Synthesis of Ag$_2$Se–graphene–TiO$_2$ nanocomposite and analysis of photocatalytic activity of CO$_2$ reduction to CH$_3$OH

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Abstract. The present work deals with the development of a new ternary composite, Ag$_2$Se–G–TiO$_2$, using ultrasonic techniques as well as X-ray diffraction (XRD), scanning electron microscopy (SEM), high transmission electron microscopy (HTEM), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy and UV–Vis diffuse reflectance spectra (DRS) analyses. The photocatalytic potential of nanocomposites is examined for CO$_2$ reduction to methanol under ultraviolet (UV) and visible light irradiation. Ag$_2$Se–TiO$_2$ with an optimum loading graphene of 10 wt% exhibited the maximum photoactivity, obtaining a total CH$_3$OH yield of 3.52 μmol g$^{-1}$ h$^{-1}$ after 48 h. This outstanding photoreduction activity is due to the positive synergistic relation between Ag$_2$Se and graphene components in our heterogeneous system.

Keywords. Graphene; photoreduction CO$_2$; semiconductors; CH$_3$OH; scavenger effect.

1. Introduction

In recent years, the significant increasing energy demand has been driven by growing world population. These days, the energy demand mostly depends on fossil fuels. Using fossil fuels produces greenhouse gases, which play the key role in global warming [1,2]. To overcome this problem, scientists are attempting to use alternative techniques to minimize the energy crisis and utilize CO$_2$. Three convenient approaches have been presented to reduce the amount of CO$_2$ in the atmosphere: (1) conversion of CO$_2$ into valuable solar fuels; (2) CO$_2$ capture and storage; and (3) CO$_2$ utilization [3–5]. Among these techniques, the photocatalytic reduction of CO$_2$ is the most promising technique to fulfill the energy crisis [6–10]. Although photocatalytic conversion of CO$_2$ using solar energy is the most convenient route for the transformation of CO$_2$, some barriers are involved in photocatalytic CO$_2$ reduction: (1) fast recombination of photo-induced electron and hole recombination; (2) slow charge consumption during redox reaction; and (3) poor light utilization [11,12]. To overcome these barriers, scientists have developed new photocatalysts such as TiO$_2$, ZrO$_2$, ZnO, ZnGa$_2$O$_4$, NaNbO$_3$ and SrTiO$_3$, which have been vastly used for CO$_2$ photoreduction [13–17]. Among these photocatalysts, TiO$_2$ is a promising candidate for CO$_2$ photoreduction due to its unique properties, including low cost, chemical stability, nontoxicity and abundance [18]. However, its usage is limited due to its large band gap (3.2 eV) and fast charge carrier recombination [19,20]. Consequently, to enhance the efficiency of TiO$_2$ towards CO$_2$ photoreduction, various methods have been used such as doping of metals or their oxides (e.g., Cu [21], Ag [22] and Pd [23] when these metals fill the interstitial sites) and replacing Ti in the substitutional sites or agglomerates formation on the surface of TiO$_2$, thus, changing the properties of TiO$_2$ [24]. Moreover, graphene is very easy to obtain from low-cost graphite using the Hummers method [25,26]. Owing to its unique properties (surface functionalities, large surface area and stability), graphene is a suitable candidate to anchor on the surface of semiconductor materials (TiO$_2$) and promote the charge transfer mechanism. The oxygen functionalities modify the particle size and shape of the semiconductor materials on the surface of graphene. Chen et al [27] reported that graphene is an excellent supporter to anchor TiO$_2$ nanocrystals for the graphene–TiO$_2$ synthesis, because graphene acts as a photosensitizer to enhance the light response of TiO$_2$ towards the visible range of the electromagnetic spectrum. Further, due to its unique electronic and optical properties, metal selenide has attracted considerable attention over the past few decades. Metal selenide has been coupled with large band gap semiconductors (TiO$_2$), which enhanced the photocatalytic efficiency [28]. Silver selenide is available in two different phases (α-Ag$_2$Se, high temperature phase and β-Ag$_2$Se, low temperature phase) with the phase transition point at 1331°C [29]. α-Ag$_2$Se is a known superionic conductor and is mostly used as a solid electrolyte in photorechargeable secondary batteries, while β-Ag$_2$Se is broadly used in thermalchromic materials as a photosensitizer due to its narrow band gap [30,31]. Zheo et al [32] prepared a TiO$_2$/Ag$_2$Se nanocomposite by interface reaction and their result suggested that the nanocomposite is an excellent photovoltaic with photocurrent properties towards visible light. On the other hand, Cao et al [33] incorporated a single-crystalline Ag$_2$Se complex nanostructure using
solvothernal techniques, the result of which indicated that the nanostructure has an excellent photocatalytic activity by the photodegradation of rhodamin B (RhB) dye using UV light irradiation. Here, we study a G–Ag₂Se–TiO₂ photocatalyst using an ultrasonication technique, and synthesize a nanocomposite characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), high transmission electron microscopy (HTEM), X-ray photoelectron spectroscopy (XPS), diffuse reflectance spectroscopy (DRS) and Raman spectroscopy. The main aim of this paper is to demonstrate an excellent photocatalytic-reduction ability of CO₂ with Ag₂Se–G–TiO₂ nanocomposites under light irradiation.

