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A new synergetic mesoporous silica combined to CdSe-graphene nanocomposite for dye degradation and hydrogen evolution in visible light

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ABSTRACT

To promote outstanding qualities of mesoporous silica and enhance photocatalytic activity of CdSe and silica nanoparticles, the combination of SiO_2 nanoparticles from silica precursor with CdSe-graphene nanoparticles was processed under catering of cetyltrimethylammonium bromide (CTAB) and sodium lauryl sulfate (SLS) as the surfactant template. The as-synthesized sample exhibited highly efficient photocatalytic effects for treatment of MB and RBB organic dye solutions at optimum conditions for this study, including pH and catalyst dosage, were at pH 11 for MB dye solution case and pH 3 for RBB dye solution case and initial amount was 0.05 g catalyst for both cases. Besides, hydrogen generation of SiO_2/CdSe-graphene was markedly higher than that of binary CdSe-graphene nanocomposite under ambient conditions with/without methanol 20% sacrificing reagents at room temperature. The SiO_2/CdSe-graphene nanocomposite is capable of photocatalytic degradation of different organic dyes under visible light irradiation as well as for developing efficient hetero-system for hydrogen production.

1. Introduction

In addition to air pollution from industrial activities, water pollution also becomes one of the issues that receives attention in the scientific community due to serious harm that it causes. Until now, the aquatic environment and marine life as well as human life have been directly or indirectly impacted by the process of rapid industrialization and modernization globally [1–3]. Semiconductor materials have attracted much concern as new approaches in the photocatalytic activity field due to highly stable and potential application to mitigate pollution of water resources globally as well as being highly efficient in achieving renewable energy [4,5]. With suitable band gap energy E_g, various semiconductor sources are capable of decomposing pollution organic material such as TiO_2, CuO, CdS, ferrates, ferrites, etc [6–8]. Cadmium selenide (CdSe) is a promising n-type semiconductor material known as potential material to improve photocatalytic activity due to its small band gap energy (1.65–1.8 eV) [9–11]. With this small band gap energy, CdSe can easily form photogenerated electrons when light wavelength of the light source is less than or equal to 730 nm [12,13]. CdSe can rapidly form the photogenerated electron-hole under any kind of irradiation (UV or visible light) and can participate in the elimination or mineralization process of organic pollutants from wastewater to reduce impact on the environment [14,15]. Regarding the other aspect, with suitable band gap energy, CdSe is also promising in achieving high hydrogen production from water splitting reaction under light irradiation [16–18].

Besides, the combination of CdSe and graphene also attracted much attention from many researchers in this field because the combination can enhance properties such as high catalytic activity and excellent electrochemical properties of each individual nanoparticle. Oh Won-Chun, et al. reported synthesis of graphene-CdSe composite by a simple hydrothermal method and photocatalytic degradation of organic dye [19]. Stephen H. Frayne et al. posits that the development of new materials for degradation of toxic waste is of major significance from an environmental perspective by surveying growth and properties of CdSe nanoparticles on ellagic acid bio templates [20].

On other aspects, mesoporous silica has received growing interest in many areas of science and technology because of multiple excellent properties such as high porosities, large specific surface areas, low densities, and large pore sizes [21,22]. From that, SiO_2 becomes a promising candidate in many different fields of nano drug carriers as well as improvement of photocatalytic performance [23–26]. Decoration of mesoporous silica nanoparticles on the graphene surface was proven the improved interfacial contact as well as development of

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conducting pathways, and suppression of charge recombination through various covalent, non-covalent and π-π interactions, that can enhance photocatalytic activity of both nanomaterials [27,28]. According to previous reports, mesoporous SiO_2/Cu_2O-graphene nanocomposites were synthesized and achieved results revealed highly efficient photocatalytic performance for dye pollutants as well as good stability during photocatalysis under visible light irradiation [29]. Synthesis of mesoporous SiO_2/CdSe-graphene nanocomposites through a facile method, such as the self-assembly method, and effective use in photocatalytic systems has not been demonstrated.

