



View Article Online

View Journal

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: W. Oh, K. Youn Cho and Z. Otgonbayar, *New J. Chem.*, 2020, DOI: 10.1039/D0NJ03150J.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/njc

4 5

10

11 12

13 14

15

16 17

18 19

₩23

10202528

27

14. August 2020 Wankaded

36

bilisheed 8

. മു

> 40 41

> 42 43

> 44 45

> 46

47 48

49 50

56 57

58

59 60

irv Accepted Manuscript B ew Journa

Enhanced Photocatalytic Activity of CO₂ Reduction to Methanol by the Use online of a Novel-structured CuCaAg₂Se-Graphene-TiO₂ Ternary Nanocomposite

Zambaga Otgonbayar¹, Kwang Youn Cho³, Won-Chun Oh^{1.2*}

¹Department of Advanced Materials Science & Engineering, Hanseo University, Seosan-si, Chungnam, Korea, 356-706

² College of Materials Science and Engineering, Anhui University of Science & Technology, Huainan 232001, PR China

³ Korea Institutes of Ceramic Engineering and Technology, Soho-ro, Jinju-Si, Gyeongsangnam-do, South Korea

Abstract. The effective charge transfer is a key factor to enhance catalytic activity for photocatalytic nanocomposite materials. In order to enhance the charge transfer of Graphene and TiO₂, we combined with Quaternary chalcogenide (CuCaAg₂Se) nanocomposite. The ternary nanocomposite was synthesized by muffle-assisted hydrothermal method which is afforded to obtaining a decent crystallinity and the polymer precursor solution was prepared by Pechini method based on metallic citrate polymerization using ethylene glycol C₂H₆O₂ (Merck) and citric acid C₆H₈O₇ (Merck) as chelate cation. The morphology structure, charge-carrier separation analysis confirmed that the combination of CuCaAg₂Se, Graphene and TiO₂ enhanced the photocatalytic activity of the ternary nanocomposite. Each results pointed-out that the ternary nanocomposite was successfully synthesized and enhanced the performance of nanocomposite. This ternary-nanocomposite showed 6-times higher photo-activity performance towards CO₂ reduction to generate methanol (CH₃OH) under the UV and Visible-light irradiation with different amount of scavenger, compared to the TiO₂, pure CuCaAg₂Se, binary nanocomposite. More importantly, the as-synthesized nanocomposite displayed excellent stability during recycling test with no obvious loss in the generation of methanol from CO₂ photoreduction. This approach presented herein offers a promising route for the rational design of a new class of ternary-nanocomposite for various applications in environmental protection and solar energy conversion.

^{*}Corresponding author

E-mail: wc_oh@hanseo.ac.kr

Tel: +82-41-660-1337, Fax: +82-41-688-3352

Keywords: Graphene, semiconductor, chalcogenide nanocomposite, photocatalytic CO View direction of the semiconductor, chalcogenide nanocomposite, photocatalytic CO View direction of the semiconductor of the semiconduc

1. Introduction

1 2 3

4

5 6

7 8 9

10 11

12

13 14

15 16

17 18

19

20 ⊉1

102025

\$26

₽7

14. August 2020 Downloaded

ම්6 මී7

<u>₹</u>38

ສັ້ງ 40

> 41 42

> 43

44

45 46

47 48

49

50 51

52 53

54

55 56

57 58

59 60

Photocatalytic reduction of CO₂ with water into renewable hydrocarbon solar fuels is considered as a promising strategy to simultaneously address the global energy and environmental issues. Furthermore, the photocatalyst has many advantages over the methods in efficiency of biodegradable pollutants, simple catalyst regeneration, low energy utilization [1]. TiO₂ has a function under UV-light irradiation with wavelength shorter than 387 nm and recombination and recombination rate of electron and holes are quickly [2]. A new challenge that scientists need to overcome is the unification of a wellstructured photocatalyst material for transforming CO₂ into a product, and the graphene-based chalcogenide photocatalyst has shown a great-deal of promising attributers in this area. Twodimensional (2D) layered materials have gained immense attention in the area of photocatalysis in recent years [3]. Compared to 0D and 1D materials, these 2D materials possess impressive properties, including large specific surface area with abundant active sites, superior electron conductivity (e.g., in the case of graphene) to facilitate charge transfer and separation, and the ability to function as excellent catalyst supports [4-6]. Graphene united with chalcogenide photocatalyst had a superb catalytic activity due to variable bandgap energy, such as WSe₂-Graphene (2.68 eV) [7], PbSe-Graphene (2.60 eV) [8], Cu₂Se-Graphene (2.80 eV) [9] which showed a high reduction activity of CO₂. Last decade year, manufacturing a ternary structure has turned into an effective tactic to enhance the absorbing of solar light and photocatalytic capability. According from published papers, the enhanced photo-activity of Cu₂ZnSnS₄/ZnO composite catalyst for photocatalytic reduction of CO₂ to CH₄ [10]. Recently, ZnV₂O₆/g-C₃N₄ [11] and Zn₂GeO₄/Mg-MOF-74 composites with enhanced photocatalytic activity for CO₂ reduction has been reported [12].

As well, ternary, and quaternary chalcogenide nanocomposite showing a semi-insolating feature was observed with band-gaps from small (< 1 eV) to large (> 3 eV) and noted a suppleness large amount of electron hole pairs. The semiconductor of Ag₂Se is also used nowadays for their excellent optical and chemical properties as well as for future potential applications. Also, two stable solid phases have been noted, one is an orthorhombic phase β -Ag₂Se (low - temperature, 0K), the second one is the cubic phase α -Ag₂Se (high - temperature, 409K) [13]. The β -Ag₂Se has a role same as a (ntype) semiconductor and the band-gap energy is 0.07 eV, α -Ag₂Se is same as a metal and the band-gap energy is 0.15 eV [14]. Zheo et al [14] prepared a TiO₂/Ag₂Se nanocomposite by interface reaction and their result suggested that the nanocomposite is an excellent photovoltaic with photocurrent properties towards visible light. Combining with copper (Cu) and into the surface of TiO₂ it is noted to

New Journal of Chemistry

Accep

/ Journal of Chemis

enhance improving the catalytic activity and prevent the recombination of an electron-hole which is also altering the band-gap energy. The state of graphene successfully joined the chalcogenide (inorganic materials) for using the proper method and due to the noted oxygen-containing functional group of graphene, take-action as a stabilizer and prevent the agglomeration [15].

This work reports the synthesis of ternary CuCaAg₂Se-Graphene-TiO₂ nanocomposite, in which a quaternary chalcogenide nanocomposite and semiconductor TiO₂ are dispersed onto the graphene exterior by muffle-assisted hydrothermal method and analyzed by some physical characteristic equipment. The photo-catalytic activity of ternary nanocomposite was studied in the CO₂ reduction with a different amount of scavenger and the main final product was methanol (CH₃OH) under the UV/Vis-light irradiation. Sodium carbonate solution as used in CO₂ photocatalytic reduction which can act as the reducing agent. More specifically, there is a two reason: (i)an increase of dissolved CO₂ amount, (ii) and reduction of the recombination of hole-electron pairs leading to a longer decay time of surface electrons and facilitation of CO₂ reduction. The ternary nanocomposite (CuCaAg₂Se-Graphene-TiO₂) exhibits superior photocatalytic activity owing to an enhanced charge carrier separation and high stability. The photostability and photoactivity of ternary nanocomposite developed the research field of photocatalytic carbon dioxide reduction. In this heterostructure, the purpose of graphene is shown to be a bridge between the quaternary chalcogenide and TiO_2 and may improve the charge-separation, and thereafter may enhance the capacity of photogenerated charge carriers. Each results pointed-out that the quaternary chalcogenide nanocomposite and TiO₂ were successfully scattered onto the graphene surface. The purpose of this study is the confirmation of exceptional photocatalytic activity during a reduction of carbon dioxide (CO₂) with a target synthesized material under the Visible light and UV light.