2. Experimental

2.1 Materials

Silver nitrate (AgNO₃), selenium powder (Se, 99%), ammonium hydroxide (NH₄OH, 25–28%), sodium sulfite (Na₂SO₃), sodium bicarbonate (NaHCO₃, 95%), and titanium (IV) n-butoxide (TNB, C₁₆H₃₆O₄Ti) were purchased from Duksan Pure Chemicals Co. Ltd., Republic of Korea. All chemicals were used without further purification. All solutions were used with distilled water.

2.2 Preparation of Ag₂Se–graphene–TiO₂ composite

Typical preparations of G–Ag₂Se–TiO₂ nanocomposite are as follows. Three grams of Na₂SO₃ and 0.3 g of selenium powder (Se, 99%) were mixed with 50 ml DI water and refluxed for 2 h to form Na₂SeSO₃ i.e., solution A. Then, 400 mg graphene oxide (GO) (which was prepared in the laboratory following the Hummers-Offeman method as reported in previous work) [34] and AgNO₃ (0.02 g) were mixed in 60 ml ethylene glycol by ultrasonication for 3 h to form a graphene oxide nanosheet (GONS)/Ag⁺² i.e., solution B. Solutions A and B were then mixed and heated at 60°C for 30 min to obtain a homogenous solution. Finally, the molar ratios of ethanol:H₂O:TNB = 35:15:4 were added to the obtained solution and sonicated at room temperature for 2 h using a controllable serial-ultrasonic apparatus (Ultrasonic Processor, VCX 750, 500 Watt, Korea, Power 500 Watt, frequency 20kHz, amplitude 50% and low intensity). The reaction solution was then left to cool and settle at room temperature after filtering with 47 mm Whatman filter paper at a pore size of 0.7 mm. The resultant powder was washed with distilled water five times, and dried in a vacuum oven at 100°C for 12 h; the solution was then transferred to an electric furnace for heat treatment at 500°C for 2 h. The same procedure was followed for the other control samples of Ag₂Se and Ag₂Se–graphene. The prepared nanocomposites were named as Ag₂Se, Ag₂Se–graphene and Ag₂Se–graphene–TiO₂.

2.3 Photocatalytic reduction of CO₂

In the photocatalytic experiments, the reduction of CO₂ with H₂O was carried out in a reactor designed in our laboratory reported in our pervious paper [35]. A typical reactor is comprised of a 500 W light irritation source (SOLAREDGE700, Perfect Light, China), closed chamber (with the dimensions of 20 cm length × 2.0 diameter), and carbon dioxide (CO₂) and nitrogen (N₂) gas (N₂ gas was used to remove gases from the reactor). One-hundred and fifty milligrams of the photocatalyst (Ag₂Se–G–TiO₂) and 0.05 mol l⁻¹ Na₂Se/Na₂S [36,37] were used as sacrificial reagents and added to 20 ml distilled water containing sodium bicarbonate (NaHCO₃, 0.04 M) and continually stirred for 2 h. Ultra-high-purity grade CO₂ gas was then purged through the reactor for 30 min. The suspension solution was then magnetically stirred and irradiated to visible light using a metal halide lamp (500 W, SOLAREDGE700, Perfect Light, China). The distance between the light source and photocatalyst was 10 cm. Moreover, the temperatures inside the reactor was maintained at 100°C using a heat sink. The reaction was continued for 2 d and at every 12 h interval, the reactor was left to cool naturally for CH₃OH desorption from the catalyst. Ten millilitres of the sample was then collected from the suspension solution using a syringe and a membrane filter. The collected sample was then analysed using gas chromatography (GC).