Based on available platforms, a set of mesoporous SiO_2/CdSe-graphene composites were prepared using a self-assembly method, by using tetraethyl orthosilicate (TEOS) as the silica precursor, with cationic surfactant cetyltrimethylammonium bromide (CTAB) and nonionic surfactant sodium lauryl sulfate (SLS) as the surfactant template. After that, structure and morphology of survey composites were characterized via XRD, SEM, EDX analysis, TEM, Raman spectroscopy, UV–vis-DRS, XPS, and FT-IR spectra. More interestingly, by using nitrogen adsorption/desorption isotherms using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, the pore diameter, pore volume, and surface area of the tested composites were determined. Photodegradation experiments were then tested with safranine O (SO), rhodamine B (RhB), methylene blue trihydrate (MB) as cationic organic dyes; methyl orange (MO), reactive black B (RBB), texbrite BA-L (TBA) as anionic organic dyes in aqueous solution under visible light irradiation with the difference of initial pH and catalyst dosage. What is more, photocatalytic hydrogen production studies of as-synthesized nanocomposites were tested from pure water and aqueous solution containing 20% methanol as sacrificial reagent.

2. Experimental

2.1. Reagents

Graphene oxide was prepared in the laboratory from natural graphite using the Hummers-Offeman method and was used to form composites. Ethanol (C_2H_5OH, 95%), methanol (CH_3OH, 99.5%), sodium hydroxide (NaOH, 93.0–100%), selenium powder (Se, 99%), sodium sulfite ($Na_2SO_3.7H_2O$, 95%), and hydrochloric acid (HCl, 35.0–37.0%) were purchased from Duskan Pure Chemicals Co. Ltd., Korea. Tetraethyl orthosilicate (TEOS, 99%) was purchased from Aldrich Chemistry, Germany. Cadmium acetate dihydrate ($(CH_3COO)_2Cd$, 98%), cetyltrimethylammonium bromide (CTAB, $C_{19}H_{42}BrN$, 99%), sodium lauryl sulfate ($C_{12}H_{25}NaO_4S$), methyl organe (MO, $C_{14}H_{14}N_3NaO_3S$), and ammonium hydroxide (NH_4OH, 25%) were purchased from Daejung Chemicals Co. Ltd., Korea. Safranine O (SO, $C_{20}H_{19}ClN_4$), texbrite TBA-L (TBA), rhodamine B (RhB, $C_{28}H_{31}ClN_2O_3$), and methylene blue trihydrate (MB, $C_{18}H_{18}ClN_3S.3H_2O$) were purchased from Samchun Pure Chemicals Co. Ltd., Korea. Reactive Black B (RBB) was purchased from JAY Chemical Industries Limited, India. All chemicals were used without further purification, and all experiments were conducted using distilled water.

2.2. Synthesis nanocomposites

2.2.1. Synthesis of the CdSe-graphene nanocomposite

A selenium salt was obtained via combination of 0.01 mol anhydrous sodium sulfite (Na_2SO_3) and 0.004 mol crude selenium (Se) powder were dispersed in 120 ml of distilled water for three hours at 80 °C. After that, 0.675 g $(CH_3COO)_2Cd$ and 2 ml NH_4OH 25% were added into the achieved selenium salt, then heated to 80 °C with magnetic stirring for one hour to form Part A. Separately, Part B was formed from sonication of graphene oxide (0.2 g) was sonicated in 20 ml of distilled water for 30 min (Ultrasonic Processor, VCX 750, 500 W, Korea, Power 500-Watt, frequency 20KHz, Amplitude 50%, low intensity). Part A was mixed with Part B, with continued vigorous stirring for two hours at 80 °C. After hydrothermal reaction occurred at 70 °C for six hours, temperature of dispersion decreased to ambient temperature. The mixture was filtered using Whatman filter paper ($\Phi = 110$ mm). Obtained solid was collected and washed with distilled water three times, and 95% ethanol twice. CdSe-graphene nanocomposites were obtained after drying in a vacuum at 105 °C for 24 h. The sample was labeled as CG corresponding to the CdSe-graphene nanocomposite.

