Preparation of Nanowire like WSe$_2$-Graphene Nanocomposite for Photocatalytic Reduction of CO$_2$ into CH$_3$OH with the Presence of Sacrificial Agents

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A nanowire-like WSe$_2$-graphene catalyst was prepared via ultra-sonication and was tested in terms of the photocatalytic reduction of CO$_2$ into CH$_3$OH under irradiation with UV/visible light. The prepared nano-composite was further characterized via XRD, SEM, TEM, Raman and XPS. The photocurrent analysis was further tested for its photocatalytic reduction of CO$_2$ using gas chromatography (GCMS-QP2010 SE). To further improve the the photo-catalytic efficiency, a sacrificial agent (Na$_2$S/Na$_2$SO$_3$) was added to the WSe$_2$-graphene nanocomposite and was found to improve the photo-catalytic efficiency, with the methanol yield reaching 5.0278 µmol g$^{-1}$ h$^{-1}$. Our present work provides a convenient way to prepare nanomaterials various morphologies that have future applications for environmental remediation.

The increase in the amount of the CO$_2$ emissions in the environment has reached an alarming level, greatly contributing to global warming$^1$, and in the last few decades, the shortage of fossil fuel resources has resulted in an increased demand for energy production from different sources, including photovoltaic and photocatalytic H$_2$ production. One such technology is photocatalytic CO$_2$ reduction, which is a most valuable approach to overcome both global environmental and energy problems due its low cost, clean energy production, and environmental friendliness$^2$. In particular, the photocatalytic reduction of CO$_2$ can convert noxious gasses (carbon dioxide) into profitable solar fuels, i.e., CO, HCHO, CH$_3$OH, and CH$_4$ by using solar energy$^4,5$. To date, many photocatalysts such as TiO$_2$, CdS, g-C$_3$N$_4$, ZnO and Bi$_2$WO$_6$ have been shown to achieve the photo reduction of CO$_2$$^6$–$^{10}$. Unfortunately, there are limits to the practical applicability of these semiconductors because the efficiency of the CO$_2$ conversion into useful products is very low due to many factors of the CO$_2$ reduction process, e.g., band gap tuning, charge carrier recombination, and light utilization$^{11}$. Due to the wide band gap energy, most materials are unable to absorb visible light, and on the other hand, small band gap semiconductors exhibit a fast recombination phenomenon. To overcome this and to find an achievable process, highly efficient, low cost transition metal dichalcogenides (TMDC) have been investigated$^{12}$–$^{15}$. The generalized formula for TMDs is MX$_2$, where M is transition metal element of group 4, 5 or 6 and X represents a chalcogen. Tungsten diselenide (WSe$_2$) is a semiconductor that belongs to the TMDC family. Its structure consists of Selenium and tungsten held together by a weak van der Waals force that allow the material to be exfoliated into monolayers$^{16,17}$. Moreover WSe$_2$ is a layered semiconductor with a small band gap of approximately 1.6 eV$^{18}$. It has unique electrical transport performance, and its use was recently reported in many advanced energy storage applications, such as in superconductors$^{19}$, lithium ion batteries$^{20}$, photodetectors$^{21}$, and photocatalytic hydrogen production$^{22}$ in solar cells. Furthermore, Li, Yanguang et al. and Merki, Daniel et al. indicated that both the theoretical calculation and experimental results for the hydrogen evolution reaction of transition metal dichalcogenide (WSe$_2$) materials appears to be from active edge sites that play an important role in hydrogen evolution reaction catalysis$^{23,24}$. However, due to the intrinsic interlayer Van der Waals attraction, the layered TMDC materials can be easily re-stacked as a result of reducing the active edge sites. Therefore, to improve photocatalytic activity, the TMDC (WSe$_2$) materials are combined with 2D carbon material such as graphene.

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Graphene has unique properties, including a large surface area, good conductivity, and high flexibility, and it is used in high-performance energy storage devices. Therefore, coupling with a photocatalyst may improve the photocatalytic reduction efficiency of CO\textsubscript{2} to fulfill the practical requirements. Liange et al. first described that coupling with a semiconductor is one of the best ways to boost the photocatalytic reduction efficiency of CO\textsubscript{2}. Recently, graphene coupled with TMDCs (WSe\textsubscript{2}) was reported for the hydrogen evolution reaction (HER), high-performance oxygen reduction reaction (ORR), and in a superconductor. However, the WSe\textsubscript{2} chalcogenide family has not yet been analyzed for the photocatalytic reduction activity of CO\textsubscript{2}. In the present study, we report on WSe\textsubscript{2}-graphene nano composites prepared via ultra-sonication. The prepared samples (WSe\textsubscript{2}-graphene) were used for CO\textsubscript{2} reduction, and the results exhibit a high efficiency for photocatalytic CO\textsubscript{2} conversion under UV and visible light irradiation.

