Novel Micro and Nanostructure of a AgCuInS$_2$–Graphene–TiO$_2$ Ternary Composite for Photocatalytic CO$_2$ Reduction for Methanol Fuel

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ABSTRACT: Photocatalytic CO$_2$ reduction into hydrocarbon fuels over photocatalysts has hypothetically and reasonably developed into a trendy exploration topic. In this study, the progress of the quaternary nanocomposite containing a graphene-based catalyst was reported; this was fabricated using the hydrothermal technique. The analysis of physical characteristics of the nanocomposite confirmed the interaction between all parts. The quaternary nanocomposite containing the graphene-based catalyst was utilized for carbon dioxide reduction to methanol (CH$_3$OH) under light irradiation. Titanium dioxide (TiO$_2$) and the quaternary nanocomposite of AgCuInS$_2$ were monotonously spread on the graphene exterior. This nanomaterial showed superior activity compared with TiO$_2$ and the binary composite for CO$_2$ conversion, and the obtained result indicates that the synthesized ternary composite enhances the properties of the photocatalyst in the reduction process.

1. INTRODUCTION

Fossil fuels are one of the largest sources of energy in the world, and their continuous combustion is among the primary contributors to carbon dioxide in the atmosphere. As such, it is important to find a way to reduce it through thermal, electrochemical, and photocatalytic reduction methods. A semiconductor-based catalyst is ecologically the cheapest, safest, and most environmentally friendly method. During the photocatalytic reduction, CO$_2$ and H$_2$O are remolded into hydrocarbon fuels using solar light, which is a source of abundant energy. In addition, H$_2$O acts as an essential proton donor during the reduction process of CO$_2$, the highest oxidation state of carbon, which can be reduced into a variety of products through obtaining different numbers of electrons and protons, such as CO, HCOOH, HCHO, CH$_3$OH, and CH$_4$. Designing a well-structured catalyst and utilizing solar light energy assess how carbon dioxide converts to carbon fuels, which has become the focus of most of the policies developed for reducing energy and nature hazards. The doping of noble metals (Pt, Pd, Rh, Ag, Cu, and Au) onto the surface of titania is noted to enhance the catalytic activity to suppress the recombination rate. Carbon-based materials, especially graphene, are used for the enhancement of photogenerated charge carriers. The oxygen characteristics adjust the particle size and shape of the semiconductor materials on the extrinsic state of graphene. The efficiency of TiO$_2$ makes it a decent electron acceptor for extricating photogenerated electrons from a semiconductor. To enhance the capacity of photogenerated charge carriers, all of the generated electrons of the semiconductors must be transported through the surface of graphene to create a higher surface electron density. Metal semiconductors perform roles such as relieving the recombination of photogenerated charges, as an electron trap for photogenerated e$^-$ from the photocatalyst, and to activate the aggregation of photogenerated electrons.

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The noble metal deposition (e.g., Pt, Au, Pd, Ag)\textsuperscript{33–37} and nonmetal doping (e.g., N, C)\textsuperscript{38–41} are important methods for modification of photoactivity. The role of silver was enhanced by H\textsubscript{2}S. The CuInS\textsubscript{2} nanocomposite containing a graphene-based catalyst is synthesized using a hydrothermal method and characterized by some physical techniques. The reduction activity of carbon dioxide with AgCuInS\textsubscript{2}–graphene–TiO\textsubscript{2} nanocomposites under light irradiation.

2. EXPERIMENTAL SECTION

2.1. Materials. Natural graphite, hydrochloric acid (Sigma-Aldrich, 36 wt %), sulfuric acid (Sigma-Aldrich, 97%), potassium permanganate (Sigma-Aldrich), titanium n-butoxide (Pure Chemical Co.), ethylene glycol (Pure Chemical Co., 99.5%), silver nitrate (Duksan Pure Chemicals Co., 98%), copper (II) chloride (Duksan Pure Chemicals Co., 99.9%), indium chloride tetrahydrate (Duksan Pure Chemicals Co., 98%), sodium bicarbonate (Duksan Pure Chemicals Co., 99%), and sodium sulfite anhydrous (Duksan Pure Chemicals Co., 97%) were used for the experiment. All solutions were made using distilled water.

2.2. Preparation of Graphene. Preparation of graphene was done in the laboratory, following a standard preparation method known as Hummer–Offeman’s method.\textsuperscript{58} First, a precise volume of graphite (20 g) and 450 mL of H\textsubscript{2}SO\textsubscript{4} were dissolved into DI water and stirred in an ice bath. Second, 45 g of KMnO\textsubscript{4} was added into the solution and stirred until a dark-brown color was obtained at 35 °C temperature. The beaker was plugged and stirred for half an hour at 100 °C. Meanwhile, 20% H\textsubscript{2}O\textsubscript{2} was added drop-by-drop for 5 min. Third, the solution was rinsed with acetone and 10% HCl three times and heat-treated at 90 °C for 12 h until obtained a graphite oxide powder was obtained. The as-prepared graphite oxide powder was dissolved into 200 mL of DI water, vigorously stirred for half an hour, and then continuously ultrasonicated for 2 h (using an ultrasonic processor, VCX 750). Finally, the solution was washed out with hot water several times and then dried for 6 h to form graphene powder.