2.4 Characterization

The crystallinity and composition of the prepared samples were characterized using monochromatic high intensity CuKα radiation (λ = 1.5406 Å) in XRD (Shimadzu XD-D1). The surface state and structures of the prepared sample were examined using SEM (JS M-5600, JEOL, Japan) and TEM (JEM-2010, JEOL, Japan). XPS was performed using VG (Scientific VISA CA Lab 2000), and a monochromatic Mg X-ray radiation source. Raman spectra of the prepared samples were observed using a spectrometer (Jasco Model Name NRS-3100) with an excitation laser wavelength of 532.06 nm.

3. Result and discussion

The phase structure of the prepared (Ag₂Se–G–TiO₂) nanocomposites was analysed by XRD. Figure 1 shows that the XRD pattern of Ag₂Se–G has diffraction peaks at around 2θ of 25.2, 30.88, 32.52, 34.63, 36.95, 39.98, 40.20, 42.65 and 43.38°, which can be indexed to the characteristic peak (101), (102), (120), (112), (121), (013), (122), (113) and (201) plane reflections, respectively, with orthorhombic Ag₂Se phase with a lattice parameter a = 4.33 Å, b = c = 7.06 Å (JCPDS PDF#00-024-1401) [38]. The TiO₂ peaks appeared at around 2θ = 25.20, 47.99, 53.82, 55.01, 62.62 and 68.75°, corresponding to the (101), (200), (105), (211), (204) and (116) diffractions as the anatase crystal phase with lattice parameter a = b = 3.78 Å and c = 9.51 Å (JCPDS PDF#00-021-1279). The TiO₂ (101) and graphene (002) peaks overlap each other in the same 2θ values; it is thus, very difficult to differentiate both peaks and the diffraction intensity peaks of the TiO₂ and graphene are very low, indicating that graphene oxides
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Figure 1. X-ray diffraction (XRD) patterns of Ag$_2$Se–G–TiO$_2$ composites.

are reduced to graphene [39,40]. Further, the fluctuation of diffraction peaks of the Ag$_2$Se–G–TiO$_2$ nanocomposites also demonstrates the increased amount of graphene and suppression of the crystalline phases. The compression in the peak intensity indicates that the lattice structure of Ag$_2$Se is distorted by the interaction with GO [41,42].

Figure 2a and b describes the overall morphology of the prepared sample obtained by SEM, which shows that the pure Ag$_2$Se particles are uniformly distributed on graphene oxide sheets, but the particle size and shape are difficult to distinguish in SEM. The graphene is shown as a sheet-like structure that is broken off in different directions, with a nanocomposite plate-like shape with a partial agglomerate; this plate-like structure demonstrated the existence of oxygen functionalities on the surface of the graphene [43]. Figure 2c and d shows the TiO$_2$ particles with an almost spherical shape, uniformly distributed on the graphene sheet. In addition, the final image clearly shows the difference between the binary and ternary composites. After the coupling of TiO$_2$, a bright spot appears in the ternary composite, showing that the synthesis of G–Ag$_2$Se–TiO$_2$ particles was successful and has a proper distribution pattern.

The microstructures of the Ag$_2$Se–G–TiO$_2$ were investigated by using high-resolution transmission electron microscopy (HRTEM). Figure 3 illustrates the HRTEM images of the prepared sample with different magnifications. The irregular dark images shown in figure 3a and b indicates that Ag$_2$Se was highly agglomerated, while TiO$_2$ nanoparticles were uniformly distributed on the graphene nanosheet, revealing the role of the Ag$_2$Se bridge-like support between TiO$_2$ and the graphene sheet [44,45]. Using the image J software, the average particle size of Ag$_2$Se ranges from

Figure 2. SEM image of Ag$_2$Se–G–TiO$_2$ composites (a) SEM images of Ag$_2$Se nanocomposites, (b) SEM images of Ag$_2$Se–G nanocomposites, (c) TiO$_2$ nanoparticles and (d) SEM images of Ag$_2$Se–G–TiO$_2$ nanocomposites.
Figure 3. TEM image of Ag$_2$Se–G–TiO$_2$ composites with different magnification.