2. Experimental

2.1. Materials

Natural graphite powder, hydrochloric acid (HCl, 36 wt%), sulphuric acid (H₂SO₄, 97 %) and potassium permanganate (KMnO₄) were purchased from Sigma Aldrich. Titanium n-butoxide (TNB, C₁₆H₃₆O₄Ti) and Ethylene glycol (99.5 %) were purchased from Samchun Pure Chemical Co., LTD., 99%), Korea. Copper nitrate trihydrate $(Cu(NO_3)_2 \cdot 3H_2O_1)$ Calcium nitrate tetrahydrate (Ca(NO₃)₂·4H₂O, 98%), Silver nitrate (AgNO₃, 98%), Selenium powder (Se). Citric acid (C₆H₈O₇, 99.5%), Scavenger (Sodium sulfite anhydrous (Na₂SO₃, 97%)) were purchased from Duksan Pure Chemicals Co. Ltd., Korea. It is noted that all solutions were used with distilled water.

ry Accepted N

Φ

ĝ

New Journ

2.2. Synthesis of Graphene

View Article Online DOI: 10.1039/D0NJ03150J

Hummer Offeman's method was used to synthesize the graphene by oxidation of graphite [16]. A certain quantity of natural graphite (20 g) was then dissolved into a sulfuric acid (450 ml) and DI-water and agitated for one hour under 0 $^{\circ}$ C in ice bath. Then, the ice bath has been removed and potassium permanganate (45 g) (graphite + H₂SO₄) was progressively added into the mixture and agitated under 35 °C until the color turned into a dim brownish color, continuously. The container was sealed and later agitated for 30 min under 100 °C, in the meanwhile hydrogen peroxide (H₂O₂) was added dropwise in the timeframe of 5 min. After that, the solution was washed with acetone and hydrochloric acid (HCl, 10%) thrice, then the product was heat-treated in an oven at 90 °C for 12 h until it formed to a graphite oxide powder. As-prepared graphite oxide powder was added into 200 ml de-ionized water and rigorously agitated for 30 min, then it was continuously ultra-sonicated for 2 h (using Ultrasonic Processor, VCX 750). The mixture was cleansed and washed with hot water for several times, then oven-dried for 6 h to form into a graphene oxide powder.

2.3. Synthesis of quaternary (CuCaAg₂Se) composite

The CuCaAg₂Se was synthesized through the use of a muffle-assisted hydrothermal method. The molar ration of precursor reagents was noted at 0.02:0.02:0.04:0.02. The precursor solution was prepared through a Pechini-method based on the metallic citrate polymerization using ethylene glycol $(C_2H_6O_2)$ and citric acid $(C_6H_8O_7)$ as chelate cation. The configuration of numerous coordination bonds between organic molecules and transition metals ion control to sequestration of the metal its meaning of chelation. The citric acid was dissolved in DI-water with a constant stirring at 60 °C to make a citric acid solution. A certain quantity of precursor reagents was dissolved into an as-prepared acid solvent and stirred until fully dissolved. After that, ethylene glycol $(C_2H_6O_2)$ was added into that solution, and the proportion ration of citric acid and ethylene glycol is noted at 60:40, and the solution can become a viscous. Under the same temperature, the solution was stirred for 5 h and put into 100 ml Teflon-lined stainless-steel autoclave. The autoclave was maintained at 150 °C for 12 h, and then allowed cool to room-temperature (25 °C). The product was rinsed several times using DI-water and dried at 100 °C for 5 h, and then obtained sample was renamed as CCAS (before). As-prepared CuCaAg₂Se powder was calcined at 700°C for 2 h to obtain, and then renamed by CCAS (after).

2.4. Synthesis of graphene-TiO2 and CuCaAg2Se-graphene-TiO2

First, the graphene-TiO₂ was prepared via the use of a hydrothermal method with calcination. A molar ratio of ethanol to H_2O to TNB of 30:15:4 was mixed and stirred continuously for 1 h. Then, 0.5 g graphene was added into that mixture and agitated for 5 h, then it was transferred into the 100 ml

Teflon-lined autoclave and maintained at 150 °C for 12 h, and then cooled to <u>poom_temperature</u> (25 °C). The product was rinsed several times with DI-water and dried at 100 °C for 5 h and calcined under 700°C for 2 h. The ternary composite of CuCaAg₂Se-graphene-TiO₂ was prepared via a muffle-assisted hydrothermal method. As-prepared CuCaAg₂Se was taking 0.50 g and dissolved into metallic citrate polymerization with agitated for 30 min and then mixed with (0.30 g) as-prepared G-TiO₂ nanocomposite and the solution was mixed continuously for 5 h. The mixture put into 100 ml Teflon-lined stainless-steel autoclave. The autoclave was maintained at 150 °C for 12 h, and then allowed cool to room-temperature (25 °C). The product was rinsed several times using DI-water and dried at 100 °C for 5 h, and then obtained sample was renamed as CCAS (before). As-prepared powder was calcined at 700°C for 2 h to obtain, and then renamed

2.5. Characterization

The phases of samples were examined using X-ray diffraction measurements (SHIMADZU XRD-6000) equipped with a Cu Ka X-ray source (1.5406 Å). The Debye-Scherrer equation (Eq. (1)) was used to analyze the particle size of CuCaAg₂Se and TiO₂ based on the data acquired via XRD analysis [17].

$$L = \frac{K\lambda}{(FWHM)\cos\theta} \qquad \qquad \left[d = \frac{0.9\,\lambda}{\beta\,\cos\theta}\right]$$

Where L is the particle size, λ is the wavelength of X-ray radiation (1.5406 Å), β is the full-width at half-maximum (FWHM) of the peak (in radians) and 2θ is the Bragg angle. The shape and structure of the nanomaterial surface were examined at high-resolution using SEM (JSM-5600 JEOL, Japan). The chemical composition was analyzed using an energy dispersive X-ray (EDX) analysis incorporated into the SEM. Transmission electron microscopy (TEM, Hitachi HT7700, operated at 100 kV) was used to evaluate the morphologies of the samples. The high-resolution transmission electron microscopic (HRTEM) images of the samples were obtained using a (Hitachi H9500) operated at 300 kV. The surface composition was studied based on the X-ray photoelectron spectra (KRATOS AXIS SUPRA) with a monochromatized Al Ka X-ray source (10 kV, 1500 W, pass energy=40 eV). UV–vis diffuse reflectance spectra (DRS) analysis was conducted using an ultraviolet–visible (UV–vis) spectrophotometer (SHIMADZU UV-2600) 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. A Raman spectroscopy was performed using a Confocal-Raman imaging system with a 633 nm excitation laser (Renishaw in Via Reflex). Additionally, the photo-electrochemical analysis was executed using a self-made photo-electrochemical system installed a

n

New Journ

250-W halogen lamp as the irradiation-source. The chemical bonds vibration and functional group of the product was confirmed by FTIR spectrometer (FTIR iS5, Thermoscience). The photo-current measurement was conducted by a computer-controlled Versa-STAT-3 electro-chemical analyzer. The photoluminescence spectroscopy (PL) was carried out at RT in a conventional PL system. The ND 10% filter united 514 nm laser was utilized as the excitation source and measurement range was noted at the 530-1000 nm region.

