]. These nanoparticles have increased band gap as compared to their bulk counterparts leading to a blue shift in the absorption and emission spectra [3]. The bandgaps of these nanoparticles are tuned by controlling the size of particles, which can tailor physical and chemical properties for various applications [4]. Among the semiconductors, Zinc Sulphide is a non-toxic II–VI semiconductor with wide and direct bandgap energy of 3.71 eV and 3.78 eV for cubic zinc blend and hexagonal wurtzite structure respectively [5]. The morphology and size play very important role in the processes of characterization and applications. The wide bandgap of semiconductors is vital for photocatalysts and optoelectronics applications due to rapid electron-hole pair generation by photo-excitation [6]. ZnS has great potential for applications in sensors, catalysis, and optoelectronics [7,8]. Recently, ZnS nanostructure with various morphologies, such as a spheres, flowers, sheets, rods, wires, tubes, tetrapods, multi-angular branched shape, and T-shaped have been synthesized by different methods are used for various application of potentials [9,10]. On the other hand, the quick recombination of photogenerated charge carriers in ZnS nanocrystals limits its photocatalytic property and decreases the efficiency rate in optoelectronics fields. When ZnS crystal reacts with a photon, which carries the energy of h equal, or more than the bandgap energy of the ZnS nanocrystals makes an electron excited from the valence band to conduction band, consequently resulting in a positive hole in the valence band and recombination of electron and holes that plays vital role in optoelectronics fields [11,12]. The photogenerated holes and electrons play a very important role in the photocatalytic activity. However, the photogenerated electrons and holes in the excited states are unstable and can easily recombine, dissipating the input energy as heat, which results in low efficiency of the photocatalyst [13].

Graphene, a single layer two-dimensional sp^2 hybrid new class of carbon structure has attracted intensive research interest due to

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its excellent electrical, mechanical and optical properties. Its notable characteristics include tunable bandgap, high mobility, efficient flexibility, excellent chemical stability and inflated specific surface area that enables it to integrate with other materials without any difficulties [13,14]. Recently, graphene-based materials decorated with metal sulphides/metal oxides nanoparticles has encouraged great interest in the treatment of organic contaminants in wastewater through photocatalytic technique, because it can destruct the pollutants completely and has broader potential optical applications [15–17]. ZnS is an a excellent photocatalysts and photoresponsive to excite electrons from valence band to the conduction band and to create electron–hole pairs which can migrate and initiate redox reactions with water and oxygen and then degrade organic molecules or reduces metal ion absorbed on the surface of ZnS owing to their large shape anisotropy and superior thermal/chemical stability in ambient environments [18,19]. In the present work, a relatively facile sol-gel method treated with microwave irradiation and assisted with hydrothermal processing were employed to deposit and to decorate the ZnS nanoparticles on 2D platform surface of graphene oxide nanosheets without the aid of any stabilizers/surfactants have been reported [20,21]. Here, Microwave irradiation provides fast and uniform heating rates that will remove the impurities and loosely bonding forces, which can reduce the reaction time and causes a rapid nucleation of particles and growth. The interfacing of materials with microwave irradiation and hydrothermal treatment [22] resulting in growth, well crystalline structure, an increase in surface area, an enrichment in porosity of materials, morphology and enhanced role in photocatalytic applications.

2. Experiments

2.1. Materials

Graphite powder (−300 mesh, 99.95%, MERCK), 95% Hydrochloric acid (HCl), 98% Sulphuric acid (H_2SO_4), 30% Hydrogen Peroxide (H_2O_2), 95% Potassium Permanganate ($KMnO_4$), Sodium Nitrate ($NaNO_3$), 95% Phosphoric acid (H_3PO_4), Zinc Sulphate ($ZnSO_4 \cdot 5H_2O$), Sodium Sulphide ($Na_2S \cdot 7H_2O$) and ethanol purchased from Sigma-Aldrich Chemical Reagent Co. Ltd. The nanopure water used for all the experiments with a resistivity of 18.2 MΩ cm purified by PURELAB Option Q7, ELGA, UK.