10–20 nm, and TiO$_2$ ranges from 12–40 nm. Figure 3c shows that the lattice spacing of the Ag$_2$Se is $\sim 0.249$ nm, corresponding to the characteristic of the (013) crystal planes of $\beta$-Ag$_2$Se nanoparticles [33,46]. Also, the lattice spacing of the anatase TiO$_2$ phase is 0.35 nm [41,47]. Hence, the layered Ag$_2$Se supports the TiO$_2$ nanoparticles on the graphene sheet and provides a bridge between TiO$_2$ and the graphene nanosheet; we thus assume that an ultrasonication technique is favourable for enhancing the photocatalytic properties of the Ag$_2$Se–G–TiO$_2$ nanocomposite [48].

XPS was used to determine the chemical bonding and composition of the Ag$_2$Se–G–TiO$_2$ nanocomposite consisting of Ag$_2$Se, graphene and TiO$_2$. The XPS survey spectrum in figure 4a shows peaks corresponding to Ag, Se, O, C and Ti consistent with the formation of Ag$_2$Se–G–TiO$_2$ nanocomposites, while figure 4b and c shows the two main peaks of the Ag core level corresponding to Ag$_2$d$_{3/2}$ and Ag$_2$d$_{5/3}$ at 374 and 368 eV, respectively. The selenium Se3d binding energy peak located at 54.8 eV indicates the presence of oxidation state of Se$^{\text{+}}$ [49,50]. From figure 4d, the C1s spectra show the presence of carbon in the Ag$_2$Se–G–TiO$_2$ composites. The C1s spectrum is located at 284.8 eV. The C1s binding energy shows C–O and C=O functional groups, which indicate that our prepared composites still contain partial oxygen functional groups [51]. These oxygen functional groups are beneficial for enhancing the light absorption towards the visible region [52]. The O1s peak is located at 531.75 eV from contributions of the C=O and O–C–OH groups (figure 4e). The O1s peak shows that after heat treatment, the conversion to other chemical species is also possible, and the other peak at 534 eV indicates that the C–OH group is still present [53–55]. Figure 4f shows the Ti2p peaks located at 459.8 and 465.7 eV, which indicate the Ti$^{4+}$ oxidation state during synthesis, where the Ti2p$_{3/2}$ peak becomes narrow and its position changes, indicating the presence of some Ti in low valance (Ti$^{3+}$) form [55].

Further, Raman spectroscopy clearly illustrates the electronic structure of the carbon materials and the structural properties of Ag$_2$Se–G–TiO$_2$. Even a minor change in the band intensity and shifting provides the complete details
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Figure 4. XPS results of the Ag$_2$Se–G–TiO$_2$ nanocomposite (a) survey scan spectra, (b) Ag peaks, (c) Se 3d, (d) C 1s, (e) O 1s and (f) Ti 2p.

of the nature of carbon–carbon bonds and defects [41]. Figure 5 shows details on the graphene oxide and Ag$_2$Se–G–TiO$_2$ nanocomposites. The strong peak observed around at the 230 cm$^{-1}$ wave could be due to the characteristic vibrations of the Ag$_2$Se band [56–58], while the peaks around 412 cm$^{-1}$ show the presence of the anatase TiO$_2$ band [59]. The characteristic D band appears at 1354 cm$^{-1}$, revealing the disorder in the atomic arrangements. This indicates the increasing modes
of the sp³ atoms in the carbon and the G bands appearing at 1584 cm⁻¹; this provides information on the in plane vibration of the sp³ bonded carbons [60]. The nature of the defects can be determined from the intensity ratio of the corresponding D–G bands. The calculated ratios of the D and G bands (I_D/I_G ratio) demonstrate that the graphene consists of several layers, as explained in the previously mentioned paper [61].