2.6. Photocatalytic CO₂ reduction

In terms of the main research field, the photocatalytic CO₂ reduction was performed in a reactor (composed of three То take a precise (100 mg) of aspart). amount prepared photocatalysts (CuCaAg₂Se-Graphene-TiO₂) and different amount of sodium sulfite (as a sacrificial scavenger) was dissolved in 50 ml DI water (0.04 M, containing sodium bicarbonate) and agitated continuously for 1 h. Then, a high purity carbon dioxide (CO₂) gas was purged to the reactor for 30 min, after the solution was agitated and the visible light turned on via a metal halide lamp (500 W, SOLAREDGE700, Perfect Light, China). The distance between the light source and the photocatalyst was constantly at 10 cm, and a heat sink was stocked on the left-side of chamber to dismiss the lamp-heat. And the reaction time carried on continuously for up to 48 h whereby the reactor was cool down congenitally for methanol (CH₃OH) desorption from the catalyst after every 12 h. The different amounts (10, 20, and 30 ml) of the samples were withdrawn from the suspension at intervals of 12 h during the light irradiation using a syringe and a membrane filter. Subsequently, the reaction product was analyzed through the "Quantitative analysis of alcohol" method. In the "Quantitative analysis of alcohol," 0.1 M CrO₃ was added to the 10 ml sample and agitated for 15 min. The sample was then centrifuged (10.000 ppm/15 min) and its concentration peak was found using a UV spectrophotometer (Optizen POP, Korea). The chemical bonds vibration and functional group of the product was confirmed by FTIR spectrometer (FTIR iS5, Thermoscience). All samples were measured by the ATR (Attenuated total-reflection) method and a diamond crystal was used. The data of transmittance was obtained at the 3800 cm⁻¹ to 400 cm⁻¹ wavenumber range.

3. Result and discussion

3.1. X-ray diffraction studies

Figure 1 shows the XRD result of as-synthesized CCAS-G-TiO₂, G-TiO₂ and pure CCAS (after).

₹1

22

Buhlished o

View Article Online DOI: 10.1039/D0NJ03150J



Figure 1. The XRD pattern CuCaAg₂Se (after), Graphene-TiO₂, CuCaAg₂Se-G-TiO₂ nanocomposite.

The XRD result basically shows the characteristic of CCAS-G-TiO₂, G-TiO₂ and pure CCAS. After calcination, the XRD peaks intensity of CCAS nanocomposites was increased and the diffraction peaks had become sharp, and it was shown that the temperature intensified atomic-mobility and grain growth after that which was observed as a decent crystallinity. The full-width half maximum amount of the X-ray diffraction pattern decreased, while the average crystallite-size became bigger, that is the reason that the CCAS nanocomposite exhibited a decent crystallinity and large crystallite size (as shown in Figure S1a). The entire diffraction peak confirmed the orthorhombic crystal phase with lattice parameters a=4.1050 Å, b=4.0700 Å, c=6.3100 Å of CCAS nanocomposite (Card № 96-9008070). In addition, the peaks were located at 2θ of 23.04°, 26.84°, 31.06°, 36.18°, 40.16°, 45.20° and 57.98°, which were assigned to the (002), (110), (102), (112), (013), (031) and (230) crystal plane and corresponded to the crystal phase with lattice parameter of a = 4.3359 Å, b = 7.0700 Å, c= 7.7740 Å of Ag₂Se (JCPDS №.24-1041). With the conclusion of G-TiO₂ nanocomposite, it is noted that the XRD pattern showed the similar peaks of anatase TiO₂ (JCPDS №.21-1272), and the characteristic peak of graphene (002) was not shown due to less quantity and peak intensity was low (as shown in Figure S1b). And the index facet of (101) was exhibited in XRD pattern of G-TiO₂. In the case of anatase TiO₂, the index facet of (101), (010) and (001) exhibit a different catalytic activity [18]. After this, it was noted that the CCAS combined with G-TiO₂, whereby the most characteristic peak of

w Journal of Chemistry Accepted Manu

two nanocomposites were overlapped. Herein, this might be due to the consolidation between CCAS and G-TiO₂. The crystallite sizes of CCAS (before and after calcination) and TiO₂ were calculated using the Debye-Scherrer equation and were found to be 46.16 nm, 54.38 nm, and 43.33 nm, individually. The crystallites size of pure Ag₂Se was noted as 35 nm [19]. After being unified with copper and calcium and treated with a heat treatment process, the crystallites size of the CCAS nanocomposite was increased.

3.2. Morphological characterization

The surface morphology structure was shown to have appeared via SEM and TEM, in Figure 2 (a)-(c) and (d)-(f) shows the SEM, TEM analysis result of all synthesized nanocomposite which included schematic diagram.



Figure 2. (a-c) SEM images, (d-f) TEM images of CuCaAg₂Se-G-TiO₂ ternary nanocomposite

The before and after muffle-calcination of pure (CuCaAg₂Se) quaternary nanocomposite result shown in Figure S2 (a)-(d). Before calcination, the pure quaternary nanoparticles showed various structures, such as resembling the shapes of a sphere and a wrinkle. After calcination, the particle structure showed it was most resembled to a plate structure, which meant that, in high temperature nanoparticles grow to slightly larger size and were characteristic in formulating the aggregation. Figure 2 (a)-(c) presents the CuCaAg₂Se quaternary nanocomposite, G-TiO₂, and CuCaAg₂Se-G-TiO₂ nanocomposite morphology analysis. The TiO₂ particle regularly dispersed on the graphene-surface, whereby it is plainly exhibited with the polygonal plates and small spherical shape structure. After, the G-TiO₂ combining with quaternary nanocomposite, both of nanocomposites deposited on the graphene exterior, in addition to that, the graphene is shown to act as a bridge and acceptor, which is helpful an

increasing the path of photogenerated electrons, and is another way towards improvementation photogenerated electrons, and is another way towards improvementation photocatalytic efficiency. The graphene was shown as a sheet-like structure that was divided in various directions. This structure indicates the being on a graphene surface has oxygen functionalities. In this result, we can realize the disparity of the binary and ternary-composite material. The pure quaternary nanocomposite showed various sphere-structure, as shown in Figure 2 (d). The round and pentagonal-shaped TiO₂ was occurred as dark-colored and it was successfully dispersed onto the graphene exterior, which was confirmed by a dark-grey colored graphene surrounded the TiO₂ as shown in Figure 2 (e). The TiO₂ was slightly agglomerated due to an oxygen-containing functional group of graphene that can prevent the metal-oxide agglomeration. The quaternary CuCaAg₂Se and TiO₂ were scattered onto the graphene, as shown in Figure 2 (f). The round-shaped quaternary nanocomposite was obtained at the black-dot, and the CCAS was slightly agglomerated compared with TiO₂ and spread onto the surface of graphene which obtained as a dark-grey colored. Furthermore, the graphene obtained like double-layer-structure and all nanoparticle were shown to be uniformly spread and strongly attached onto the exterior during the muffle-assisted hydrothermal method.

The atomic structure and information of crystallographic structure of nanocomposite was analyzed via HRTEM. **Figure 3 (a)** and **(c)** indicated the lattice space of TiO₂. The spacing values can be 0.350 and 0.357 nm which corresponds to the (101) crystal planes in unary and ternary nanocomposites. The lattice fringes with di-spacing of CuCaAg₂Se was 0.235 nm which corresponding to the (102) crystal planes, as shown in Figure 3 (b). Figure 3 (d-f) shows the inter-active 3D surface-plot of TiO₂, Graphene and CCAS. From this result, the roughness state of each nanoparticle can be analyzed. The roughness states of the quaternary nanoparticle were normal, and another two nanoparticles states were shown to be uneven, which was the same as the sunken and convex result. The particle size histograms of TiO₂ and CCAS nanoparticles at different filtered sizes are shown in Figure 3 (g-h).

View Article Online DOI: 10.1039/D0NJ03150J

New Journal of Chemistry











4

5

6

7 8

9 10

11

12

13

14 15

16 17

18

19 20

₹1 **7**22

40 41

42

43 44

45 46

47 48

49

50 51

52 53

54 55

an

Figure 3. The HRTEM images of (a) G-TiO₂, CuCaAg₂Se-G-TiO₂ (b, c) nanocomposite, (d-f) Interactive 3D surface plot and (g-h) nanoparticle size histogram of TiO₂, CCAS Graphene-TiO₂ in CuCaAg₂Se-G-TiO₂.These histograms show the noted calculated average nanoparticle diameter distributions with 5.28 \pm 1.3 nm (TiO₂ in G-TiO₂), 2.93 ± 0.8 nm (CCAS in CCAS-G-TiO₂). After CuCaAg₂Se united with G-TiO₂ binary nanocomposite, the average core diameter of TiO₂ was reduced during a hydrothermal muffle-assisted synthesis process. The average particle diameter of TiO₂ was 3.39 ± 1.02 nm (TiO₂ in CCAS-G-TiO₂), as shown in Figure S3.

