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A green and direct synthesis of photosensitized CoS_2–graphene/TiO_2 hybrid with high photocatalytic performance

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ABSTRACT

CoS_2, CoS_2–graphene and CoS_2–graphene/TiO_2 composite was synthesized by a facile sonochemical and hydrothermal method. X-ray diffraction, scanning electron microscopy with energy-dispersive X-ray analysis, transmission electron microscopy, FT-IR, UV–vis and BET surface area was calculated by nitrogen adsorption were used. The FT-IR results illuminated that CoS_2 and TiO_2 band transfers electrons to graphene with functional groups attached. UV–vis patterns indicated that CoS_2–graphene/TiO_2 have good photoinduction effects in visible light region. The photocatalytic activity of sample was evaluated by measuring the degradation of organic pollutants such as methylene blue (MB), and industrial dyes such as Texbrite BA-L (TBA) under visible light.

Introduction

Employing titania (TiO_2) as a photocatalyst in degradation of organic and inorganic pollutants in air and water offers a viable approach for solving environmental pollution problems. This is due to its unique properties which include high oxidizing capacity, low cost, non-toxicity, chemical robustness and high photostability [1]. However, practical application of this great substance is impeded by its high recombination rate of photo induced charge carriers and wide band gap (3.2 eV for anatase polymorph) [2]. TiO_2 only shows photo-response to UV light, hence making it more costly to use it because of the need for a UV light source [3]. A more cost effective way will be the use of renewable energy (solar energy) for the purpose of environmental cleanup due to its abundance and environmental friendliness. TiO_2 can only absorb UV light ($\lambda < 387$ nm), which accounts for less than 5% of sunlight, thus restricting its practical applications [4].

Two strategies have been employed to improve the sunlight utilization efficiency. One is the use of modification techniques on TiO_2 to shift its light absorption capacity toward visible light wavelengths, such as ion doping, noble metal loading, metal ion-implantation, dye sensitization, and conjugated polymer modification. The other is the development of new oxide photocatalysts with visible light-driven activity [5].

Transition metal dichalcogenide compounds with pyrite structure, MX_2 (M = Mn, Fe, Co, Ni; X = S, Se, Te), show various magnetic and electronic properties. Among them, CoS_2 is an itinerant ferro-magnet with the Curie temperature of $T_c = 120$ K. The crystal structure is pyrite-type cubic and represented by the space group $T^6{}_h$ (Pa3). The Co atom is octahedrally surrounded by six covalently bonded S–S pairs. The Co 3d electrons are in the low spin state with the nominal $t^6{}_{2g}e^1{}_g$ configuration. The electronic structures of the pyrites have been studied by photoemission and band calculations. Some transition-metal dichalcogenides are semiconductor materials with narrow band gap, high sunlight utilization efficiency. They have been proven to be efficient in the degradation of pollutants and/or the production of photocatalytic hydrogen [6].

Carbon-based materials, such as graphite, carbon nanotubes, graphene sheets and fullerene have been widely studied. Two-dimensional (2-D) graphene has emerged as high potential material and increasingly attracted attention owing to its fascinating physical properties including quantum electronic transport, extremely high mobility, high elasticity, and electromechanical modulation. As a simple and facile method, hydrothermal method has shown its advantages in the preparation of nanomaterials [7].

In this study, CoS_2–graphene/TiO_2 has been prepared via sonochemical and hydrothermal method using cobalt chloride

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and anhydrous purified sodium thiosulphate. Interesting phenomena were also found in which the enhancement of photoactivity was attributed the photosensitization of graphene and the enhanced interfacial charge separation between graphene and CoS_2 particles.

Experimental

Materials

Graphene oxide which was prepared d by a Hummers–Offeman method in our previous works was used as another carbon nanomaterial [8]. In brief, graphite powder (10 g) was dispersed in cold concentrated sulphuric acid (230 mL, 98 wt%, dry ice bath), and potassium permanganate ($KMnO_4$, 30 g) were gradually added with continuous vigorous stirring and cooling to prevent the temperature from exceeding 293 K. The dry ice bath was removed and replaced by a water bath, and the mixture were heated to 308 K for 30 min with gas release under continuous stirring, followed by slow addition of deionized water (460 mL), which produced a rapid increase in solution temperature up to a maximum of 371 K. The reaction was maintained for 40 min in order to increase the oxidation degree of the GO product; then the resultant bright-yellow suspension was terminated by addition of more distilled water (230 mL), followed by a hydrogen peroxide solution (H_2O_2, 30%, 250 mL). The solid products was separated by centrifugation at 3000 rpm, was washed initially with 5% HCl until sulphate ions were no longer detectable with barium chloride ($BaCl_2$), were then washed three times with acetone, and were air dried overnight in vacuum oven. After sonication for 30 min under 308 K, the graphite oxide was transformed into graphene oxide sheet.