For the eradication of environmental pollutants, we need an ideal photocatalyst with a maximum efficiency (UV and visible) in the range of the electromagnetic spectrum. DRS is used to understand the absorption response in the Ag₂Se–G–TiO₂ nanocomposites to the electromagnetic spectrum. Figure 6 illustrates that our nanocomposites are mostly in the visible part of the electromagnetic spectrum and the total spectra are similar to carbon-based semiconductor materials [62]. Figure 6 shows that after the introduction of graphene with Ag₂Se and TiO₂, the absorption edge shifts towards the visible region. Due to the carbon-based structure of graphene, the unpaired π electron merges with the metal nanoparticles, causing a shift in the band edges and enhancing the light absorption towards the visible region. Therefore, the attachment of graphene with Ag₂Se and TiO₂ increases the absorption intensities in the entire visible region, confirming the improved efficiency of the light-harvesting activity as shown in figure 6. To calculate the band gap of the Ag₂Se–G–TiO₂ nanocomposite, the Kubelka–Munk function \( F(R) = (1 - R)^2/2R \) [63] is used. The obtained plot in figure 6 shows that the banding energy of the Ag₂Se–G–TiO₂ nanocomposites was 2.6 eV, which was almost less than that of pure TiO₂ and Ag₂Se. The reducing banding energy of the Ag₂Se–G–TiO₂ nanocomposite is due to the distribution of the Ag₂Se and TiO₂ nanocomposites on the graphene sheets. Moreover, the partial agglomeration can change the absorption property, reducing the band gap of the nanocomposite [64,65].

The yield of methanol according to the time of irradiation in the photocatalytic experiments is shown in figure 7a. The reaction quantum yield (QE) is estimated using the CH₃OH yield, considering that six electrons are required to reduce CO₂ to CH₃OH. The equation is as follows [66,67]:

\[
\text{Methanol (\%)} = \frac{100 \times (6 \times \text{mole of CH₃OH yield})}{(\text{mole of photon absorbed by catalyte}) - \text{mole of photon}} = \frac{I \times S}{N_A \times E},
\]

where \( I \) is light intensity (0.12 mW cm⁻²), \( S \) the irradiated area of the reactor (30 cm × 15 cm), \( E \) the photon energy (4.97 × 10⁻¹⁹ J at 400 nm) and \( N_A \) the avogadro number (6.02 × 10²³ mol⁻¹).

The result reveals that the photocatalytic efficiency of TiO₂ can be greatly enhanced through the attachment of graphene and Ag₂Se to the TiO₂ structure. In addition, CH₃OH was detected as a major product from the photoreduction of CO₂ over the Ag₂Se–G–TiO₂ photocatalysts. The total methanol yield and quantum yield of the photocatalysts for 48h using a UV/visible light source was calculated and are shown in table 1a and b. The photocatalytic reduction of CO₂ under UV light is more active than under visible light irradiation, and the maximum CH₃OH yield of Ag₂Se–G–TiO₂ after 48h was found to be 1.3420 μmol g⁻¹h⁻¹ without using any sacrificial reagents. Further, to improve the catalytic activity of the photoreduction of CO₂, Na₂SO₃ is used as a scavenger as shown in figure 7b. Generally, Na₂SO₃ was used to increase the photocatalytic activity of the semiconductors and to avoid the oxidation of the reduction products in liquid phase. Na₂SO₃ is a highly efficient electron donor, which is used as a cycling electron donor to combine CO₂ photoreduction with water splitting to improve the overall efficiency [68].
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Figure 7. The methanol yield in the photocatalytic reduction of CO$_2$ under UV/visible light irradiation of different nanocomposites. (a) methanol yield under UV/visible light irradiation without scavenger, (b) methanol yield under UV/visible light irradiation using Na$_2$SO$_3$ and (c) weight percentage of graphene in Ag$_2$Se–G–TiO$_2$ nanocomposite.