In conjunction with UV-vis DRS results, the slight changes in the feature of nanoparticles support the light response of main material, considering their average core diameter after the coupling reaction as shown in HRTEM studies. The considerable average diameter of nanoparticle was produced with an increased polydispersity.

The quantitative as well as the qualitative main elements of the catalyst was detected via EDX analysis and every element has their characteristic peak (sharp K α and K β). Figure 4 displays the micro-analysis result of assynthesized all samples, which reveals the presence of the main elements.

The Cu, Ca, Ag, Se, Ti and O view Article Caline from the main precursor reagents and C element was obtained from graphene, which was one of the absorbent materials in the catalyst. The strong K α and K β of C and O element peak observed at 0.28 keV and 0.53 keV [20]. Other main elements peaks were appeared in characteristic regions. Figure S4 shows the EDX result and diagram of pure quaternary nanocomposite (before and after calcination) which exhibited each element percent.

New Journal of Chemistry Accepted Manuscrip



View Article Online DOI: 10.1039/D0NJ03150J

Figure 4. The quantitative analysis results.

To explore the detailed surface chemical state of the elements and interactions between CuCaAg₂Se, graphene, and TiO₂, XPS an analysis was conducted over CCAS-G-TiO₂. The binding energies depend on the chemical structure and elemental formation of sample. **Figure 5** (a) presents the XPS survey spectrum, which expresses the existence of C1s, O1s, Ca2p, Ti2p, Cu2p, Se3d and Ag3d,

and it is confirmed that there is the successful formation of CCAS-G-TiO₂.



New Journal of Chemistry Accepted Manuscrip







4

5

6

7

8

9

10

11

12

13 14

15

16

17

18

19 20 2€

22

14. August 2020 Wankaded

36

- lalished

<u>ā</u>9

40 41

42 43

44

45 46

47 48

49

50 51

52 53

54 55

56

57 58

59 60



Figure 5. (a) XPS survey spectra and the high-resolution XPS spectra of (b) C1s, (c) O1s, (d) Ca2p, (e) Ti2p, (f) Cu2p, (g) Se3d and (h) Ag3d.

The electron configuration of C1s is shown to consist of three peaks and those peaks are corresponding to the [C-C], [C-C] aliphatic and C-OX groups, as shown in Figure 5 (b). In addition, the existence of C-OX group confirms from the synthesized ternary composite contains the oxygencontaining functional group [21] which confirms the existence of the chemical-bond between oxygen and metal, and the X-is the state of metal. The O1s spectrum is shown to compose of two peaks which are located at the 530.26 and 532.19 eV regions. The first peak indicated the carbonyl group [-C=O], whereby the second peak are corresponding to the one of the metal carbonates forms, Ti-O-C as shown in Figure 5 (c) [22]. The Ca2p XPS spectrum consisted of two characteristic peaks which are located at a 346.59 and 351.30 eV, and those peaks corresponding to the formation of Ca-O, Ca- TiO_2 bonding [23], as shown in Figure 5 (d). The formation of the TiO_2 expressed two sharp peaks, which were centered at the 458.81 and 464.57 eV binding energy regions, and it was assigned to spin-orbital of Ti $2p_{3/2}$, Ti $2p_{1/2}$. In addition, $2p_{3/2}$ clearly defined the Ti (IV) (TiO₂) and the intensity ratios of two peaks are also constrained to 2:1, as shown in Figure 5 (e). The $Cu2p_{3/2}$ and $Cu2p_{1/2}$ spin orbital peak of ternary composite divided into two major and two satellites peaks, as shown in Figure 5 (f). The first major peak was defined the Cu(I) oxide and Cu(I) selenide [24]. Se3d is consist of two characteristic peaks of $\text{Se3d}_{5/2}$ and $\text{Se3d}_{3/2}$ spin orbital which are located at a binding energy of 53.83 and 54.37 eV regions. In addition, two more peaks were observed in the 58.53 and 58.21 eV regions, which assigned to the Se-Se, Se-O form [25], as shown in Figure 5 (g). Finally, the Ag3d XPS spectrum of composite consisted of two characteristic peaks which corresponds to the $3d_{5/2}$ and $3d_{3/2}$ spin orbital, as shown in Figure 5 (h). These two sharp peaks located at 368.12 and 374.06 eV binding-energy regions and those two peaks correspond to the state of Ag (I) in Ag₂O and

 Ag₂Se, respectively [26]. The binding energy shifts indicate the strong bond-interaction article $G_{0,1}$ transfer among the CuCaAg₂Se quaternary nanocomposite, bridge element of graphene, and TiO₂ in the synthesized ternary CCAS-G-TiO₂ nanocomposite.

The charge-separation and transfer process and photo-electro-chemical capacity of sample was investigated via DRS, PL, and photocurrent analysis. UV-vis DRS analysis was conducted to explore the optical absorption-properties of prepared sample, as shown in **Figure 6** (**a**).

View Article Online DOI: 10.1039/D0NJ03150J



≩1

12:42:10203228 an isotropy 2020727878 and 22:202012928 and 22:202012928 and 22:202012928 and 22:202020 and 22:202020

 View Article Online DOI: 10.1039/D0NJ03150J

G-TiO2





To get the relation of the energy (E_g) and optical absorption, according to the, the absorption spectra can be analyzed by using (Eq. (2)) equation [27]:

$$[hvF(R_{\infty})]^{1/n} = A(hv E_g)$$
 [2]

where $hv=hc/\lambda$ is the energy of the incident photon, $F(R)(1 R)^2/2R$ is the Kubelka-Munk function, Eg is the energy of the band gap and A is the constant of proportionality, F(R) is the absorption coefficient. The composites are exhibit the obvious absorption in the solar-light region of 300-600 nm. The pure quaternary nanocomposite has light-absorption under near-Visible light region and Kubelka-Munk function was exhibited at 449.27 nm. The synthesized G-TiO₂ nanocomposite has photo-absorption from UV-light to Visible light range and Kubelka–Munk function was exhibited at 417.50 nm. The TiO₂ is n-type semiconductor which usually used for photocatalytic CO₂ reduction due can possess a light absorption property under the UV-light region

New Journal of Chemistry Accepted Manuscri

(UVA, 315–400 nm, UVB, 280–315 nm, and UVC, 180–280 nm) [28]. After_D the officiency characterina common characterina common composite (CuCaAg₂Se) united with Graphene-TiO₂, the light absorption range was changed to 441.48 nm. The reason is: the conglomeration can act on the light-absorption performance resulting to modify the bandgap. Figure 6 (a) shows the bandgap of CCAS, G-TiO₂ and CCAS-G-TiO₂, which was expected to be 2.76, 2.97 and 2.79 eV, respectively. The pure CuCaAg₂Se quaternary nanocomposite, G-TiO₂ binary and CuCaAg₂Se-G-TiO₂ ternary nanocomposite showed the lower bandgap condition existed rather than a pure anatase TiO₂, which can show a high catalytic activity and can be able to practice application. Furthermore, the ternary CuCaAg₂Se-G-TiO₂ nanocomposite can be able to generate more electron-hole pairs under the UV/Vis-light which can exhibit high catalytic efficiency.