**Results and Discussion**

**Characterization of catalytic materials.** The XRD patterns of the WSe\textsubscript{2}-graphene nanocomposites is shown in Fig. 2(a), the diffraction peaks at 13.54, 32.50, 38.45, 41.86, 47.75, 56.25, 58.10, 66.77, 69.45, 72.55 and 76.78° correspond to (002), (100), (103), (006), (105), (112), (200), (203), (116) and (205) directions, respectively \( (a = b = 0.329 \text{ nm}, c = 1.298 \text{ nm}, \text{ JCPDS PDF# 00-38-1388}) \). However, no other diffraction peaks form any other chemical species were observed in the prepared sample. For the GO analysis, a sharp peak (002) occurs at 13.44°, revealing that the graphite power was converted into graphene oxide by expanding the d-spacing from 3.5 to 6.78 Å. Moreover, the results indicate that the XRD signals of GO are very weak and are overlapped with those of WSe\textsubscript{2}-graphene at 13.54°. Therefore, the measurements were unable to detect the weaker diffraction peaks of GO. Further EDX spectra confirm the presence of the main elements in the catalyst composites. The Fig. 2(b) shows the presence of the prime elements C, O, W, and Se. The C elemental peak is derived from graphene sheet, and W, Se and O are the precursor material.

SEM observations were carried out to investigate the surface and structural morphology. Figure 3 shows the SEM images of WSe\textsubscript{2}-graphene at different magnifications. Figure 3(a) shows the wire-like and nanoscale WSe\textsubscript{2} morphology composed of interlaced and ultrathin nanosheets uniformly dispersed on the graphene nanosheet. Figure 3(b) and (c) show that graphene has an irregular structure that is broken off in different directions. Figure 3 also indicates that the WSe\textsubscript{2} nanowires extensively grow on the surface of the graphene nanosheet.
Figure 3. SEM images of WSe$_2$-graphene composite with different magnification.

Figure 4. TEM image of WSe$_2$-graphene.
depicts bright nanowire WSe₂ shapes that are properly coated on the graphene surface, indicating that graphene nanosheets provide a good platform for the nucleation and successive growth of WSe₂ layers, and growth on WSe₂ in graphene is possible due to the precursors that are attached to the graphene oxide through functional groups ²³, ³⁴–³⁶. Figure 4(a–d) shows transmission electron microscopy (TEM) that further confirms the morphology and shape of the WSe₂-graphene nanocomposites. Figure 4(a–c) shows the WSe₂-graphene nanocomposites at different magnifications. The WSe₂ is clearly seen to have dark imaged compounds that are almost very small in a spherical form, layer form, and a highly agglomerated structure attached to the surface of the graphene sheets. Moreover, several layers of the WSe₂ are covered with the graphene nano sheets, and the average size of the WSe₂ is measured to be approximately 6 to 10 μm using the ImageJ software.

Figure 4(d) shows the formation of single-crystalline and few-layered WSe₂ nanosheets. Different WSe₂ flakes indicating that the particles sizes fluctuate between 30 nm to 190 nm. When compared to the bulk material, the size of the WSe₂ layers decreases, which is may be due to the discontinuity of the particles induced by sonication and particle selection by centrifugation ³⁷. The precise structural properties of the WSe₂-graphene were analyzed via Raman spectroscopy. Figure 5 provides comprehensive detail of the GO and WSe₂ nanocomposites (e.g., crystal structure and no. of layers), Fig. 5 shows the Raman signature energy band of the WSe₂ located at 200 to 400 cm⁻¹. The typical Raman spectra for WSe₂ shows a band at the A₁g (out-of-plane) (255 cm⁻¹) and E₁2g (in-plane) mode (250 cm⁻¹)³⁸.

Figure 5 also shows that the characteristics of the graphene Raman shifts for the D, G, and 2D bands. The D band is located at 1360 cm⁻¹, which shows the presence of disorder in the atomic arrangements or edge effect of graphene, while the G band appears at 1590 cm⁻¹. Both the G and D band show the vibration of the carbon atoms in disorder or defect sites and the in-plane vibration of sp² and sp³ bonded carbon atoms ³⁹. These two bands (D 1360 cm⁻¹, G 1590 cm⁻¹) indicate an interaction between rGO and selenide nanosheets, which improves the stability of the catalyst interface and provides a high stability for the nanocomposites. A 2D band appears at 2690 cm⁻¹ to express the degree of graphitization. Moreover, the 2D band is smaller than the G band in our spectrum, which indicates the presence of a few layers of graphene sheets ⁴⁰–⁴³.