2.2.2. Synthesis of the SiO_2/CdSe-graphene nanocomposite

3.6 g TEOS, 80 ml ethanol, and 5 ml NH_4OH 25% were mixed under vigorous stirring to form Part C. Conversely, 0.36 g CTAB was dissolved in 57 ml distilled water, then stirred with magnetic stirring for 30 min to form Part D. Part E was obtained via ultrasonication of a certain amount of CdSe-graphene nanocomposite in 20 ml distilled water for 30 min. Vigorous stirring of mixture of Parts C, D, and E was continued for six hours at room temperature. Meanwhile, pH value was adjusted with NH_4OH 25%, until reaching pH 9.5–10. The above dispersion was transferred to an autoclave for a hydrothermal reaction at 100 °C for 24 h. Finally, the temperature of the mixture was reduced to room temperature, and the mixture was filtered using Whatman filter papers ($\Phi = 110$ mm). The obtained solid was collected and washed several times with 95% ethanol and distilled water and then drying under a vacuum at 105 °C for 24 h. The achieved powder was kept in furnace to calcine at room temperature to 550 °C for 8 h, then it was heated at 550 °C for 6 h to completely remove a surfactant as well as a volatile matter and destroy impurity materials. Samples were labeled as SCG-1, SCG-2, and SCG-3, corresponding to the CdSe-graphene and TEOS mass ratios of 5:100, 10:100, and 15:100, respectively.

With the catalytic base (pH = 9.5–10), the hydrolysis reaction of TEOS easily forms $Si(OH)_4$ with OH^- ions that can directly penetrate toward the Si atoms and replace every part of the $-OC_2H_5$ group in the TEOS molecule. Therefore, condensing the $\equiv Si(OH)$ group of silica gel made up with structural hierarchical priorities for all sides, resulting in nanosilica material that often-formed spherical structures [8].

Replaced 0.36 g CTAB with 0.2 g SLS as the surfactant template, as well as structure creator, and conducted with the same experimental conditions as above description, we will obtain samples that were labeled as SCG-A, SCG-B, and SCG-C, corresponding to the CdSe-graphene and TEOS mass ratios of 5:100, 10:100, and 15:100, respectively.

2.3. Characterization

An X-ray diffraction (XRD, Shimadzu XD-D1) using monochromatic high-intensity Cu Kα radiation ($\lambda = 1.5406$ Å). SEM (JSM-5600 JEOL, Japan) was used to analyze the shape and structure of the nanomaterial surface at high-resolution. A UV–vis diffuse reflectance spectra (DRS) analysis was obtained by UV–vis spectrophotometry (Neosys-2000) by using $BaSO_4$ as a reference at room temperature and converted from reflection to absorbance by the Kubelka-Munk method. Transmission electron microscopy (TEM) was also used to investigate the size and distribution of the nanoparticles deposited on the graphene surface of the various samples. The XPS analysis was observed using a VG Scientific ESCALAB250 XPS system equipped with a monochromatic AlKα X-ray source ($h\nu = 1486.6$ eV) with charge compensation. The Raman spectra were achieved by a spectrometry (Jasco Model Name NRS-3100) with an excitation laser wavelength of 532.06 nm. Nitrogen adsorption/desorption isotherms studies were investigated by a Micromeritics ASAP 2020 M + C operating at 77 K, the surface area was calculated by using the Brunauer-Emmett-Teller (BET) method. and the pore size distribution was calculated according to the Barrett-Joyner-Halenda (BJH) method. The photodegradation experiments were analyzed by a UV-spectrophotometry (Opizen POP, Korea).