Figure 6 (b) shows the photo-current response of ternary composite, during four on-off cycles of light illumination. The ternary composite and pure quaternary nanocomposite showed swift and velocity current response for each light irradiation. The photo-current state decayed immediately in the no-light condition and recovered once the light was on. When the light was switched on, the current-state increased with time in 30 s. This process can be explained in reference to the existence of charge carriers transfer from the VB to the CB under the light irradiation. The current-state of CuCaAg₂Se was slightly decreased after two on-off cycle (Fig.S5a). The current state of G-TiO₂ was stable during a four-on-off cycles which can confirm the binary nanocomposite showed fluent current capability. In the case of ternary CuCaAg₂Se-Graphene-TiO₂ composite, the photo-current state was obviously amplified after four on-off cycle tests (Fig.S5b). The photocurrent state of G-TiO₂ was 3.90*10⁻⁶ A. The photocurrent-time (I-t) curves of quaternary nanocomposite expose the high-separation capacity for charge-carrier under the light illumination and photocurrent state was 5.45*10⁻⁶. In the case of ternary nanocomposite, the photo-current state was almost reached to the quaternary nanocomposite state. It is shown that it can improve the catalytic activity, after being combined with Graphene-TiO₂ to make a ternary composite. This hypothesis approved in characterization of UV-vis DRS analysis; the band-gap energy of CCAS was 2.76 eV, G-TiO₂ was 2.97 eV, and CCAS-G-TiO₂ was 2.79 eV.

Photoluminescence (PL) spectroscopy was conducted to investigate the separation efficiency, and recombination process of the photo-excited electrons. The PL spectra of composites are displayed in **Figure 6** (c). The unary, binary, and ternary nanocomposite showed a light response to 514 nm laser which is shown in Figure 6 (c) (I-III). The emission-spectra of metal oxide are categorized into two groups: [1] Near-band-edge (**NBE**) UV-emission, [2] Deep-level (**DL**) defect-related Visible-emission [29]. A broad emission peak was observed in the range between 570 nm to

60

625 nm with 514 nm laser. The quaternary nanocomposite has wide-emission peak at 603 to 603 t

Raman spectroscopy is the chemical-analysis method which can analyze the chemical structure phase and molecular interaction of matter. The principle of Raman spectroscopy is a light-scattering technique, where the light interact to the molecule bond and the result provides the information of carbon material (D and G-band), structural characteristic between CuCaAg₂Se, graphene and TiO₂ due to the strong scatter.



Page 20 of 35

₹1

View Article Online DOI: 10.1039/D0NJ03150J



Figure 7. The Raman full spectra (a) of G-TiO₂ (b) and CuCaAg₂Se-G-TiO₂ (c) nanocomposite.

Figure 7 (**a**) shows the full Raman spectroscopy of all composites in detail. The G-TiO₂ binary composite included four different peaks which obtained at 149.92 cm⁻¹, 254.51 cm⁻¹, 408.75 cm⁻¹ and 607.41 cm⁻¹ shift region, as shown in Figure 7 (**b**). All occurred peaks are assigned to the TiO₂.

New Journal of Chemistry

60

In the case of binary composite, there is no peak (D and G-peak) of graphene due to variable down to be a concentration of graphene. The TiO₂ had three different phases: anatase, rutile and brookite. The asprepared TiO₂ was corresponded to the anatase phase. The anatase TiO₂ had four Raman band at 100-700 cm⁻¹ shift region [30, 31], such as E_g mode at 144, 183 cm⁻¹ region and 639, 629 cm⁻¹, B_{1g} mode at 399, 382 cm⁻¹, the last one is A_{1g} mode at the 520 cm⁻¹ region. The first intense and sharp peak assigned to the (left side) E_g mode which obtained at the 149.92 cm⁻¹ shift region. The other (right side) E_g mode is an asymmetric bend of O-Ti-O bond on the (001) crystal plane, and this peak was commonly obtained in the Raman spectra of TiO₂.

In the center of Figure 7b, other Raman modes were observed. The asymmetric bend of O-Ti-O bond on the (001), (110) and (101) crystal planes of TiO₂ was corresponded to the B_{1g} mode and this peak was obtained at 408.75 cm⁻¹. Furthermore, the weak and broad peak was observed at 254.51 cm⁻¹ shift region which renamed by SEO mode and the peak is shown to belong to the motion of atoms. Figure 7 (c) shows the Raman spectra of ternary composite (CCAS-G-TiO₂) which included four peaks. In 142.99 and 591.34 cm⁻¹ shift regions, these two weak and broad peaks were obtained, and those peaks are belonging to the Eg mode peak of TiO2. The peak position was shifted to the left side due to the structural characteristic and asymmetric bend of O-Ti-O bond of TiO₂ was changed which graphene-TiO₂ joined with quaternary nanocomposite. There were another two peaks which were assigned to the Raman band of quaternary nanocomposite at 100-700 cm⁻¹ shift region. The characteristic peak position of quaternary composite was overlapped with the peak of TiO₂ at 200-600 cm⁻¹. The pure silver selenide had four characteristic peaks at 200-840 cm⁻¹ shift region [32]. Copper and copper oxide had three Raman peaks at 295 cm⁻¹, 342 cm⁻¹, 628 cm⁻¹ shift regions [33]. The combination of Ag₂Se with Cu and Ca, the structural property of each part was changed, and the Raman peaks were indicated at 274.55, 388.35 and 591.34 cm⁻¹. All peak position was shifted to the (left side) red shift, which means that the peak belongs at the low Raman shift side. In Raman spectra, the shifting of peaks towards lower or higher-wavenumber is related to the chemical bond and symmetry of molecules were changed in quaternary nanocomposite and Graphene-TiO₂.

New Journal of Chemistry Accepted Manuscrip

Metal oxygen and functional group in the composites were confirmed by FTIR spectra. The FTIR spectra of the synthesized nanocomposites are show in **Figure 8**.

New Journal of Chemistry Accepted Manuscrip

View Article Online DOI: 10.1039/D0NJ03150J



Figure 8. FTIR spectra of CuCaAg₂Se, G-TiO₂ and CuCaAg₂Se-G-TiO₂ nanocomposite.

The adsorption band of O-H stretching (R-C(O)-OH) at around 3236.12 cm⁻¹, 2379.06 cm⁻¹ corresponds to CH₂, C=O stretching (C(O)-OH) at 1403.87 cm⁻¹, and CH₂ rocking at 872.86 cm⁻¹. The result is attributed to the vibrational modes of citric acid molecule [34]. Moreover, the other appearance bands confirmed the evidence of successful chemical bonding state of CuCaAg₂Se. More specifically, 710.07 cm⁻¹ corresponding to Se-O, Se-Se vibration [35]. Additionally, the Graphene exhibited the C-H stretching at 2989.15 cm⁻¹, C-OH stretching at and 1213.63 cm⁻¹, and C-O stretching at and 1074.41 cm⁻¹, implying the vibration of hydroxyl group and carboxyl group of Graphene [36]. The strong absorption band at 1575.49 cm⁻¹ is corresponding to the Ti-O-Ti bond in TiO₂. All functional groups confirmed the strong chemical formation of Graphene and TiO₂. After quaternary nanocomposite (CuCaAg₂Se) combined with G-TiO₂ via muffle-assisted hydrothermal method. The peak intensity and position were changed, indicating the formation of due to formation of CuCaAg₂Se-G-TiO₂ bonding.

Recently, some of research papers with Ag₂Se-based nanocomposites for the CO₂ reduction have not been published. There are several silver doped or silver-based photocatalyst for the CO₂ reduction such as Ag-Cu₂O core-shell nanoparticles [37], Ag₃PO₄ [38], novel Ag/Ag₂WO₄/ZnWO₄ [39] heterojunctions. Generally, Ag₂Se and Ag₂Se-graphene nanocomposite were used in solar cells, sensor, and conductor due to high chemical and optical properties. Some of techniques were applied to the fabrication of silver selenide nanostructures include combination of the precursors at high

 temperatures [40], hydrothermal method, microwave [41], and molecular precursor methods in the polymer precursor method in the polymer precursor solution was prepared which is afforded to obtaining a decent crystallinity and the polymer precursor solution was prepared by Pechini method based on metallic citrate polymerization using ethylene glycol $C_2H_6O_2$ (Merck) and citric acid $C_6H_8O_7$ (Merck) as chelate cation. The surface and morphology structure of pure $A_{g2}Se$ is spherical type and diameter of particles were around 5–10 nm. The Ag_2Se -rGO possesses good conductivity and considerably low charge transfer resistance (Rct) due to the high synergistic effect, which can confirm that silver chalcogenide with graphene nanocomposite exhibit a high catalytic activity. The Ag_2Se -rGO possesses good conductivity and considerably low charge transfer resistance (Rct) due to the high synergistic effect, which can confirm that silver chalcogenide with graphene nanocomposite exhibit a high catalytic activity.