XPS measurements were carried out to assess the elemental composition of the WSe₂-graphene nanocomposite. Figure 6(a) shows the XPS spectrum, which indicates the presence of W, Se, C and O and shows the formation WSe₂-graphene nanocomposite. Figure 6(b) shows the XPS spectrum of W and the binding energies of W⁴f⁷/₂, W⁵f⁵/₂ and W⁵p⁳/₂ at positions of 31.90, 34.80 and 37.90 eV, respectively. The W⁴f⁷/₂ and W⁵f⁵/₂ binding energy peaks express the elemental chemical binding state of W, while the peak positioned at 37.70 eV is attributed to the core level of W⁵p⁳/₂ from WO₃ due to the partial oxidation of the WSe₂ layers ⁴⁴, ⁴⁵. The binding energy for the Se 3d⁵/₂ core level peak of 54.90 eV confirms a lattice Se⁻² of the WSe₂-graphene hybrid (Fig. 6c). The core peak level of Se3d between 50 to 56 eV shows the absorbance of pure Se in a catalysts, which is conclude that WSe₂-graphene nanocomposite is free from any impurity ⁴⁶, ⁴⁷. Figure 6(d) shows the core level XPS spectrum of the O1s, peak located at 532.90 eV, which shows the carbonyl and carboxyl groups, while the C1s (Fig. 6(e)) spectrum is located at 284.5 eV. These results show that the spectra can fit with oxygen containing functional groups (C=O, C-O), which is evident in the reduction of GO to rGO ⁴⁶–⁵².

The UV-vis diffuse reflectance spectrum of the WSe₂-graphene nanocomposite was displayed in Fig. 7(a). The band gap energy value was achieved where the straight line approaching the curve intersects the horizontal axis. As the results from Fig. 7(a), the band gap energy values of the WSe₂-graphene nanocomposite was 2.68 eV. The photoelectrochemical current response was investigated by employing different materials to decorate the ITO sheet used as a photoanode. The photocurrent of each prepared sample was calculated in a 0.1 M KCl solution containing 0.1 M TEA under “on-off” light illumination cycles at a bias of 0 V vs. Ag/AgCl, as shown in Fig. 7(b). The photorepons for graphene was non-existent because graphene could not be excited, as shown in curve a⁴³ to the nature of graphene, which requires further reduction steps to generate a photocurrent signal ⁴⁴. This Fig. 7(b) displays the photocurrent response of the ITO/WSe₂-graphene based on time, which was repeatedly measured.
five times at 20-s intervals under visible irradiation. No current was observed in the dark, which clearly suggests that no photoinduced charge separation took place. When the light was turned on, the photocurrent intensity was significantly increased to 121.21 $\mu$A. This may have been due to the photoinduced electron–hole separation at the WSe$_2$, in which the holes were scavenged by the TEA, and graphene acted as an electron transfer medium. Thus, the electrons were transported to the ITO electrode, resulting in photocurrent generation. The electrode showed a pronounced and stable photocurrent response during the light “on-off” condition, which it maintained.

**Photocatalytic performance.** We assessed the photocatalytic activity of the pure WSe$_2$ and WSe$_2$-graphene composites for 48 h during UV ($\lambda > 300$) and visible ($\lambda > 400$) light irradiation, and every 12 h interval sample withdraw manually from the reactor using a gas-tight syringe, then the collected sample was centrifuged and characterized via gas chromatography. Figure 8 displays the CH$_3$OH yield for the pure WSe$_2$ and WSe$_2$-g nanocomposites. The control experiment determined that no methanol yield was produced in the absence of photocatalysts or light irradiations or both. The gas chromatographic study shows that only CH$_3$OH was successfully achieved as a reduction product. Furthermore, graphene is an electron donor for the reduction of CO$_2$ as a substitute carbon source to produce CH$_3$OH, and H$_2$O was a reactant of the CO$_2$ reduction. Figure 8(a) shows that the effect of the photocatalytic reduction of CO$_2$ with pure WSe$_2$ and WSe$_2$-graphene under UV light was higher than that for the same composite under visible light.