Table 1. Effect of preparation method on methanol yield and quantum yield.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CH$_3$OH yield ($\mu$mol g$^{-1}$ h$^{-1}$)</th>
<th>Quantum yield (QE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Visible light</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag$_2$Se–G–TiO$_2$ (12 h)</td>
<td>0.3665</td>
<td>0.0530</td>
</tr>
<tr>
<td>Ag$_2$Se–G–TiO$_2$ (24 h)</td>
<td>0.5734</td>
<td>0.0770</td>
</tr>
<tr>
<td>Ag$_2$Se–G–TiO$_2$ (36 h)</td>
<td>0.9020</td>
<td>0.1487</td>
</tr>
<tr>
<td>Ag$_2$Se–G–TiO$_2$ (48 h)</td>
<td>0.9255</td>
<td>0.1504</td>
</tr>
<tr>
<td>(b) UV light</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag$_2$Se–G–TiO$_2$ (12 h)</td>
<td>0.8623</td>
<td>0.1395</td>
</tr>
<tr>
<td>Ag$_2$Se–G–TiO$_2$ (24 h)</td>
<td>0.9814</td>
<td>0.1647</td>
</tr>
<tr>
<td>Ag$_2$Se–G–TiO$_2$ (36 h)</td>
<td>1.2821</td>
<td>0.2090</td>
</tr>
<tr>
<td>Ag$_2$Se–G–TiO$_2$ (48 h)</td>
<td>1.3420</td>
<td>0.1522</td>
</tr>
</tbody>
</table>

Table 2. Effect of preparation method on methanol yield and quantum yield.

<table>
<thead>
<tr>
<th>Sample after Na$_2$SO$_3$</th>
<th>CH$_3$OH yield ($\mu$mol g$^{-1}$h$^{-1}$)</th>
<th>Quantum yield (QE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Visible light</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag$_2$Se–G–TiO$_2$ (12 h)</td>
<td>1.3380</td>
<td>0.2237</td>
</tr>
<tr>
<td>Ag$_2$Se–G–TiO$_2$ (24 h)</td>
<td>1.5450</td>
<td>0.2054</td>
</tr>
<tr>
<td>Ag$_2$Se–G–TiO$_2$ (36 h)</td>
<td>1.6100</td>
<td>0.2613</td>
</tr>
<tr>
<td>Ag$_2$Se–G–TiO$_2$ (48 h)</td>
<td>1.9170</td>
<td>0.3141</td>
</tr>
<tr>
<td>(b) UV light</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag$_2$Se–G–TiO$_2$ (12 h)</td>
<td>1.8862</td>
<td>0.3061</td>
</tr>
<tr>
<td>Ag$_2$Se–G–TiO$_2$ (24 h)</td>
<td>2.4682</td>
<td>0.4005</td>
</tr>
<tr>
<td>Ag$_2$Se–G–TiO$_2$ (36 h)</td>
<td>2.9683</td>
<td>0.4817</td>
</tr>
<tr>
<td>Ag$_2$Se–G–TiO$_2$ (48 h)</td>
<td>3.5262</td>
<td>0.5722</td>
</tr>
</tbody>
</table>

The methanol yield of Ag$_2$Se–G–TiO$_2$ under UV (VL-4.LC, 8 W, 365 nm)/visible light is almost higher than that of without using a scavenger. The CH$_3$OH yield of Ag$_2$Se–G–TiO$_2$ with different time intervals is shown in table 2a and b. The photoreduction rate of the pure TiO$_2$ and Ag$_2$Se–graphene nanosheets is smaller than that of the Ag$_2$Se–G–TiO$_2$ nanocomposites. This shows that a strong interaction between graphene and the attached semiconductor materials, Ag$_2$Se supported by TiO$_2$, allows good interfacial contact with the graphene sheet by enhancing the synergistic effect between Ag$_2$Se and the
graphene sheet, which plays an important role in photoreduction activity. Hence, graphene plays an important role in the catalytic photoreduction of CO$_2$. The optimum content of graphene in the Ag$_2$Se–G–TiO$_2$ system was found to be 8 wt% as shown in figure 7c. The further increase in the amount of graphene in the ternary system was found to decrease the photocatalytic performance, possibly due to the increased light absorption of graphene itself, which affects the excitation of Ag$_2$Se and TiO$_2$ in the composites [66].