2.3. Synthesis of AgCuInS\textsubscript{2}. Generally, the AgCuInS\textsubscript{2} nanocomposite was prepared through a hydrothermal technique, which can be described as follows: silver nitrate (0.025 mmol, AgNO\textsubscript{3}), copper (II) chloride (0.025 mmol, CuCl\textsubscript{2}·2H\textsubscript{2}O), indium chloride tetrahydrate (0.025 mmol, InCl\textsubscript{3}·4H\textsubscript{2}O), and sodium thiourea anhydrous (0.05 mmol, Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3}) were made into a solution and agitated for half an hour at room temperature. The solution was prepared using DI water and ethylene glycol in the ratio of 60:40. Then, the solution was poured into a 100 mL stainless-steel Teflon autoclave and kept at 150 °C for 12 h. Then, the autoclave was cooled down and the final product was washed out with water several times and dried at 100 °C for 4 h.

2.4. Synthesis of AgCuInS\textsubscript{2}-G and Ternary AgCuInS\textsubscript{2}-G-TiO\textsubscript{2} Composites. First, AgCuInS\textsubscript{2}-G was prepared through a hydrothermal method. The as-prepared 0.55 g of AgCuInS\textsubscript{2} was dissolved in DI water and ethylene glycol (50:50) and then agitated for half an hour. At this point, 0.3 g of graphene was mixed into the solution and stirred for 5 h. Thereafter, the mixture was poured into a Teflon cup and kept under the same condition. The resultant binary nanocomposite was collected, rinsed with DI water thrice, and dried at 100 °C for 5 h, and labeled as ACISG. Second, the AgCuInS\textsubscript{2}-G-TiO\textsubscript{2} ternary composite was obtained via the hydrothermal method using the binary nanocomposite and TiO\textsubscript{2} and following a similar procedure. Ethanol, water, and TNB in a mole proportion of 30:15:4 were put together and agitated for 1 h. Then, a certain amount of binary nanocomposite was added and then agitated for 5 h. Thereafter, the final product was dried at 100 °C for 5 h and labeled as ACISGT.

2.5. Characterization. The surface morphology structure and atomic structure of nanocomposites were analyzed using a scanning electron microscope (SEM)/transmission electron microscope (TEM) and a high-resolution transmission electron microscope (HRTEM) (JSM-5600 JEOl, Japan; TEM, Hitachi HT7700, operated at 100 kV; Hitachi H9500 operated at 300 kV). The crystal state was investigated by X-ray diffraction measurements (SHIMADZU XRD-6000). The Debye–Schererr equation (eq 1) was used to determine the crystallite sizes.

\[
D = \frac{(K\lambda)}{β \cos θ}
\]

where \(D\) is the particle size, \(λ\) is the wavelength of X-ray radiation (1.5406 Å), \(K\) is the crystallite size factor (constant factor \(K = 0.9\)), \(β\) is the full width at half-maximum (FWHM) of the peak (in radians), and \(θ\) is the Bragg angle. The presence of main elements was analyzed using an energy-dispersive X-ray (EDX) spectrometer incorporated into the SEM. The surface composition was examined based on the X-ray photoelectron spectra (Kratos AXIS Supra). The UV–vis diffuse reflectance spectra (DRS) were recorded on a Shimadzu UV-2600 spectrophotometer ranging from 200 to 800 nm. The band gap energies of the photocatalysts were calculated through the application of a modified Kubelka–Munk function obtained from UV–vis DRS data. The electronic structure and phase analyses were conducted using Raman spectroscopy with a 633 nm excitation laser (Renishaw inVia Reflex).

The electrochemical tests were conducted on a PGP201 potentiostat/galvanostat (A41A009 apparatus. The tests were performed in a three-electrode system, where the carbon electrode was utilized as the working electrode, Ag/AgCl was used as the reference electrode, and platinum was used as the counter electrode.