For the oxidization of carbon material, 3-chloroperoxybenzoic acid (TCPBA) was chosen as the oxidizing agent and was purchased from Acros Organics, New Jersey, USA. Benzene (99.5%) was used as the organic solvent and was purchased from Samchun Pure Chemical Co., Ltd., Seoul, Korea. Cobalt chloride ($CoCl_2$) was purchased from DaeJung Chemicals & Metal Co., Ltd., Korea. Anhydrous purified sodium thiosulphate ($Na_2S_2O_3$, 95%) was purchased from Duksan Pharmaceutical Co., Ltd., Korea. Titanium(IV) *n*-butoxide (TNB, $C_{16}H_{36}O_4Ti$) as the titanium source for the preparation of the CoS_2–graphene/TiO_2 composites was purchased as reagent-grade from Acros Organics, USA. Methylene blue (MB $C_{16}H_{18}N_3S{\cdot}Cl$) was purchased from Samchun Pure Chemical Co., Ltd., Korea. Texbrite BA-L (TBA) was purchased from Texchem Co. Ltd., Korea. Titanium oxide nanopowder (P25, <25 nm, 99.7%) with anatase structure used as control sample was purchased from Sigma–Aldrich Chemistry, USA. All chemicals were used without further purification, and all experiments were carried out using distilled water.

Synthesis of CoS_2–graphene composite

The graphene nanosheets (54 mg) were under ultrasonication 1 h. After then added to $CoCl_2$ and $Na_2S_2O_3$ mixture solutions, after ultrasonication the mixture was added into a 100 ml Teflon-line autoclave and maintained at 423 K for 12 h. The solvent was evaporated and the CoS_2–graphene powders were obtained after being dried.

Synthesis of CoS_2–graphene/TiO_2 composite

CoS_2–graphene/TiO_2 was prepared using pristine concentrations of TNB for the preparation of CoS_2–graphene composites. CoS_2–graphene powder (3 g) was ultrasonicated (750 W, Ultrasonic Processor VCX 750, Korea) for 30 min, and then mixed with 3 ml TNB. The solutions were homogenized under reflux at 343 K for 5 h, while being stirred in a vial. After stirring, the solution transformed to CoS_2–graphene/TiO_2 gels and heat treated at 673 K to produce the CoS_2–graphene/TiO_2 composites.

Characterization

XRD (Shimadzu XD-D1, Uki, Kumamoto, Japan) was used to identify the crystallinity of the composite with monochromatic high-intensity CuKα radiation (l = 1.5406 Å). SEM (JSM-5600, JEOL Ltd., Tokyo, Japan) was used to observe the surface state and structure of the prepared composite. The N_2 adsorption isotherm was measured at 77 K using a BEL sorp Analyzer (BEL, Japan). Then, the BET surface area was calculated by nitrogen adsorption. The pore size distribution was calculated by the BJH method. Transmission electron microscopy (TEM, JEOL, JEM-2010, Japan) was used to determine the state and particle size of the prepared composite. TEM at an acceleration voltage of 200 kV was used to investigate the number and the stacking state of graphene layers on the various samples. TEM specimens were prepared by placing a few drops of sample solution on a carbon grid. The elemental mapping over the desired region of the prepared composite was determined by an EDX analyzer attached to the SEM. Fourier transform infrared (FT-IR) study of the photocatalysts and the monitoring of the photoactivity tests were carried out using a NICOLET IR 200 spectrophotometer. Intervals of 4000–400 cm^{-1}, a resolution of 4 cm^{-1} and a forward and reverse moving mirrors speed of 10 and 6.2 kHz, respectively were used.

UV–vis diffuse reflectance spectra were obtained using an UV–vis spectrophotometer (Neosys-2000, Sinco Co. Ltd., Seoul, Korea) using $BaSO_4$ as a reference at room temperature and were converted from reflection to absorbance spectra by the Kubelka–Munk method.

Photocatalytic degradation of dyes

Photocatalytic activity was evaluated by dye degradation in aqueous media under visible-light irradiation. For visible-light irradiation, the reaction beaker was located axially and held in a visible lamp box (8 W, halogen lamp, KLD-08L/P/N, Korea). The luminous efficacy of the lamp was 80 lm/W, and the wavelength was 400–790 nm. The lamp was located at a distance of 100 mm from the aqueous solution in a dark box. The amount of photocatalytic composite used was 0.05 g/(50 ml solution). The initial concentration of the dyes was set at 2×10^{-5} mol/L in all experiments. On the other hand, 0.001 v/v aqueous solution of TBA was also prepared with deionized water in 1 L measuring flasks, respectively. The concentrations of the stocks solutions of the three dye solutions depended on various factors such as color intensity of the dyes, molecular structure complexity of the dyes, intensity of visible light falling on the solutions and activity of the photocatalysts.

The reactor was placed for 2 h in the dark box to make the photocatalytic composite particles adsorb as many dye molecules as possible. After the adsorption phase, the visible-light irradiation was restarted to make the degradation reaction proceed. To perform dye degradation, a glass reactor (diameter = 4 cm, height = 6 cm) was used, and the reactor was placed on the magnetic churn dasher. The suspension was then irradiated with visible light for a set irradiation time. Visible-light irradiation of the reactor was performed for 90 min. Samples were withdrawn regularly from the reactor, and dispersed powders were removed in a centrifuge. The clean transparent solution was analyzed by a UV–vis spectrophotometer (Optizen POP, Mecasys Co., Ltd., Korea). The dye concentration in the solution was determined as a function of the irradiation time.