2.2. Synthesis of graphene oxide nanosheets

Graphene Oxide is prepared from graphite powder by improved Hummer's method [23]. In brief, 9:1 pre-cooled mixture of Conc. H_2SO_4/H_3PO_4 slowly poured under continuous stirring into the mixture of 1 g of graphite powder and 0.5 g of $NaNO_3$ powder taken in 1 L conical flask. Then 6 g of $KMnO_4$ was slowly added in steps maintaining the temperature of the mixture at 25 °C and stirring continuously for 2 h produces an exothermic reaction by which raise in temperature up to 80 °C–100 °C is observed. After making the solution cool to room temperature, now gradually add 280 ml of deionized water containing 10 ml (30% of H_2O_2) and kept overnight for decantation to obtain a solid precipitation. The product is washed 5 to7 times with 5% warm solution of HCl to remove the metal ions and impurities. The solutions are centrifuged for 30 min at 4000 rpm, wash with ethanol, and filtered to obtain a black powder. Finally, the resultant powder is vacuum dried at 80 °C for 24 h to obtain a black pure graphene oxide nanosheet.

2.3. Synthesis of ZnS

For the synthesis of ZnS (1 mol, 3.6 g, of $ZnSO_4 \cdot 5H_2O$) and (1 mol, 1.56 g, $Na_2S \cdot 7H_2O$) powders were dissolved separately in 20 ml of deionized water and stirred at room temperature for 30 min. Then, the solutions were mixed by dripping the Na_2S solution in drops into $ZnSO_4$ solution at 80 °C and stir for 2 h to form a white gel. The white gel is firstly irradiated with microwave radiation for 120 s at 450Wand then the irradiated solutions is transferred to 30 ml General Purpose stainless steel (SS-316) Teflon-lined autoclaves. The autoclaves were kept at 150 °C in hot air oven for 24 h and then allowed to cool down to room temperature. The products were washed several times with deionized water and ethanol followed by centrifuging at 4000 rpm for 20 min. The final resultant products were kept for drying in a vacuum oven for 24 h at 80 °C to yield ZnS nanoparticles [24].

2.4. Synthesis of ZnS-RGO nanocomposite

To prepare ZnS-RGO nanocomposite, 0.2 g of GO was dispersed in 100 ml of nanopure water and ultrasonication for 60 min to form homogenous GO solution and for further exfoliation of graphene oxide. Then, 1 mol of ZnS = Zinc Sulphide (1 mol, 3.62 g, $ZnSO_4$) and Sodium Sulphide (1 mol, 1.56 g, Na_2S) was gradually dissolved in above homogenous exfoliated GO solution at 80 °C under magnetic stirring conditions for 1 h. The different ZnS-RGO nanocomposites solutions underwent firstly with microwave irradiation treatment for 120 s at 450 W and then the irradiated solutions were soon after transferred to 30 ml General Purpose stainless steel (SS-316) Teflon lined autoclaves. The autoclaves were kept at 150 °C in hot air oven for 24 h (temperature and time duration were optimized before doing the experiment and found the suitable conditions to conduct the experiment in mild hydrothermal processing which increased the surface area, re-crystallization and structural properties of composites. The binding energies are well established with no agglomeration of ZnS particles decoration on the surface of GO. In addition the reduction of GO is moderated which make slow oxidization process resulting in increase in content of graphene transformation which yields in higher amount without much loss of mass formulating to single layers structure) and then allowed to cool down to room temperature. The products are washed with water, ethanol and followed by centrifuging at 4000 rpm for 30 min. The final products were kept for drying in a vacuum oven for 24 h at 90 °C to form ZnS-RGO nanocomposite, 1ZGS and 2ZGS respectively [25]. The schematic sketch for the synthesis of hybrid ZnS-GO nanocomposite synthesis is illustrated in Fig. 1.

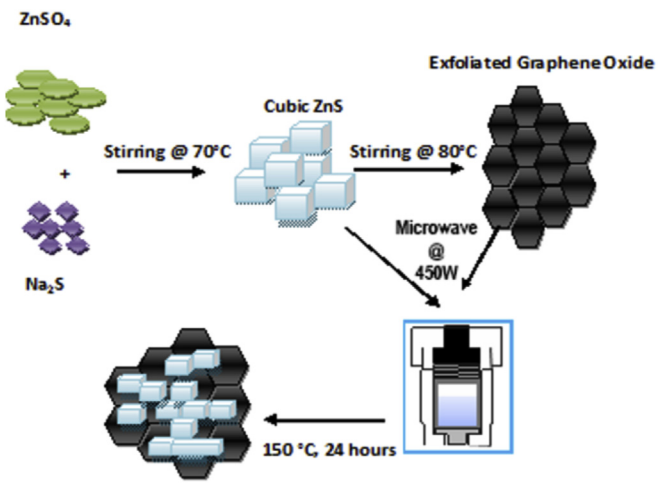

Fig. 1. Schematic sketch of synthesis of ZnS-RGO by microwave assisted hydrothermal process.

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