Primarily, it is known that the photocatalytic properties of semiconductors are due to the formation of photogenerated charge carrier (holes and electrons), which is due to the absorption of photon with energy greater or equal than the band energy ($E_g$) of separating the valence band (VB) from the conduction band (CB) [69,70]. From the proposed mechanism shown in figure 8 that the energy of the photon is equal or greater than the band gap energy ($E_g$), and thus, photogenerated electrons and holes diffuse to the surface of the semiconductor for desire chemical reaction; however, due to the absence of co-catalysts or lack of active sites, the number of excited electrons rapidly decreases. This increases the electron–hole recombination on the surface of the semiconductors. To overcome this deficiency and enhance the overall efficiency of the semiconductor, a different strategy needs to be used, such as doping of the nanostructure of the semiconductor, semiconductor heterojunction or nanocarbon material (graphene) on the semiconductor. This not only minimizes the recombination rate, but also enhances the visible light response. Further, metal ion (Ag) doping generates impurity levels in the forbidden region of the wide gap of TiO$_2$. In addition, the metal ion (Ag) can act as an electron trap and an active site for highly favourable CO$_2$ photoreduction; TiO$_2$ doped with silver has an excellent ability to reduce CO$_2$ to CH$_3$OH [71,72]. For better photocatalytic activity, a heterogeneous system needs to be introduced. The main advantage of the heterogeneous system is that it greatly improves the electron–hole separation and increases the lifetime of the charge carrier. Attachment of nanoparticles on the graphene sheet is helpful for converting CO$_2$ to CH$_3$OH [73] under the UV/visible light irradiation. The photogenerated electron in the VB of Ag$_2$Se easily transfers to the graphene sheet, which slows down the recombination of electron–hole pairs and enhances the electron transport to the catalytic sites for the reduction of CO$_2$. Due to its large surface area and various defective sites, graphene can easily absorb CO$_2$, and the photogenerated electron on Ag$_2$Se is then transferred to the active sites of graphene. The absorbed CO$_2$ is then reduced to CH$_3$OH [74]. The photocatalytic CO$_2$ reduction to convert the CH$_3$OH mechanism is expressed in equations (1–8).

Equations (1)–(4) explain the reaction mechanism of Ag$_2$Se, TiO$_2$ and graphene, exhibiting the production of the photoexcited electron–hole pair and their subsequent reaction (equations (5–8)) [75] reveal the oxidation and reduction processes, in which the holes are used for oxidation, while the electrons are used for the reduction of CO$_2$. In the photoreduction mechanism, the generated electron reacts with the dissolved oxygen modules and produces oxygen peroxides.
radicals. The positive holes are absorbed in water, resulting in the production of hydroxyl radicals (OH) and hydrogen ions (H\(^+\)) and then reacts with the excited electrons, leading to the formation of 'H, while CO\(_2\) simultaneously reacts with the excited electron and CO\(_2^-\) is formed. CO\(_2^-\) is finally converted to CH\(_3\)OH.

4. Conclusion

Heterogeneous Ag\(_2\)Se--G--TiO\(_2\) was prepared using ultrasonic techniques. The SEM and HRTEM images of the prepared sample demonstrate that the Cu\(_2\)Se and TiO\(_2\) are uniformly dispersed on graphene sheets. The average particle sizes of Ag\(_2\)Se ranged from 10 to 20 nm, while those of TiO\(_2\) ranged from 12 to 40 nm. The attachment of Ag\(_2\)Se and graphene to TiO\(_2\), the absorption and reducing CO\(_2\) to CH\(_3\)OH. DRS results reveal that after the attachment of graphene to Ag\(_2\)Se and TiO\(_2\), the absorption edge shifts towards the visible region, promoting an excited electron charge carrier, and the interface of Ag\(_2\)Se and graphene was found to be due to the synergistic effect of graphene and Ag\(_2\)Se by increasing the recombination time. It is also concluded that the different wt% also affected the photocatalytic efficiency. The optimum content of graphene to Ag\(_2\)Se and TiO\(_2\) is finally reached 3.523\,μmol g\(^{-1}\)h\(^{-1}\). It is expected that the present research will facilitate new methods of using graphene-based materials to promote an efficient heterosystem for CH\(_3\)OH production.

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