2.6. Photocatalytic CO\textsubscript{2} Reduction. The photo reduction of CO\textsubscript{2} with water was carried out in a three-part composed reactor (Scheme S2). A metal halide lamp of 500 W was used as the light source. First, 100 mg of the photocatalyst (AgCuInS\textsubscript{2}-G and AgCuInS\textsubscript{2}-G-TiO\textsubscript{2}) with a sacrificial scavenger was dissolved in 0.04 M NaHCO\textsubscript{3} containing 50 mL of solvent and stirred for 1 h. Then, the reactor was filled with pure CO\textsubscript{2} gas for 30 min and light was turned on. After 48 h of reaction, different amounts of final samples were withdrawn from the reactor every 12 h using a syringe and...
membrane filter. The final samples were analyzed through the “quantitative analysis of alcohol” method and electrochemical test.

3. RESULTS AND DISCUSSION

3.1. X-Ray Diffraction Studies. Figure 1 shows the XRD patterns of ACISG and ACISGT nanocomposites. The XRD pattern basically shows the characteristics of ACISG and ACISGT. Figure 1a presents the XRD pattern of AgCuInS2, and this result confirms that the quaternary nanocomposite was successfully synthesized using the hydrothermal method. AgCuInS2 was composed of CuInS2 (chalcogenide composite), silver, and copper sulfide. Diffraction peaks at 2θ of 28.13, 37.26, and 59.91° were ascribed to the (202), (204), and (312) crystalline planes, corresponding well to the quaternary AgCuInS2 nanocomposite. Diffraction peaks of CuInS2 located at 2θ of 26.59, 29.78, 43.80, 48.25, and 53.08° were assigned to the (112), (200), (220), (103), and (116) planes of the tetragonal crystal phase, respectively, with lattice parameters \( a = 5.5230 \) Å and \( c = 11.1200 \) Å (JCPDS card no. 85-1575). Moreover, the peak of Ag located at 2θ of 34.84, 41.21, 64.21, and 70.25° are assigned to the (111), (200), (220), and (311) crystal planes, respectively. In addition, the diffraction peak of CuS located at 2θ of 32.20° was assigned to the (103) crystal plane. In this study, the Ag and CuS showed similar peak locations. Additionally, a cubic crystal phase with a lattice parameter \( a = 4.1440 \) Å of Ag and an orthorhombic crystal phase with \( a = 3.7630 \), \( b = 6.5680 \), and \( c = 16.2250 \) Å of CuS (JCPDS card no. 06-0464) were observed. As shown in Figure 1, after combining with graphene, the diffraction peak of the graphitic material (002) was not observed due to very low quantities. Moreover, the peaks were located at 2θ of around 27.28, 63.43, and 66.62° corresponding to the (101), (204), and (220) crystal planes. These obtained results showed similar diffraction peaks and a crystal phase with lattice parameters \( a = b = 3.7892 \) Å and \( c = 9.5370 \) Å as an anatase TiO2 (JCPDS file no. 21-1272). In the case of anatase TiO2,

![Figure 1. XRD result of binary ACISG and ternary ACISGT composites.](image)

![Figure 2. SEM analysis result of (a) ACISG binary and (b) ACISGT ternary composites, and (c–e) EDX elemental analysis result and bit graph of binary and ternary nanocomposites.](image)
the index facets of (101), (010), and (001) show different catalytic activities. The (112) crystal plane overlapped with the (101) crystal plane of TiO₂. Herein, this might be due to the integration between TiO₂ and CuInS₂. The crystallite sizes of AgCuInS₂ and TiO₂ particles were calculated using the Debye–Scherrer formula and were found to be 0.95 and 0.59 nm, respectively. In addition, the lattice parameters (d-spacing) of AgCuInS₂ and TiO₂ were calculated from the XRD pattern. The corresponding d-spacing of CuInS₂ was calculated to be d₁₁₂, 3.34 Å; d₂₀₀, 2.99 Å; d₂₂₀, 2.06 Å; d₁₀₃, 1.88 Å; and d₂₁₆, 1.72 Å. In the d-spacing of Ag assigned to the d₁₁₁, 2.57 Å; d₂₀₀, 2.18 Å; d₂₂₀, 1.45 Å; and d₃₁₁, 1.34 Å. Finally, the anatase TiO₂ was assigned to the d₁₀₁, 3.26 Å; d₂₀₄, 1.95 Å; and d₂₂₀, 1.60 Å.

3.2. Morphological Characterizations. Figure 2a,b presents the general morphology of the as-prepared ACISG and ACISGT nanocomposites obtained via SEM. After the hydrothermal method, AgCuInS₂ particles uniformly grew and covered the entire surface of graphene, making it difficult to distinguish the various particle sizes and shapes. Also, the quaternary nanocomposite was sufficiently grown on the surface of graphene. This indicates that graphene provided a sufficient area for growth also in addition to the precursor reagents forming a chemical bond with the functional groups of graphene. Graphene had a sheetlike structure that was divided into several directions. This structure indicates the existence of oxygen functional groups on the surface of graphene. Figure 2b shows the deposition of TiO₂ particles on the surface of graphene. Herein, the difference between binary and ternary composites can be clearly observed. The TiO₂ particle had an irregular spherical shape and was deposited on the surface of graphene. EDX spectra certified the presence of the main elements in the nanocomposite. Figure 2c,d shows the result of microanalysis of ACISGT, which reveals the presence of the main elements, namely, C, O, Ag, Cu, In, S, and Ti. The C elemental peak was obtained from graphene, and O, Ag, Cu, In, S, and Ti peaks were derived from the precursor material. Figure 2e expresses the bit graph of the elemental analysis result of ACISG and ACISGT with surface states.