The methanol yields and quantum yields for the WSe$_2$-graphene nanocomposite with different time intervals and different conditions under UV/Visible light irradiation are shown in Tables 1 and 2. The methanol yield and quantum yield with WSe$_2$-graphene (12 h), WSe$_2$-graphene (24 h), WSe$_2$-graphene (36 h) and WSe$_2$-graphene (28 h) under visible light were 2.2434 (0.3285), 2.7021 (0.4435), 3.3243 (0.5346) and 3.5509 (0.5779) $\mu$mol g$^{-1}$h$^{-1}$, and under UV light were 2.8854 (0.4596), 3.1835 (0.3165), 3.7778 (0.6040) and 4.3257 (0.7053) $\mu$mol g$^{-1}$h$^{-1}$.
**Figure 8.** The methanol yields in the photocatalytic reduction of CO₂ under UV/visible light irradiation by using pure WSe₂ and WSe₂-graphene nanocomposites as photocatalyst (a) without Na₂SO₃, (b) with Na₂SO₃ (c) GC chromatogram of photoreaction using WSe₂-graphene, after 48 h and (d) 13C NMR (Proton decoupled).

| WSe₂-graphene (visible light) | CH₃OH yields (µmol g⁻¹ h⁻¹) | Quantum yields (QE) |
|-------------------------------|-------------------------------|---------------------|
| WSe₂-graphene (12h)           | 2.2434                        | 0.3285              |
| WSe₂-graphene (24h)           | 2.7021                        | 0.4435              |
| WSe₂-graphene (36h)           | 3.3243                        | 0.5346              |
| WSe₂-graphene (48h)           | 3.5509                        | 0.5779              |
| WSe₂-graphene + Na₂SO₃ (visible light) | CH₃OH yields (µmol g⁻¹ h⁻¹) | Quantum yields (QE) |
| WSe₂-graphene (12h)           | 2.8854                        | 0.4596              |
| WSe₂-graphene (24h)           | 3.1835                        | 0.3165              |
| WSe₂-graphene (36h)           | 3.7778                        | 0.6040              |
| WSe₂-graphene (48h)           | 4.3257                        | 0.7053              |

**Table 1.** Methanol Production condition with methanol yields and quantum yields under visible light.

| WSe₂-graphene (UV light) | CH₃OH yields (µmol g⁻¹ h⁻¹) | Quantum yields (QE) |
|--------------------------|-------------------------------|---------------------|
| WSe₂-graphene (12h)      | 2.5134                        | 0.3776              |
| WSe₂-graphene (24h)      | 3.2686                        | 0.4294              |
| WSe₂-graphene (36h)      | 3.7746                        | 0.5672              |
| WSe₂-graphene (48h)      | 3.5233                        | 0.3535              |
| WSe₂-graphene + Na₂SO₃ (UV light) | CH₃OH yields (µmol g⁻¹ h⁻¹) | Quantum yields (QE) |
| WSe₂-graphene (12h)      | 3.1848                        | 0.4115              |
| WSe₂-graphene (24h)      | 3.7765                        | 0.5606              |
| WSe₂-graphene (36h)      | 4.3246                        | 0.6530              |
| WSe₂-graphene (48h)      | 5.0278                        | 0.8159              |

**Table 2.** Effect of preparation method on methanol yields and quantum yields under UV light.
g−1h−1, respectively. Na2SO3 was used as a sacrificial reagent to further enhance the catalytic activity of the binary graphene-based nanocomposites in the photoreduction of CO2, as shown in Fig. 8. Figure 8(b) shows that the efficiency of the methanol yield of the pure WSe2 and WSe2-graphene nanocomposite under UV/visible light is almost two times greater than that of the nanocomposite without using scavenger (Na2SO3), and Fig. 8(c) shows a GC calibration curve for the quantification of methanol after 48 hours. The sacrificial reagent plays a crucial role in attaining the stability of the photocatalysts because of the well-known process of photocorrosion of sulfides. For further confirmation of final product CH3OH, the products were recovered after 18 h and 24 h of irradiation and analyzed by 13C NMR (Proton decoupled) (Fig. 8d). A single peak was obtained at 48.96 ppm for both, as it is due to methanol, it is verified that photocatalytic conversions of CO2 yield mainly CH3OH. It is also substantiated by GC. For stability and recyclability, the WSe2-graphene nanocomposite was tested for photocatalytic conversion of CO2 into CH3OH under UV/Visible light irradiation. The WSe2-graphene (48 h) was reused for six consecutive runs, and only a minor change in the CH3OH yield rate was found, indicating that the prepared nanocomposite is highly stable and can be used for a continuous photocatalytic reduction system of CO2.

