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## Highly efficient visible light driven photocatalytic activities of the LaCuS<sub>2</sub>-graphene composite-decorated ordered mesoporous silica



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### ABSTRACT

A combination of mesoporous silica with an LaCuS<sub>2</sub>-graphene composite has been prepared by a self-assembly method in support of the CTAB surfactant as the structure creator and basic medium. The characterization was investigated using XRD, SEM, TEM, HR-TEM, EDS, XPS, Raman, and DRS analysis. The pore size of the as-fabricated composite was calculated to be 5.83 nm by the nitrogen adsorption/desorption isotherms. In addition, the photocatalytic properties revealed that the mesoporous SiO<sub>2</sub>/LaCuS<sub>2</sub>-graphene catalyst presented a good result for the photocatalytic activity of organic dyes and gallic acid under visible light irradiation. Moreover, the as-prepared mesoporous SiO<sub>2</sub>/LaCuS<sub>2</sub>-graphene nanocomposite exhibited a good photodegradation rate for a cationic organic dye group under a pH medium of 11. The photocatalytic performance of the phenol compound representation presented a good result, and the optimum amount of the catalytic for the gallic acid photocatalytic activity is 0.05 g. In addition, the mesoporous SiO<sub>2</sub>/LaCuS<sub>2</sub>-graphene catalyst can be exploited for the application of solar energy conversion with high hydrogen production capacity.

### 1. Introduction

Ordered mesoporous silica has been determined as the potential material source for the removal of organic and inorganic pollutants due to its high surface area, uniform pore size distribution, ordered structure, and high pore volume [1–4]. With the presence of numerous outstanding properties, the mesoporous structure promises to provide a large interaction surface area. The increasing active site population and accessibility to active sites leads to an increase in the reactivity capability of the photocatalyst and harmful organic molecular, which can help to enhance its photocatalytic performance [5–8]. As a supporter material, the mesoporous silica is used in much different applications, such as in sensing, separation, and photocatalyst fields [9,10]. In the photocatalyst field, the combining mesoporous silica with graphene oxide or other semiconductor materials is proven to achieve high photocatalytic performance [11,12]. Our previous research also indicated that the combination of mesoporous silica and a Cu<sub>2</sub>O-graphene composite to form a ternary photocatalyst material can improve the photodegradation efficiency of the organic dyes under visible light irradiation [13].

In the development of various new material source processes, the

potential semiconductor source, which can be used as a photocatalyst for the degradation as well as the decomposition of harmful organic pollutants in industrial and civil wastewater, is now receiving much consideration by many researchers. To the best of our knowledge, lanthanum copper sulfur (LaCuS<sub>2</sub>) is a semiconducting ternary chalcogenide that has not been studied extensively. The combination of lanthanum copper sulfur (LaCuS<sub>2</sub>) with other supporting materials, such as graphene oxide and/or other semiconductors, is promising as a way to overcome the drawback point itself and for its ability to enhance the photocatalytic field, as well as for its use in solar energy conversion and environmental purification.

In this present paper, a combination of lanthanum copper sulfur (LaCuS<sub>2</sub>) with mesoporous silica and graphene oxide by a simple self-assembly method to form a new ternary catalyst is prepared, which can help to explore the photocatalytic application under visible irradiation, such as the photodegradation of organic dyes, the photocatalytic activity of a phenol compound, and hydrogen evolution. In addition, the photodegradation of organic dyes was proceeded by the representation of a cationic dye group and the representation of an anionic dye group under visible light irradiation. Moreover, the degradation of gallic acid under visible light irradiation was carried out to determine the capacity

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of the achieved materials to create the photocatalytic activity of phenol compound. The recycling experiments were carried out for five repeated cycles to prove the stability of the photocatalysts. Photocatalytic hydrogen evolution also was studied to establish the wide application of the as-fabricated SiO<sub>2</sub>/LaCuS<sub>2</sub>-graphene catalyst for use in energy conversion.