The morphology and shape of the ternary (AgCuInS₂-G-TiO₂) composite were observed using TEM and HRTEM and the various magnifications of images are presented in Figure 3. Figure 3a,b shows that the synthesized AgCuInS₂ nanocomposite was uniformly distributed on the surface of graphene and observed as a round-shaped black spot. Figure 3c,d shows that the TiO₂ particles were normally spread on the surface of graphene and were similarly observed as spherical forms. In addition, the quaternary nanocomposite acts as a bridge between TiO₂ and graphene such that the TiO₂ particle spreads evenly on the surface of graphene. The particle size histograms of TiO₂ and ACIS nanoparticles at different filter sizes are shown in Figure 3e,f. These histograms show the calculated average nanoparticle diameter distributions of 5.5 nm (ACIS) and 1.99 ± 0.59 nm (TiO₂). The crystallographic structure of the nanocomposite was analyzed via HRTEM. The HRTEM image shows the lattice fringes with d-spacings of $d = \ldots$
0.241 and 0.326 nm, which corresponded to the AgCuInS₂ (204) and TiO₂ (101) crystal facets. Additionally, the EDS elemental mappings of ACISG and ACISGT (Figure 4a−o) revealed the coexistence of Ag, Cu, In, S, C, Ti, and O in the ternary nanocomposite. The corresponding elemental mapping spatial distribution for binary and ternary nanocomposites and the uniform dispersion of these elements further confirmed the successful construction of the ternary nanocomposite.

For surface chemical state of the elements and interactions among AgCuInS₂, graphene, and TiO₂, XPS analysis was conducted over ACISGT. Figure 5a shows the presence of C 1s, O 1s, S 2p, Ti 2p, Cu 2p, In 3d, and Ag 3d and demonstrates the successful formation of ACISGT. Figure 5b shows the C 1s spectrum consisting of two peaks located at binding energies of 283.98 and 285.19 eV corresponding to the C=C and C=O groups. It also shows that the as-synthesized ternary composite contains the oxygen functional groups. It also shows that the as-synthesized ternary composite contains the oxygen functional groups.61 Figure 5c shows the spectrum of O 1s, and the peak was located at the 530.43 eV region, which indicated the Ti−O−C form. In addition, this peak indicated the formation of a chemical bond between graphene and TiO₂.62 Figure 5d shows the XPS spectrum of S, including two peaks that are located at binding energies of 160.93 and 162.06 eV belonging to spin-orbital forms S 2p3/2 and S 2p1/2. In anatase TiO₂, the titanium atom shows two distinct peaks for the Ti 2p1/2 and Ti 2p3/2 spin-orbital splitting electrons located at binding energies of 458.81 and 464.57 eV.63 Figure 5e shows the formation of TiO₂ with two sharp peaks, located at 458.58 and 464.48 eV binding energy regions and corresponding to Ti 2p1/2 and Ti 2p3/2, respectively. In Figure 5f, Cu 2p exhibits two sharp peaks located at 931.08, 931.83, and 951.39 eV regions, and these two peaks describe the 2p3/2 and 2p1/2 spin-orbital forms of Cu₂O. In the case of the In element, the peak located at 458.50 eV is assigned to In 3d5/2 of In₃⁺, as shown in Figure 5g. Finally, Figure 5h exhibits two sharp peaks located at binding energies of 368.44 and 374.46 eV, which correspond to Ag 3d5/2 and Ag 3d3/2, respectively. The binding energy shifts indicate the strong interaction and charge transfer among the AgCuInS₂, graphene, and TiO₂ in the as-synthesized ACISGT nanocomposite.