A further explanation of the proposed photocatalytic mechanism is given in Fig. 9, which shows that the WSe2 nanomaterial absorbs light of the solar spectrum and creates photo-generated charge carriers (holes and electrons). However, due to the narrow bandgap of the WSe2 nanocomposite, these electron-holes recombine very quickly, and their photocatalytic efficiency is therefore limited. To improve the photocatalytic efficiency, the WSe2 nanocomposite was attached to a graphene nanosheet since graphene is an electron acceptor/transporter that plays an important role in the separation of the transport electron-hole pairs in the binary system55. The excited electron and hole in the conduction band of WSe2 can be conveniently shifted to the graphene nanosheet, which decelerates the recombination of the electron-hole pairs and thus promotes the electron transport to the catalytic sites for the photo reduction of CO2. The graphene with a large surface area and many defective sites absorbs the CO2, and the photo-generated electrons on the WSe2 and the photo-generated electrons on the WSe2 are transmitted to the catalytic sites of the graphene and then reduce the absorbed CO2 into CH3OH2,56. However, the photocatalytic reduction mechanism contains a series of water oxidation and the reduction processes, as shown in Fig. 9. The photo-induced holes on the WSe2-g VB could absorb water molecules to form hydroxyl radicals (OH·), and then the hydroxyl radicals further oxidize the protons (H+) and oxygen. In the meantime, electrons in the conductor band transfer and absorb CO2 to form ·CO2−. The ·CO2− reacts with ·H radical, which then leads to the formation of a series of radicals, finally producing CH3OH.

**Reaction Mechanism.**

\[ \text{WSe}_2^+ + \text{hv} \rightarrow \text{WSe}_2(e^- + h^+) \]
\[ \text{WSe}_2(h^+) + \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH} \]
\[ \text{Graphene}(e^-) + \text{O}_2 \rightarrow \text{O}_2 \]
\[ \text{Graphene}(2e^-) + 2\text{H}^+\text{O}_2 \rightarrow \text{H}_2\text{O}_2 \]
\[ \text{H}_2\text{O}_2 + \text{Graphene}(e^-) \rightarrow \text{OH} \]

**CO2 reaction.**
\[ 2\text{CH}_3^-\text{OH} + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 4\text{H}_2\text{O} \]
\[ 2\text{CO}_3^- + \text{H}_2\text{O} + 2e^- \rightarrow \text{HCO}_3^- + \text{HCO}_3^- \]

**Methods**

**Experimental setup and Materials.** Tungsten (VI) oxide (WO3), selenium powder (Se, 99%), ammonium hydroxide (NH4OH, 25–28%), Sodium sulfite (Na2SO3 · 7H2O, 95%), Nitric acid (HNO3) and ethyl alcohol (94%) were purchased from Duksan Pure Chemical Co. Ltd., Korea. All chemicals were used without further purification, and all dilutions were carried out using distilled water.
Preparation of Graphene. Graphene oxide was prepared in the laboratory following Hummer-Offeman’s method, as previously reported in the literature. A typical preparation method for graphene is as follows. First, 20 g of natural graphite and H2SO4 (450 ml) are put in de-ionized (DI) water and are stirred continuously for one hour at 0 °C. After that, 45 g of KMnO4 are slowly mixed with the solution (graphite + H2SO4) and are constantly stirred at a temperature of 35 °C until it becomes a dim brownish color. Then, the container is sealed and kept at 100 °C with vigorous stirring for 30 min. Meanwhile 20% H2O2 is added drop wise within 5 min. After that, the solution is washed with acetone and 10% HCl several times to remove the residual metal ions. The solution was then heat-treated in a dry oven at 90 °C for 12 h to obtain the graphene oxide, then 250 mg graphene oxide powder were added to 200 ml DI water, were vigorously stirred for 30 min, and were then ultrasonicated (using Ultrasonic Processor, VCX 750) for 2 h. Finally, the resulting solution was refined and washed several times with hot water and kept in a dry oven for 6 h to obtain the graphene oxide powder.