## 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<sub>2</sub>H<sub>5</sub>OH, 95%), methanol (CH<sub>3</sub>OH, 99.5%), sodium hydroxide (NaOH, 93.0–100%), and hydrochloric acid (HCl, 35.0–37.0%) were purchased from Duskan Pure Chemicals Co. Ltd., Korea. Tetraethyl orthosilicate (TEOS, 99%) and Folin-Ciocalteu's reagent were purchased from Aldrich Chemistry, Germany. Copper (II) acetate (Cu(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O, 95%) was purchased from Junsei Chemical Co., Ltd., Japan. Lanthanum (III) chloride heptahydrate (LaCl<sub>3</sub>·7H<sub>2</sub>O, 98%), sodium sulfide pentahydrate (Na<sub>2</sub>S·5H<sub>2</sub>O, 98%), cetyltrimethylammonium bromide (CTAB, C<sub>19</sub>H<sub>42</sub>BrN, 99%), ammonium hydroxide (NH<sub>4</sub>OH, 25%), sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>), N, N-dimethylformamide (HCON(CH<sub>3</sub>)<sub>2</sub>, 99.5%), ethylene glycol (C<sub>2</sub>H<sub>6</sub>O<sub>2</sub>, 99%), and gallic acid (C<sub>7</sub>H<sub>6</sub>O<sub>5</sub>, 98%) were purchased from Daejung Chemicals Co. Ltd., Korea. Safranin O (SO, C<sub>20</sub>H<sub>19</sub>ClN<sub>4</sub>), rhodamine B (RhB, C<sub>28</sub>H<sub>31</sub>ClN<sub>2</sub>O<sub>3</sub>), and methylene blue trihydrate (MB, C<sub>18</sub>H<sub>18</sub>ClN<sub>3</sub>S·3H<sub>2</sub>O) 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

*Synthesis of the LaCuS<sub>2</sub>-graphene nanocomposite:* in a typical procedure, 0.1 mmol copper(II) acetate and 0.1 mmol lanthanum (III) chloride heptahydrate were added to 50 mL N,N-dimethylformamide. After vigorous stirring for 1 h at 40 °C to form the transparent dispersion, 20 mL ethylene glycol was dropped into the above dispersion. The temperature of the achieved solution was raised to 120 °C and stirring continued for 1 h. Then 0.2 mmol sodium sulfide pentahydrate was added to the dispersion, and the mixture continued to be stirred until homogenization was achieved.

Separately, 0.2 g graphene oxide, which was dispersed in 20 mL ethylene glycol using an ultrasonication (250 W) for 30 min was added drop by drop to the above dispersion to obtain the final dispersion. The obtained dispersion was subjected to hydrothermal treatment at 150 °C for 12 h and then naturally reduced to ambient temperature. The mixture was filtered through Whatman filter paper (Φ = 110 mm). The product was washed with distilled water 3 times and with 95% ethanol twice. After drying under a vacuum at 105 °C for 24 h, the LaCuS<sub>2</sub>-graphene material was synthesized and labeled as LCSG.

*Synthesis of the SiO<sub>2</sub>/LaCuS<sub>2</sub>-graphene nanocomposite:* In a typical procedure, 3.6 g tetraethyl orthosilicate was added drop by drop to the mixture of 5 mL ammonium hydroxide and 80 mL ethanol under vigorous stirring to form part A. Part B was formed by the dissolution of 0.36 g cetyltrimethylammonium bromide in 57 mL distilled water, and continuously stirred with magnetic stirring for 30 min. At the same time, the LaCuS<sub>2</sub>-graphene solution was obtained by the ultrasonication of 0.4 g of the as-fabricated LaCuS<sub>2</sub>-graphene in 20 mL distilled water for 30 min. Then, parts B and C were added to part A drop by drop at ambient temperature. The achieved dispersion was continuously stirred for 6 h. Meanwhile, the pH value was adjusted with ammonium hydroxide until it reached pH (9.5–10). The final dispersion was placed in a Teflon-lined autoclave for a hydrothermal reaction at 100 °C for 24 h. The temperature of the mixture was naturally reduced to room

temperature, and the mixture was filtered using Whatman filter papers (Φ = 110 mm). The obtained solid was collected, washed several times with 95% ethanol and distilled water, and then dried under a vacuum at 105 °C for 24 h. The achieved powder was calcined from room temperature to 550 °C for 8 h, followed by heating at 550 °C for 6 h. Samples were labeled as SLCSG, corresponding to the obtained SiO<sub>2</sub>/LaCuS<sub>2</sub>-graphene.