The optical absorption properties of the prepared samples were evaluated using UV−vis DRS analysis, as shown in Figure 6. To obtain the relation of the energy (Eg) and optical absorption, according to the Kubelka−Munk function, the absorption spectra can be analyzed using eq 2:

\[ \alpha = c(h\nu - E_g)^2 \]  

where \( \alpha \) is the absorption coefficient, \( h \) is Planck’s constant, \( \nu \) is the frequency of the light, \( c \) is the proportional constant, and \( E_g \) is the energy of the band gap. Absorption coefficient \( \alpha \) is given by

\[ (1 - R)^2 / 2R \]  

where \( R \) is the reflectance and \( A \) is an optical absorption in which is given by \( 10^{-A} \). Figure 5 shows the band gap energies of ACISG and ACISGT, which were expected to be 1.25−52 and 1.96 eV, respectively. The pure CuInS₂ has a direct band
gap energy of 1.50 eV, which is close to the optimal band gap (1.45 eV). After combining with a silver (Ag), the band gap energy was decreased (1.25 eV), since the silver increases the electron density of lower energy compared to the conduction band of CuInS$_2$, and if the electron density is adequate then it suitably acts as the conduction band. After binding with TiO$_2$, the band gap energy was increased; however, it exhibited lower band gap energy than pure anatase TiO$_2$, while the band gap
energy of pure (n-type) TiO$_2$ is 3.20 eV. This is because agglomeration can have an effect on the absorption property, resulting in a change in the band gap energy. Raman spectroscopy shows the formation of the electronic structure of carbon materials, phase, and structural properties of AgCuInS$_2$, TiO$_2$, and graphene owing to the strong scattering properties as presented in Figure 7a. As-synthesized samples exhibited several characteristic peaks. First, two types of feature peaks were observed at 1363 and 1602 cm$^{-1}$ corresponding to the sp$^3$ defects of the D band (structural defect) and the in-plane vibration of sp$^2$-bonded carbons of the G band (graphite) correlated with graphene as shown in Figure 7b. The D-band is at the 1390 cm$^{-1}$ shift region. The G-band is at about 1583 cm$^{-1}$ and is due to the E$_2g$ mode of graphene. In this result, the two bands were observed in different regions due to the quaternary nanocomposite and TiO$_2$ effect on the formation of graphene. In addition, the intensity ratio of two peaks ($I_D/I_G$) showed that they were due to layers of graphene, as described in this article. The ratio of $I_D/I_G$ was 0.88. Also, two characteristic peaks were observed at 229 and 1333 cm$^{-1}$ shift regions, which correspond to silver (Ag). In the case of CuInS$_2$, two peaks were observed at 290 and 332 cm$^{-1}$ shift regions, which correspond to the CA-ordering to CH-ordering phase of chalcopyrite CuInS$_2$. CA is a second-ordered phase, while CH is a first-ordered phase, and the formation energy and structure of these two peaks were very close. The very sharp and intense peak observed at around 159 and 636 cm$^{-1}$ regions corresponded to the anatase TiO$_2$ as displayed in Figure 7c.

3.3. Photocatalytic Performance and Reduction of CO$_2$. The photocatalytic activity of the as-synthesized photocatalyst (ACISG and ACISGT) was determined for 48 h under the UV-light ($\lambda > 300$) and visible ($\lambda > 400$) light irradiation. The sample was taken out of the reactor at intervals of 12 h using a syringe. The samples were collected and centrifuged (10,000 ppm/15 min), after which they were analyzed through quantitative analysis of alcohol and the electrochemical test. Figure 8 presents the result of the quantitative analysis of alcohol, for which the as-synthesized samples were used under light irradiation. The synthesized ACISG and ACISGT nanocomposites showed excellent photocatalytic activity with a very high final product yield (CH$_3$OH). Under the visible light irradiation, the methanol (CH$_3$OH) yield of the ACISG and ACISGT nanocomposites was low compared to that of the as-synthesized nanocomposite without using a scavenger (Na$_2$SO$_3$), as shown in Figure 8a. Without using a scavenger, the methanol yields of the ACISG nanocomposite were 0.48, 1.46, 2.76, and 4.78%, while those of the ACISGT nanocomposite were 1.51, 2.72, 3.74, and 6.35%. With the scavenger, the methanol yields of the ACISG nanocomposite were 2.35, 3.22, 4.34, and 7.63%, while those of the ACISGT nanocomposite were 4.71, 7.11, 8.09, and 11.92%, under visible light irradiation after 12–48 h. As shown in Figure 8b, under UV light irradiation, all synthesized samples showed a higher product yield compared to that under visible light irradiation. In the case of the as-synthesized nanocomposite without using a scavenger, the methanol yields of the ACISG nanocomposite were 1.53, 2.51, 4.01, and 7.49%, while those of the ACISGT nanocomposite were 2.06, 5.71, 8.94, and 14.35%. With the scavenger, the methanol yields of the ACISG nanocomposite were 2.16, 4.28, 4.68, and 7.63%.
The stability and reproducibility of the photocatalyst are the main factors for the practical application. In the cycling test, the photocatalysts were recycled four times under the same conditions. In three cycling tests, the methanol yields of ACISG reached 7.63, 7.97, 8.26, and 9.70%, while those of the ACISGT nanocomposite were 11.92, 12.34, 13.69, and 15.32% under vis light irradiation. The methanol yields of ACISG reached 9.78, 10.45, 11.04, and 11.79%, while those of the ACISGT nanocomposite were 15.21, 15.63, 16.28, and 16.46% under UV light irradiation, as shown in Figure 8c. According to the recyclability test, the prepared binary and ternary nanocomposites showed high stability and catalytic activity for photocatalytic CO2 reduction.