Preparation of the WSe2 composite. In a typical synthesis process, 0.675 g tungsten (VI) oxide (WO3) are dispersed in deionized water, 0.5 M nitric acid are then added drop wise in a three-necked flask (100 ml), and the mixture is heated to 120 °C to eliminate H2O and O2. In a separate flask, 1.5 g of anhydrous sodium sulfite (Na2SO3) and 0.3 g crude selenium (Se) powder were dispersed in 200 ml of ethylene glycol with continuous magnetic stirring at 80 °C until a selenium salt was obtained. In the next step, both solutions are transferred to a stainless steel autoclave with a Teflon liner with 20 ml capacity for 24 h at 250 °C in an electric furnace. Finally, the WSe2 precipitates are cooled to room temperature, the prepared solution is filtered using 47-mm Whatman filter paper, and the remaining material is heated to a temperature of 350 K for 12 h to obtain a WSe2 power.

Preparation of WSe2-graphene nanocomposite. Graphene oxide (200 mg) was added in 150 ml ethylene glycol and was then exfoliated to generate a graphene oxide nanosheet (GONS) dispersion solution via ultrasonication for 30 min. The WSe2 powder from the above solution is mixed at equal volumetric ratios of 1:1, and the mixture is sonicated at room temperature for 6 h using a controllable serial-ultrasound apparatus (Ultrasonic Processor, VCX 750, 500 Watt, Korea, Power 500 Watt, frequency 20 KHz, Amplitude 50%, low intensity). The reaction solution was allowed to cool and settle at room temperature after filtering with 47-mm Whatman filter paper with a pore size of 0.7 mm. The resulting powder was washed with distilled water multiple times and was dried in a vacuum oven at 80 °C for 12 h before heat treatment at 500 °C for 1 h with (Ar) inert atmosphere. The prepared sample was then labeled as WSe2-graphene.

Characterization. The crystal structure and morphology of the prepared samples were measured using monochromatic high intensity Cu Kα radiation (λ = 1.5406 Å) in XRD (Shimadzu XRD-D1), Energy dispersive X-ray spectrometer (EDX) was used to measure the atomic percentage of W, Se, and C elements, SEM (JSM-5600 JEOIL, Japan) and TEM (JEOL, JEM-2010, and Japan) observations. X-ray photoelectron spectroscopy (XPS) was performed using a VG Scientific VISACA Lab 2000 device with a monochromatic Mg X-ray radiation source, and the Raman spectra of the prepared samples were observed using a spectrometer (Jasco Name NRS-3100) with an excitation laser wavelength of 532.06 nm. For quantitative analysis of the CH3OH, a Standard Gas Chromatograph-Mass Spectrometer (GCMS-QP2010 SE) was used with a long column. Photoelectrochemical measurements were performed using a self-made photoelectrochemical system installed a 250-W halogen lamp as the irradiation source. The photocurrent measurement was performed by a computer-controlled Versa-STAT-3 electrochemical analyzer. A WSe2-graphene modified photoelectrode with an active area of 1 cm2 was used as the working electrode, and a Pt wire and saturated Ag/AgCl were used as the counter and reference electrodes, respectively. All the photocurrent measurements were conducted by dipping the WSe2-graphene modified photoelectrode into a mixture of 0.1 M KCl and 0.5 M TEA at a constant potential of 0 V vs. Ag/AgCl.

Photocatalytic reduction of CO2. The reduction of CO2 with H2O in the photocatalytic experiments was carried in a reactor designed in our laboratory, as shown in Fig. 1. The reactor consists of three parts: (1) light source, (2) closed chamber, (30 cm length × 2.0 diameter), (3) CO2 + N2 gas (N2 gas was used to remove gases from the reactor). 100 mg of photocatalyst (WSe2-graphene) and Na2SO3 as hole scavenger were added in 20 ml distilled water containing sodium bicarbonate (NaHCO3, 0.04 M) and were constantly stirred for one hour. Ultra-high-purity grade CO2 gas was purged through the reactor for 30 min, and then the suspension solution was magnetically stirred and irradiated with visible light using a metal halide lamp (500 W, SOLAREDGE700, Perfect Light, China). The distance between the light source and the photocatalyst remained at 10 cm, and a heat sink was equipped in the left side of the chamber to remove the lamp heat. Furthermore, the temperatures inside the reactor were kept at 283.15 K. The reaction continued up to 48 h, and in every 12 h interval, the reactor was allowed to cool down naturally for CH3OH desorption from the catalyst. Then, the reaction product was taken from the reactor for GC analysis (GCMS-QP2010 SE).