3.3. Photocatalytic performance and reduction of CO₂

Figure 9 shows the result of the "Quantitative analysis of alcohol" which used an as-synthesized ternary composite for using a different amount of scavenger. Besides, to investigate the role of ternary nanocomposite, the photocatalytic CO₂ reduction process was carried out for a unary and binary nanocomposites, such as TiO₂, CuCaAg₂Se, G-TiO₂.

New Journal of Chemistry Accepted Manuscrip

New Journal of Chemistry Accepted Manuscript



₹1

Buhlished o



Figure 9. (a) Quantitative analysis of the Alcohol result of unary, binary, and ternary composite under the Visible light, (b) UV light for using a different amount of scavenger.

The first comparison made with as-prepared TiO₂, under identical experimental conditions. However, TiO₂ exhibited rather poor CO₂ reduction activity (Figure 9 (a, b)) owing to its UV-only light absorption and unmatched CB potential to drive the CO₂ reduction effectively. The improved CO₂ conversion efficiency of the TiO₂ is due to facilitated charge transfer and separation property of graphene. More importantly, the methanol evolution over CCAS-G-TiO₂ is also superior to graphene-based nanocomposite, TiO₂ photocatalytic systems. Under the Vis-light, the ternary composite exhibited high final product yield (CH₃OH), and when increasing the amount of scavenger (0.1 to 0.6 g) the yield was increased. With (0.1 g) scavenger, the methanol yield was 4.24, 6.04, 10.17 and 12.28 % while with (0.6 g) scavenger, the methanol yield was 4.62, 7.28, 10.88 and 12.68 %

₹21

Buhlished o

under the vis-light after 12 to 48 hours as shown in Figure 8 (a). Figure 8 (b) shows the vis-state $\Omega_{1503}^{\text{me}}$ methanol yield under the UV-light, the target ternary composite exhibited high methanol (CH₃OH) yield with various quota of scavenger. With (0.1 g) scavenger, the methanol yield was 2.35, 5.00, 6.38 and 8.71 %. When using a (0.3 g), the yield was 4.82, 7.31, 11.08 and 15.53 % while using a (0.6 g) scavenger the methanol yield was 7.13, 11.02, 15.35 and 16.84 % under the UV-light after 12 to 48 hours.

To analyze the consequence of "Quantitative Analysis of Alcohol," the ternary composite showed a good catalytic activity and reduction performance for CO_2 into methanol (CH₃OH) with using various amount of scavenger. Sodium sulfite (Na₂SO₃) was applied as the scavenger since it is a great efficient electron provider and cycling electron donor, to combine the Carbon dioxide (CO₂) compound to photo-reduction with water to enhance all potency. In addition, the scavenger boosts the photo-catalytic activity of graphene-based ternary composite in CO_2 reduction. Under the UVlight irradiation, the final product quota was high with using a high amount of scavenger. Moreover, with using a 0.3g and 0.6g scavenger affects was not high.

In the practical application of a reusable state, the reproducibility and sturdiness of a photocatalyst never be dismissed. In the cycling test, the photocatalyst (CCAS-G-TiO₂) was recycled for 9 times (432 h) under UV/Vis-light irradiation with scavenger (0.3 g) in CO₂ reduction. As can be seen in **Figure 10**,



√⊋1

 Figure 10. Photocatalytic activity of CO₂ reduction using CuCaAg₂Se-Graphene-TiO⁴ are arrived after 432 h (9 days) illumination in the cycling experiment. the ternary nanocomposite retains its notable activity after nine cycle under identical conditions with no significant deactivation towards to Methanol evolution. According from recycling test, the synthesized ternary nanocomposite is stable for practical application in generating solar fuel.

The FTIR spectrum of first intermediate product (after 4 h) and final product (after 12 h of reaction) was shown in **Figure 11**.

Table 1. Characteristic vibrational group of the intermediate and final-product from the FTIR measurement.

N⁰	Vibrational state	Mode	Experimental (cm ⁻¹)	Theoretical (cm ⁻¹)
1	Hydroxyl group	(O-H)	3294.57 cm ⁻¹	$3400-3300 \text{ cm}^{-1}$
2	Carbonyl group	C=O	1648.3 cm ⁻¹	$1715-1700 \text{ cm}^{-1}$
3	Alcohol group	C-O-H	1274.41 cm ⁻¹	1440-1220 cm ⁻¹
4	Methyl group	(C-H) in	1402.32 cm ⁻¹	1450 and 1375 cm ⁻¹
		(CH3) δ		



Figure 11. The FTIR result and result of the final product: reference (red line), final methanol product (blue line), formic acid (black line).

New Journal of Chemistry Accepted Manuscri

The first intermediate product (formic acid) and final product consisted of hydroxyl group (C=O), alcohol group (C-O-H), methyl group (CH₃-deformation) and the peak appeared at the exact wavenumber region which can confirm the state of each product. Table 1 summarized the results of each obtained peak position with the theoretical key data. The position of hydroxyl and carbonyl group was noted as the same. The intensity and position of C-H in (CH₃)-deformation was different in methanol as compared with Formic acid. In addition, the FTIR result of the final product was compared with the result of commercial methanol. Each peak position was overlapped, and it can prove that photocatalyst material can convert the CO₂ into a methanol.

Figure 12 shows the morphology and crystal structure of photocatalyst after UV/Vis-light irradiation which analyzed via SEM and XRD. After the experiment, it was possible to collect the photocatalyst, and it was rinsed with DI-water and dried at 100 °C.



⊉1

Z2

<u>ā</u>9



Figure 12. (a-b) The formation mechanism of CuCaAg₂Se-G-TiO₂ ternary nanocomposite with the SEM images of after Vis-light irradiation, and (c-d) after UV-light irradiation, (e) the XRD pattern of ternary photocatalyst after light irradiation.

The morphology structure of the photocatalyst was clear and each peak position is noted as the same as a fresh photocatalyst in SEM and XRD. The total result showed no apparent retrogression as compared to the pure-photocatalyst which can prove the high stability and reusability of this material.

For the suggested photocatalytic reduction mechanism, the light (photon) interacts onto the exterior of TiO₂ absorbing the energy. When the light energy (Ev) is equal or greater than the bandgap energy (Eg) of semiconductor, then the electron can be excited from the VB to CB creating an electron-hole pair. During a reaction, an excited electron and hole move to the semiconductor-exterior. Nevertheless, the absence of a co-catalyst, or an insufficient active site determines that the electron-hole recombines very quickly on the semiconductor-surface and shows that the catalytic-efficiency was modified. During a photocatalytic reaction, the role of graphene is an electron acceptor/transporter, whereby this presents the most important part of the partition of electron-hole transport. The oxygen-function of graphene were bonded by un-paired π -electrons with Ti-atoms on the exterior of TiO₂, which affecting the band-gap of graphene-TiO₂ nanocomposites. The photocatalytic activity can be further enhanced through the contributions of a junction/interaction between the co-catalyst and the semiconductor to increase the electron-hole partition or charge transport. In the heterogeneous system, the performance of the co-catalyst acts as an electron-trap to

₹1

22

Buhlished o

increase the photo-generated electron-hole pairs as well as to boost the catalytic activity for the CO_2 reduction. During a UV/Visible-light irradiation, the graphene and CuCaAg₂Se are concurrently excited thereby migrating the electrons. These electrons are able to act reciprocally through the graphene with the VB electrons of TiO₂ in the composite and create a donor-level. Therefore, the semiconductor materials bound on the sheet-like structured graphene are able to act as electron assimilates in the photocatalytic reaction mechanism which is shown in **Scheme 1**. The reaction mechanism is expressed as in the equation below:



Scheme 1. The mechanism (a) and chemical reaction (b) of the photocatalytic CO_2 reduction.