The reaction quantum yield (QE) is estimated using the CH3OH yield, considering that six electrons are required to reduce CO2 to CH3OH. The equation (eq 4) is as follows:

\[
2\text{CO}_2 + 4\text{H}_2\text{O} \rightarrow 2\text{CH}_3\text{OH} + 3\text{O}_2 \]

\[
\text{methanol (\%)} = 100 \times \left( \frac{6 \times \text{mole of CH}_3\text{OH yield}}{\text{mole of photon absorbed by catalyst}} \right) 
\]

\[
= \frac{\text{mole of photon}}{\text{photons absorbed by catalyst}} = \frac{I \times S \times E}{N_A} 
\]

where \(I\) is the light intensity (0.12 mW cm\(^{-2}\)), \(S\) is the irradiated area of the reactor (30 cm \(	imes\) 15 cm), \(E\) is the photon energy (4.97 \times 10\(^{-19}\) J at 400 nm), and \(N_A\) is the Avogadro number (6.02 \times 10\(^{23}\) mol\(^{-1}\)). The total methanol yield and quantum yield of the photocatalysts for 48 h using a UV/visible light source were calculated and are shown in Table 1 and 2.

Table 1. Methanol Yield without the Scavenger and Quantum Yield

| sample (without scavenger) | methanol yield | quantum yield (QE) |
|---------------------------|----------------|-------------------|
| Visible Light             |                |                   |
| AgCuInS\(_2\)-graphene (12 h) | 0.48          | 0.069             |
| AgCuInS\(_2\)-graphene (24 h) | 1.46          | 0.211             |
| AgCuInS\(_2\)-graphene (36 h) | 2.76          | 0.399             |
| AgCuInS\(_2\)-graphene (48 h) | 4.38          | 0.570             |
| AgCuInS\(_2\)-graphene-TiO\(_2\) (12 h) | 1.51     | 0.198             |
| AgCuInS\(_2\)-graphene-TiO\(_2\) (24 h) | 2.72     | 0.293             |
| AgCuInS\(_2\)-graphene-TiO\(_2\) (36 h) | 3.74     | 0.441             |
| AgCuInS\(_2\)-graphene-TiO\(_2\) (48 h) | 6.35     | 0.793             |
| UV Light                  |                |                   |
| AgCuInS\(_2\)-graphene (12 h) | 1.53          | 0.221             |
| AgCuInS\(_2\)-graphene (24 h) | 2.61          | 0.367             |
| AgCuInS\(_2\)-graphene (36 h) | 4.01          | 0.579             |
| AgCuInS\(_2\)-graphene (48 h) | 7.49          | 0.813             |
| AgCuInS\(_2\)-graphene-TiO\(_2\) (12 h) | 2.06     | 0.239             |
| AgCuInS\(_2\)-graphene-TiO\(_2\) (24 h) | 5.71     | 0.629             |
| AgCuInS\(_2\)-graphene-TiO\(_2\) (36 h) | 8.94     | 0.892             |
| AgCuInS\(_2\)-graphene-TiO\(_2\) (48 h) | 14.35    | 1.175             |

The final ternary photocatalyst exhibited an excellent photoactivity toward CO2 reduction into methanol with and without the scavenger. Sodium sulfate with a cyclic electron donor/supplier can boost the photoactivity of the graphene-based ternary photocatalyst because it allows CO2 to combine with water. With the scavenger, the methanol yield was practically twice as higher as that without the scavenger (Na\(_2\)SO\(_3\)). In methanol concentration analysis, CrO\(_3\) was used as an oxidizing agent, which can oxidize methanol, and the color of CrO\(_3\) solution was changed due to increased methanol concentration.

The Fourier-transform infrared (FTIR) spectra of methanol after one cycle (after 48 h) and after four cycles (after 192 h) are shown in Figure 9. The final product consisted of main four peaks, which are located at exact peak regions. Moreover, the experiment and theoretical key data are given in Table 3. The peak location and intensity were same each other which can confirm the ternary photocatalyst reduced the CO\(_2\) into methanol.
Currently, no research paper has been published on quaternary chalcogenide-based nanocomposites for CO₂ reduction. There are several ternary chalcogenide photocatalysts for CO₂ reduction such as ZnO/ZnSe, CeO₃/ZnInS₂, and CuInS₂–TiO₂ heterojunctions. It can be found that AgCuInS₂–graphene and AgCuInS₂–graphene–TiO₂ exhibit high photocatalytic CO₂ conversion activities compared with other ternary chalcogenide photocatalysts. Therefore, noble-metal-combined quaternary chalcogenide catalysts can still achieve high-efficiency CO₂ reduction.