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

\[
\phi_{\text{Methanol}}(\%) = 100 \times \left(6 \times \text{mole of CH}_3\text{OH yield}\right) \\
/(\text{mole of proton absorbed by catalyte})
\]

- Mole of proton = (I \times S)/(N_A \times E)

where: I is light intensity (0.12 mW cm\(^{-2}\))
- S is the irradiated area of the reactor (30 cm \times 15 cm)
- E is the photon energy (4.97 \times 10^{-19} J at 400 nm)
- NA is Avogadro’s constant (6.02 \times 10^{23} mol\(^{-1}\))
Conclusion

In summary, the TMDC (WSe$_2$) materials are attached to the graphene nanosheet via ultra-sonication. The SEM and TEM images of the prepared samples show that the WSe$_2$ have nanowire morphology that is uniformly distributed on the graphene sheets, and the average size of the nanowires is verified to be from 30 to 130 nm. The graphene sheet-supported WSe$_2$ nanowire resulting from the binary structure present excited charge carriers with the combined effect of WSe$_2$ and graphene, improving the recombination time. Raman spectroscopy and XPS measurements show an intimate contact and chemical binding interaction between the WSe$_2$ and GO. Graphene plays a role as an electron mediator to support a binary system and to help provide stable photocatalyst materials. The CO$_2$ photo reduction experiment was carried out to investigate the photo catalytic reduction of CO$_2$ with the WSe$_2$–G nanocomposite, achieving a maximum photocatalytic efficiency after 48 h. The WSe$_2$–graphene with added Na$_2$SO$_4$ (48 h) showed the highest photocatalytic efficacy and obtained a total CH$_3$OH yield of 5.0278 μmol g$^{-1}$ h$^{-1}$. Our present work indicates that the attachment of WSe$_2$ on the graphene sheet can further increase the photocatalytic performance, opening new ways to deploy novel, next-generation heterojunction photocatalysts for environmentally-related applications.