### 2.3. Characterization

An X-ray diffraction (XRD, Shimadzu XD-D1) was made using monochromatic high-intensity Cu Kα radiation (λ = 1.5406 Å). Nitrogen adsorption/desorption isotherm studies were investigated using a Micromeritics ASAP 2020 M + C operating at 77 K. The surface area was calculated by the Brunauer-Emmett-Teller (BET) method, and the pore size distribution was calculated according to the Barrett-Joyner-Halenda (BJH) method. The morphology, shape, structure, size, and distribution of the nanoparticles of the products were investigated using SEM (JSM-5600 JEOL, Japan) and TEM analysis. The EDS analysis was used to test the element mapping of the as-fabricated materials (attached to the SEM analysis). The XPS analysis was observed using a VG Scientific ESCALAB250 XPS system equipped with a monochromated AlKα X-ray source (hν = 1,486.6 eV) with charge compensation. A UV-vis diffuse reflectance spectra (DRS) analysis was obtained by UV-vis spectrophotometry (Neosys-2000) by using BaSO<sub>4</sub> as a reference at room temperature. The analysis was converted from reflection to absorbance by the Kubelka-Munk method. The Raman spectra were achieved by spectrometry (Jasco Model NRS-3100) with an excitation laser wavelength of 532.06 nm. The photodegradation experiments were analyzed by UV-spectrophotometry (Opizen POP, Korea). A PGP 201 Potentiostat Galvanostat (VoltaLab, Germany) was used for the electrochemical tests of the electrodes at 25 °C.

### 2.4. Photocatalytic activity of contaminants

The photodegradation experiment was processed under ambient conditions of atmospheric pressure at room temperature without any sacrificial material. 0.05 g SiO<sub>2</sub>/LaCuS<sub>2</sub>-graphene nanocomposite was dissolved in a 100-ml organic dye solution or gallic acid solution. The visible light source was made from an 8-watt lamp (Fawoo, Lumidas-H, Korea, λ ≥ 420 nm) with a filter (Kenko Zeta, transmittance > 90%) to make sure that the photocatalytic activity proceeded under visible light irradiation. First, the mixture solution of nanocomposite and organic dye was kept in a dark box for 2 h, to ensure the establishment of the adsorption/desorption equilibrium of organic dyes gallic acid solution. Then the mixture solution was irradiated under visible light irradiation (λ ≥ 420 nm). The first sample was taken out at the end of the dark adsorption period, and then the light was turned on to confirm the organic dye concentration of the mixture solution after dark adsorption. The starting point (t = 0) of the reaction was described as the point at which the concentration of the dye solution was recorded as c<sub>0</sub>. After that, other samples were taken from the mixture solution in the reactor at regular intervals of 30, 60, 90, 120, and 180 min. Then a centrifuge machine (10,000 ppm/10 min) was used to remove the powders.

The dye concentration in the solution was measured as a function of the irradiation time. Photodegradation of the SO, MB, RhB, RBB, and TBAC solution proceeded following the above process, with concentrations of (1 × 10<sup>-4</sup>, 5 × 10<sup>-4</sup>, 5 × 10<sup>-4</sup>, 5 × 10<sup>-4</sup>, and 5 × 10<sup>-4</sup>) mol/l, respectively.

Also, the effect of the pH (3–11) was examined while keeping the other parameters constant. This was followed by the photodegradation test. The effects of the above factors were expressed through the percent of dye removal. To investigate the stability of the photocatalytic performance under ambient conditions and neutral pH, the recycling experiments were carried out for five repeated cycles. After each cycle, the catalyst was centrifuged, washed with ethanol, deionized water,

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