Z2

 View Article Online DOI: 10.1039/D0NJ03150J

(5)

(6)

$TiO_2 + h\nu \rightarrow e^- (TiO_2) + h^+ (TiO_2)$	(1)
$CuCaAg_2Se + h\nu \rightarrow e^- (CuCaAg_2Se) + h^+(CuCaAg_2Se)$	(2)
$e^{-}(TiO_{2}) + Graphene \rightarrow TiO_{2} + e^{-}(Graphene)$	(3)
$e^{-}(Graphene) + CuCaAg_2Se \rightarrow Graphene + e^{-}(CuCaAg_2Se)$	

 $H_2O + h^+ \rightarrow H^+ + OH^-$

$$\mathcal{CO}_2 + e^- \rightarrow \mathcal{CO}_2^{\bullet^-}$$

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$$
 (Carbon monoxide) (7)

$$CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O$$
 (Formaldehyde) (8)

$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$$
 (Methanol) (9)

Equations (1) to (4) describe the reaction mechanism of CuCaAg₂Se, TiO₂, and graphene and define the production of the photoexcited electron-hole pair. The subsequent reactions (equations 6 to 9) shows the oxidation and reduction processes, where holes are used for oxidation, while the electrons are used for the photocatalytic CO₂ reduction. In the reduction mechanism, the generated electron reacts with the dissolved oxygen to produce the oxygen peroxide radicals. The positive holes are assimilated in water, resulting in the production of hydroxyl radicals (OH) and hydrogen ions (h⁺), which then react with the excited electrons, managing the configuration of •H, while CO₂ concurrently reacts with the excited electron and CO_2^- forms CO_2^{-} , which is finally commuted to CH₃OH.

4. Conclusion

In summary, the graphene-based ternary composite containing quaternary nanocomposite (CuCaAg₂Se) was successfully synthesized via the use of a muffle-consisted hydrothermal technique, and the photo-catalytic activity was analyzed for CO₂ reduction using a various amount of scavenger. The average crystallite size of CuCaAg₂Se (before and after calcination) and TiO₂ were 46.16, 54.38 and 43.33 nm, respectively. The TEM image suggested that quaternary nanocomposite and TiO₂ spread onto the exterior of graphene surface and the Raman and XPS characterization showed the strong chemical interaction among all particles. The photo-catalytic performance of ternary composite was analyzed for CO₂ reduction under the UV/Vis-light irradiation. The final product quota was 12.68 and 16.84 % under the Vis and UV-light after 48 h when using a 0.6 g scavenger. Besides, the reusability of a photocatalyst was checked and it was reported the photocatalyst could support activity. The role of the scavenger was to have provided the electron and cycling electron

New Journal of Chemistry Accepted Manuscri

donor an opportunity to combine the CO₂ to reduce with water. The chemical bonds vibration and the functional group of intermediate and final product was confirmed by the use of a FTIR spectrometer. The main functional group was obtained in the exact wavelength region. Furthermore, we compared the FTIR result of the final methanol with commercial methanol. Each peak position was overlapped, and it can prove that the photocatalyst material can convert the CO₂ into a methanol. In this work, the quaternary composite loaded graphene-based photo-catalyst was used to support the benefits of heterogeneous system and developed the production rate of final product (CH₃OH).

Reference

- Hu, X., Zhang, Q., Nan, H., Wang, M., Qiao, L., & Tian, H. Heterojunction Cu₂O/RGO/BiVO₄ Ternary Nanocomposites with Enhanced Photocatalytic Activities towards Degradation of Rhodamine B and Tetracycline Hydrochloride. *New Journal of Chemistry*, (2019), 43, 18240.
- [2] Tian, H., Shen, K., Hu, X., Qiao, L., & Zheng, W N, S co-doped graphene quantum dotsgraphene-TiO₂ nanotubes composite with enhanced photocatalytic activity, *Journal of Alloys* and Compounds, (2017), 691, 369–377.
- [3] Luo, B., Liu, G., Wang, L, Recent advances in 2D materials for photocatalysis, *Nanoscale*, (2016), 8, 6904–6920.
- [4] Eda, G., Fanchini, G., Chhowalla, M. Large-area ultrathin films of reduced graphene oxide as a transparent and flexible electronic material, *Nature Nanotechnology*, (2008), 3, 270-274.
- [5] Stankovich, S., Dikin, D.A., Dommett, G.H.B., Kohlhaas, K.M., Zimney, E.J., Stach, E.A., Piner, R.D., Nguyen, S.T., Ruoff, R.S. Graphene-based composite materials. *Nature*, (2006), 442, 282-286.
- [6] Tian, H., Wan, C., Xue, X., Hu, X., Wang, X. Effective Electron Transfer Pathway of the Ternary TiO₂/RGO/Ag Nanocomposite with Enhanced Photocatalytic Activity under Visible Light, *Catalysts*, (2017), 7, 156.
- [7] Biswas, M. R. U. D., Ali, A., Cho, K. Y., Oh, W. C. Novel synthesis of WSe₂-Graphene-TiO₂ ternary nanocomposite via ultrasonic technics for high photocatalytic reduction of CO₂ into CH₃OH, Ultrasonics – Sonochemistry, (2018), 738-746.
- [8] Ali, A., Oh, W. C. A simple ultrasono-synthetic route of PbSe-graphene-TiO₂ ternary composites to improve the photocatalytic reduction of CO₂, Fullerenes, Nanotubes and Carbon Nanostructures, (2017), 449-458.
- [9] Ali, A., Nguyen, D. C. T., Cho, K. Y., Oh, W. C. A simple ultrasonic-synthetic route of Cu₂Se-graphene-TiO₂ ternary composites for carbon dioxide conversion processes, Fullerenes, Nanotubes and Carbon Nanostructures, (2018), 26:12, 827-836.