Table 2. Methanol Yield with Scavenger and Quantum Yield

| Sample (with scavenger) | Methanol Yield | Quantum Yield (QE) |
|-------------------------|----------------|-------------------|
| **Visible Light**       |                |                   |
| AgCuInS₂–graphene (12 h) | 2.35           | 0.239             |
| AgCuInS₂–graphene (24 h) | 3.22           | 0.365             |
| AgCuInS₂–graphene (36 h) | 4.34           | 0.427             |
| AgCuInS₂–graphene (48 h) | 7.63           | 0.703             |
| AgCuInS₂–graphene–TiO₂ (12 h) | 4.71 | 0.581             |
| AgCuInS₂–graphene–TiO₂ (24 h) | 7.11           | 0.628             |
| AgCuInS₂–graphene–TiO₂ (36 h) | 8.09           | 0.859             |
| AgCuInS₂–graphene–TiO₂ (48 h) | 11.92          | 1.023             |
| **UV Light**            |                |                   |
| AgCuInS₂–graphene (12 h) | 2.16           | 0.212             |
| AgCuInS₂–graphene (24 h) | 4.28           | 0.518             |
| AgCuInS₂–graphene (36 h) | 6.32           | 0.691             |
| AgCuInS₂–graphene (48 h) | 9.78           | 0.914             |
| AgCuInS₂–graphene–TiO₂ (12 h) | 2.64 | 0.281             |
| AgCuInS₂–graphene–TiO₂ (24 h) | 7.87           | 0.738             |
| AgCuInS₂–graphene–TiO₂ (36 h) | 10.49          | 1.016             |
| AgCuInS₂–graphene–TiO₂ (48 h) | 15.21          | 1.219             |

Table 3. Characteristic Vibrational Group of the Final Product from the FTIR Measurement

| No. | Vibrational State | Mode | Experimental (cm⁻¹) | Theoretical (cm⁻¹) |
|-----|------------------|------|---------------------|-------------------|
| 1   | Hydroxyl Group   | (O–H) | 3293.16             | 3400–3300         |
| 2   | Carboxyl Group   | C–O  | 1014.09             | 1300–1000         |
| 3   | Alcohol Group    | C–O–H | 1358.14            | 1440–1220         |
| 4   | Methyl Group     | C–H in (CH₃)δ | 1637.89          | 1450              |

Figure 9. FTIR result of the final product: reference (olive line) and the final methanol product (blue and red lines).

Figure 10 shows the result of the electrochemical test, for which the solution withdrawn from the suspension irradiated by UV/visible light during photocatalytic CO₂ reduction was used. The irradiation time consisted of a total of 48 h with an interval of 12 h where samples were withdrawn from the suspension. The cyclic voltammetry tests were carried out in a three-electrode assembled glass reactor with a scan rate of 100 mV s⁻¹ at ambient room temperature. The anodic and cathodic current state and peak-to-peak separation were high when the alcohol solution was withdrawn from the suspension irradiated by visible light during photocatalytic CO₂ reduction, as shown in Figure S1a,b. As shown in Figure S1c,d, the anodic and cathodic peak separation was low when the alcohol solution was withdrawn from the suspension irradiated by visible light during a reduction process. The peak-to-peak separation is relevant to the electron transfer kinetics. Without a scavenger, the highest oxidation peak appeared at 1.28 and 3.64 A and the reduction peak appeared at –0.52 and –2.86 A. With a scavenger, the highest oxidation peak appeared at 0.61 and 0.66 A and the reduction peak appeared at –0.49 and –0.21 A, revealing the characteristics of the alcohol solution. As in Figure 10a, the study without a scavenger under UV/visible light irradiation, the current density of the ACISGT nanocomposite was higher than that of the ACISG nanocomposite. In the case with a scavenger, the current density of the ACISGT nanocomposite was lower compared to that of the ACISG nanocomposite under UV light as shown in Figure 10b.
Under light irradiation, the semiconductors absorb the photon energy, while electrons can be excited from the valence band (VB) to the conduction band (CB), creating an electron–hole pair. In a chemical reaction, graphene acts as an electron acceptor/carrier and can suppress the recombination of charges. The surface functional group of graphene forms a chemical bond between TiO\textsubscript{2} and the quaternary nanocomposite, and it can form a band gap and increase the charge transport. Under the light irradiation, AgCuInS\textsubscript{2} and graphene are parallelly activated and the electrons transfer through the graphene to reach the VB of TiO\textsubscript{2} to form the donor level (Figure 11). The semiconductor materials bound on sheetlike-structured graphene act as electron assimilates in the photocatalytic reaction mechanism shown in Figure 12. The possible CO\textsubscript{2} reduction mechanism of AgCuInS\textsubscript{2}-G-TiO\textsubscript{2} is proposed below:

\begin{align}
\text{TiO}_2 + h\nu & = \text{TiO}_2(e^- + h^+) \quad (5) \\
\text{AgCuInS}_2 + h\nu & = \text{AgCuInS}_2(e^- + h^+) \quad (6) \\
\text{TiO}_2(e^-) + \text{AgCuInS}_2 & = \text{TiO}_2 + \text{AgCuInS}_2(e^-) \quad (7) \\
\text{graphene} + \text{AgCuInS}_2 & = \text{AgCuInS}_2(e^-) \quad (8)
\end{align}

\begin{align}
\text{AgCuInS}_2 + \text{Ti}^{4+} & = \text{AgCuInS}_2 + \text{Ti}^{3+} \quad (9) \\
\text{AgCuInS}_2(e^-) + \text{O}_2 & = \text{AgCuInS}_2 + \text{O}_2^- \quad (10) \\
\text{H}_2\text{O} + \text{H}^+ & = \text{OH}^- + 2\text{H}^+ \quad (11) \\
2\text{H}^+ + 2e^- & = \text{H}_2 \quad (12) \\
\text{CO}_2 + e^- & = \text{CO}_2^- \quad (13) \\
\text{CO}_2^- + 2\text{H}^+ + 2e^- & = \text{HCO}_2\text{H} \quad \text{(formic acid)} \quad (14) \\
\text{CO}_2 + 2\text{H}^+ + 2e^- & = \text{CO} + \text{H}_2\text{O} \quad (15) \\
\text{CO}_2 + 4\text{H}^+ + 4e^- & = \text{HCHO} + \text{H}_2\text{O} \quad \text{(formaldehyde)} \quad (16) \\
\text{CO}_2 + 6\text{H}^+ + 6e^- & = \text{CH}_3\text{OH} + \text{H}_2\text{O} \quad \text{(methanol)} \quad (17)
\end{align}

Equations 5–12 show the fabrication of photoexcited electron–hole pair and water oxidation. Equations 13–17 express the redox process: the holes in VB have strong oxidizing ability, and electrons in CB reduce CO\textsubscript{2} from a hydrocarbon fuel. Water oxidation produces hydrogen ions and hydroxyl radicals, and then CO\textsubscript{2} reacts with excited electrons and hydrogen ions, which finally result in the formation of methanol. The schematic diagram of this mechanism is shown in Figure 11.

4. CONCLUSIONS

Briefly, we used the hydrothermal method to effectively synthesize the unique ternary composite (AgCuInS\textsubscript{2}-G-TiO\textsubscript{2}) and analyze the catalyst activity for photocatalytic carbon dioxide (CO\textsubscript{2}) reduction. The prepared ternary composite was analyzed via the techniques such as XRD, SEM, HRTEM, XPS, Raman, and DRS. Raman and XPS characterizations showed a strong contact and chemical bonding interaction among AgCuInS\textsubscript{2}, TiO\textsubscript{2}, and graphene. The result of the SEM and HRTEM morphological analyses demonstrates that AgCuInS\textsubscript{2} and TiO\textsubscript{2} are irregularly dispersed on the surface of graphene, and the average sizes of the quaternary nanocomposite and TiO\textsubscript{2} were around 5.5 and 1.99 nm, respectively. The band gap energy of the binary (AgCuInS\textsubscript{2}-graphene) composite was 1.25 eV and of the ternary (AgCuInS\textsubscript{2}-graphene-TiO\textsubscript{2}) composite was 1.96 eV. The catalytic activity of the quaternary
nannocomposite containing a graphene-based catalyst was studied for carbon dioxide reduction in the reactor under UV light and visible light irradiation. Additionally, the primary product identified was methanol (CH₃OH). The AgCu₃N₅−graphene−TiO₂ ternary composite showed the highest photocatalytic activity after 48 h and a total methanol amount of 15.21% using a scavenger. In this work, the quaternary nannocomposite containing a graphene-based catalyst was used to avail the benefits of a heterosystem and determined the production rate of methanol (CH₃OH).

**ASSOCIATED CONTENT**

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c02498.

Additional information about the cyclic voltammetry result of ACIS-G and ACIS-G-TiO₂ ternary nanocomposites under visible light and the schematic diagram of the device for photocatalytic CO₂ reduction (PDF)

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Notes
The authors declare no competing financial interest.

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