4 5

6

7 8

9 10

11

12 13

14 15

16 17

18

19 20

₹1 722

\$26 \$27

14.August 2020 Downloaded

36

37

Sublag8

40 41

42

43 44

45 46

47 48

49

50 51

52 53

54 55

56

57 58

- [10] Zubair, M., Razzaq, A., Grimes, C.A., In, S.I,Cu₂ZnSnS₄ (CZTS)-ZnO: A noble meral infection hybrid Z-scheme photocatalyst for enhanced solar-spectrum photocatalytic conversion of CO₂ to CH₄, *J. CO₂ Util.*, (2017), 20, 301-311.
- [11] Bafaqeer, A., Tahir, M., Amin, N.A.S, Well-designed ZnV₂O₆/gC₃N₄ 2D/2D nanosheets heterojunction with faster charges separation via pCN as mediator towards enhanced photocatalytic reduction of CO₂ to fuels. *Appl. Catal.*, *B*, (2019), 242, 312–326.
- [12] Zhao, H., Wang, X., Feng, J.F., Chen, Y., Yang, X., Gao, S., Cao, R. Synthesis, and characterization of Zn₂GeO₄/Mg-MOF-74 composites with enhanced photocatalytic activity for CO₂ reduction, *Catal. Sci. Technol.*, (2018), 1288-1295.
- [13] Santhosh, K. M. C., Pradeep, B. Electrical properties of silver selenide thin films prepared by reactive evaporation, *J. Bull Mater Sci.*, (2002), 25, 407-411.
- [14] Zhao, J., Jiang, B., Zhang, S., Niu, H., Jin, B., Tian, Y. Preparation and photoelectrochemical performance of TiO₂/Ag₂Se interface composite film, *Sci. China Ser. B: Chem.* (2009), 52, 2213.
- [15] Low, J., Yu, J., Ho, W. Graphene-based photocatalysts for CO₂ reduction to solar fuel, *J. Phys. Chem. Lett.*, (2015), 6, 4244–4251.
- [16] Xu, T., Hu, J., Yang, Y., Que, W., Yin, X., Wu, H., Chen, L. Ternary system of ZnO nanorods/reduced graphene oxide/CuInS₂ quantum dots for enhanced photocatalytic performance, *J. Alloys Compd.*, (2018), 734, 196–203.
- [17] Yan, Y., Sun, S., Song, Y., Yan, X., Guan, W., Liu, X., Shi, W. Microwave-assisted in situ synthesis of reduced graphene oxide–BiVO₄ composite photocatalysts and their enhanced photocatalytic performance for the degradation of ciprofloxacin, *J. Hazard. Mater.*, (2013), 250, 106–114.
- [18] Gan, W., Fu, X., Zhang, J. Ag@AgCl decorated graphene-like TiO₂ nanosheets with nearly 100% exposed (001) facets for efficient solar light photocatalysis, *Mat. Sci.Eng.* B., (2018), 229, 44–52.
- [19] Helman, P. R. J., Mohanraj, K., Sivakumar, G. Synthesis and characterization of β-Ag₂Se and β-AgCuSe nanoparticles via facile precipitation route, *Trans. Nonferrous Met. Soc. China.*, (2015), 25, 2241-2246.
- [20] Ali, A., Nguyen, D. C. T., Cho, K. Y., Oh, W. C. A simple ultrasonic-synthetic route of Cu₂Se-graphene-TiO₂ ternary composites for carbon dioxide conversion processes, *Fullerenes*, *Nanotubes and Carbon Nanostructures.*, (2018), 26:12, 827-836.
- [21] Hui, L., Shuang, L., Zhiling, Z., Xiaonan, Ali, A., Nguyen, D. C. T., Cho, K. Y., Oh, W. C. A simple ultrasonic-synthetic route of Cu₂Se-graphene-TiO₂ ternary composites for carbon

4 5

6

7 8

9 10

11

12 13

14 15

16 17

18

19 20

₹1 722

\$26 \$27

14.August 2020 Downloaded

36

37

Sublug 8

40 41

42

43 44

45 46

47 48

49

50 51

52 53

54 55

56

57 58

59 60 dioxide conversion processes, *Fullerenes, Nanotubes and Carbon Nanostructures*, View 2018 Police 26:12, 827-836.

- [22] Demri, B., Muster, D. XPS study of some calcium compounds, Journal of Materials Processing Technology., (1995), 55, 311-314.
- [23] Dong, J., Ye, J., Ariyanti, D., Wang, Y., Wei, S., Gao, W. Enhancing photocatalytic activities of titanium dioxide via well-dispersed copper nanoparticles, *Chemosphere.*, (2018), 204, 193.
- [24] Abdallah, W. A., Nelson, A. Characterization of MoSe₂ (0001) and ion-sputtered MoSe₂ by XPS. *Journal of materials science.*, (2005), 40, 2679–2681.
- [25] Helman, P. R. J., Mohanraj, K., Sivakumar, G. Synthesis and characterization of β-Ag₂Se and β-AgCuSe nanoparticles via facile precipitation route, *Trans. Nonferrous Met. Soc. China.*, (2015), 25, 2241-2246.
- [26] Atta, N. F., El-Kady, M. F. Novel poly(3-methylthiophene)/Pd, Pt nanoparticle sensor: Synthesis, characterization, and its application to the simultaneous analysis of dopamine and ascorbic acid in biological fluids, *Sens. Actuators B Chem.*, (2010), 145, 299-310
- [27] Pyrgiotakis, G., Wolfgang, S. M. X-Ray Photoelectron Spectroscopy of Anatase-TiO₂ Coated Carbon Nanotubes, *Solid State Phenomena.*, (2010), 162, 163-177.
- [28] Qi, K., Cheng, B., Yu, J., Ho, W. A review on TiO₂-based Z-scheme photocatalysts, *Chin. J. Catal.*, (2017), 38, 1936–1955.
- [29] Kumar, S., Bhunia, S., Singh, J., Ojha, A. K. Absence of room temperature ferromagnetism in Fe stabilized ZrO₂ nanostructures and effect of Fe doping on its structural, optical and luminescence properties, J. Alloy. Compd., (2015), 649, 348–356.
- [30] Tian, F., Zhang, Y., Zhang, J., Pan, C. Raman spectroscopy: A new approach to measure the percentage of anatase TiO₂ exposed (001) facets, *J. Phys. Chem. C.*, (2012), 116, 7515–7519.
- [31] Hui, W., Jingwei, Z., Wenzhen, X., Xiawei, C., Anshun, H., Jung, H. Y., Lianzhou, W., Han, H., Sihai, J., Li, H., Suoquan, Z., Zhengyi, J. Analysis of TiO₂ nano-additive water-based lubricants in hot rolling of microalloyed steel, *J. Manuf. Processes.*, (2017), 26-36.
- [32] Pandiaraman, M., Soundararajan, N. Micro-Raman studies on thermally evaporated Ag2Se thin films, *Journal of Theoretical and Applied Physics.*, (2012), 6:7.
- [33] Xu, J. F., Ji, W., Shen, Z. X., Li, W. S., Tang, S. H., Ye, X. R., Jia, D. Z., Xin, X. Q. Raman spectra of CuO Nanocrystals, *J. Raman Spectrosc.*, (1999), 30, 413–415.
- [34] Nguyen, T. T., Dang, L. M. Size Effect on the Structural and Magnetic Properties of Nanosized Perovskite LaFeO₃ Prepared by Different Methods, *Advances in Materials Science and Engineering.*, (2012), 3803-3806.

- [35] Dukstiene, N., Tatariskinaite, L., Andrulevicius, M. Characterization of electrochientical solution deposited thin Mo–O–C–Se film layers, *Mater. Sci. Poland.*, (2010), 28, 93.
- [36] Bansal, A., Kumar, A., Kumar, P., Bojja, S., Chatterjee, A. K., Ray, S. S., Jain, S. L. Visible light-induced surface-initiated atom transfer radical polymerization of methyl methacrylate on titania/reduced graphene oxide nanocomposite, *RSC Advances.*, (2015), 5(27), 21189–21196.
- [37] Changsoo, L., Kihyun S., Yung, J. L., Chanwon, J., Hyuck M. L. Effects of shell thickness on Ag-Cu 2 O core-shell nanoparticles with bumpy structures for enhancing photocatalytic activity and stability. *Catalysis Today*, (2018), 303, 313-319.
- [38] Difa, X., Bei, C., Weicheng, W., Chuanjia, J., Jiaguo, Yu. Ag₂CrO₄/g-C₃N₄/graphene oxide ternary nanocomposite Z-scheme photocatalyst with enhanced CO₂ reduction activity, *Applied Catalysis B: Environmental*, (2018), 231, 368-380.
- [39] Huanhuan, L., Jiao, H., Jiufu, C., Junbo Z., Jianzhang, L., Ran, D. Preparation and characterization of novel Ag/Ag₂WO₄/ZnWO₄ heterojunctions with significantly enhanced sunlight-driven photocatalytic performance, *Solid State Sciences*, (2019), 95, 105923.
- [40] Sahu, A., Qi, L., Kang, M. S., Deng, D., Norris, D. J. Facile synthesis of silver chalcogenide (Ag₂E; E = Se, S, Te) semiconductor nanocrystals, *Journal of the American Chemical Society*, (2011), *133*(17), 6509-6512.
- [41] Sundar M. S., John P. S. Elefant, K. J., Schneider, C. M. Magnetoresistance in microwave synthesized Ag_{2+δ}Se, Phys. Rev. B (2001) 63, 212405.
- [42] Jinwoo, C., Jeffrey I. Z. Gas Phase Photochemical Synthesis of II/VI Metal Sulfide Films and *in Situ* Luminescence Spectroscopic Identification of Photofragments, . *Am. Chem. Soc.* (1997), 119, 16, 3838–3839.