References

1. Lacis, A. A., Schmidt, G. A., Rind, D. & Ruedy, R. A. Atmospheric CO$_2$: Principal control knob governing Earth’s temperature. Science 330, 356–359, doi:10.1126/science.1190653 (2010).
2. Yu, J., Low, J., Xiao, W., Zhou, P. & Jaroniec, M. Enhanced photocatalytic CO$_2$-reduction activity of anatase TiO$_2$ by coexposed [001] and [101] facets. Journal of the American Chemical Society 136, 8839–8842, doi:10.1021/ja0447877 (2014).
3. Maginn, E. J. What to Do with CO$_2$. The Journal of Physical Chemistry Letters 1, 3478–3479, doi:10.1021/jz101582c (2010).
4. Li, X., Wen, J., Low, J., Fang, Y. & Yu, J. Design and fabrication of semiconductor photocatalyst for photocatalytic reduction of CO$_2$ to solar fuel. Science China Materials 57, 70–109, doi:10.1007/s11431-014-1000-3 (2014).
5. Habib, T., Schmidt-Mende, L. & Stolarczyk, J. K. Photocatalytic reduction of CO$_2$ on TiO$_2$ and other semiconductors. Angewandte Chemie International Edition 52, 7372–7408, doi:10.1002/anie.201207199 (2013).
6. Ramesha, G. K., Brennecke, J. F. & Kamar, P. V. Origin of catalytic effect in the reduction of CO$_2$ at nanostructured TiO$_2$ films. ACS Catalysis 4, 3249–3254, doi:10.1021/ac5009076 (2014).
7. Yuan, L. & Xu, Y.-J. Photocatalytic conversion of CO$_2$ into value-added and renewable fuels. Applied Surface Science 342, 154–167, doi:10.1016/j.apsusc.2015.03.050 (2015).
8. Yu, J., Wang, K., Xiao, W. & Cheng, B. Photocatalytic reduction of CO$_2$ into hydrocarbon solar fuels over g-C$_3$N$_4$–Pt nanoparticle photocatalysts. Physical Chemistry Chemical Physics 16, 11492–11501, doi:10.1039/c4cp01333h (2014).
9. Elsah, M. F. & He, T. In situ synthesis of ZnO/ZeNi common cation heterostructure and its visible-light photocatalytic reduction of CO$_2$ into CH$_4$. Applied Catalysis B: Environmental 166, 345–352, doi:10.1016/j.apcatb.2014.11.058 (2015).
10. Markiewski, M., Cao, S., Yu, J. & Jaroniec, M. Semiconductor-based photocatalytic CO$_2$ conversion. Materials Horizons 2, 261–278, doi:10.1039/C4MH00176A (2015).
11. Gojocar, B. Band gap effect on the photocatalytic activity of supramolecular structures obtained by entrapping photosensitizers in different inorganic supports. Physical Chemistry Chemical Physics 11, 5569–5577, doi:10.1039/b902348h (2009).
12. Voiry, D. et al. Enhanced band gap effect in strained chemically exfoliated WS$_2$ nanosheets for hydrogen evolution. Nature materials 12, 850–855, doi:10.1038/nmat3703 (2013).
13. Kibsgaard, J., Chen, Z., Reinecke, B. N. & Jaramillo, T. F. Engineering the surface structure of MoS$_2$ to preferentially expose active edge sites for electrocatalysis. Nature materials 11, 963–969, doi:10.1038/nmat3439 (2012).
14. Cheng, L. et al. Ultrathin WS$_2$ nanoflakes as a high-performance electrocatalyst for the hydrogen evolution reaction. Angewandte Chemie International Edition 53, 7860–7863, doi:10.1002/anie.201402315 (2014).
15. Lukowski, M. A. et al. Enhanced hydrogen evolution catalysis from chemically exfoliated metallic MoS$_2$ nanosheets. Journal of the American Chemical Society 135, 10274–10277, doi:10.1021/ja40523x (2013).
16. Li, H. et al. Mechanical Exfoliation and Characterization of Single- and Few-Layer Nanosheets of WSe$_2$, TaS$_2$, and TaSe$_2$. Small 9, 1974–1981, doi:10.1002/smll.v9i11.2 (2013).
17. Matte, H. R., Flomman, B., Datta, R. & Rao, C. Graphene analogues of layered metal selenides. Dalton Transactions 40, 10322–10325, doi:10.1039/c1dt10865j (2011).
18. Wang, Q. H., Kalantar-Zadeh, K., Kis, A., Coleman, J. N. & Strano, M. S. Electronics and optoelectronics of two-dimensional transition metal dichalcogenides. Nature nanotechnology 7, 699–712, doi:10.1038/nnano.2012.193 (2012).
19. Cao, L. et al. Direct Laser-Patterned Micro-Supercapacitors from Paintable MoS$_2$ Films. Small 9, 2905–2910, doi:10.1002/smll.v9i17.2 (2013).
20. Chen, D. et al. In situ nitrogrenated graphene–few-layer WS$_2$ composites for fast and reversible Li$^+$ storage. Nanoscale 5, 7890–7896, doi:10.1039/c3nr02920d (2013).
21. Yin, Z. et al. Single-layer MoS$_2$ phototransistors. ACS nano 6, 74–80, doi:10.1021/nn2024557 (2011).
22. Li, Y., Li, Y.-L., Araujo, C. M., Luo, W. & Ahuja, R. Single-layer MoS$_2$ as an efficient photocatalyst. Catalysis Science & Technology 3, 2214–2220 (2013).
23. Li, Y. et al. MoS$_2$ nanoparticles grown on graphene: an advanced catalyst for the hydrogen evolution reaction. Journal of the American Chemical Society 133, 7296–7299, doi:10.1021/ja2012096 (2011).
24. Merki, D., Fierro, S., Vrubel, H. & Hu, X. Amorphous molybdenum sulfide films as catalysts for electrochemical hydrogen production in water. Chemical Science 2, 1262–1267, doi:10.1039/C1SC00117E (2011).
25. Chang, H. & Wu, H. Graphene-based nanocomposites: preparation, functionalization, and energy and environmental applications. Energy & Environmental Science 6, 3483–3507 (2013).
26. Zhang, H. et al. Large-Scale Production of Nanographene Sheets with a Controlled Mesoporous Architecture as High-Performance Electrochemical Electrode Materials. Chem Sus Chem 6, 1084–1090, doi:10.1002/cssc.v6.i6.3 (2013).
27. Liang, Y. T., Vijayan, B. K., Gray, K. A. & Hersam, M. C. Minimizing graphene defects enhances titania nanocomposite-based photocatalytic reduction of CO$_2$ for improved solar fuel production. Nano letters 11, 2865–2870, doi:10.1021/nn2012906 (2011).
28. Liu, Z. et al. Assembled 3D electrocatalysts for efficient hydrogen evolution: WSe$_2$ layers anchored on graphene sheets. Inorganic Chemistry Frontiers 3, 313–319, doi:10.1039/C3QI00216H (2016).
29. Guo, J., Shi, Y., Bai, X., Wang, X. & Ma, T. Atomically thin MoSe$_2$/graphene and WSe$_2$/graphene nanosheets for the highly efficient oxygen reduction reaction. Journal of Materials Chemistry A 3, 24397–24404, doi:10.1039/C3TA06909B (2015).
30. Chakravarty, D. & Late, D. J. Microwave and hydrothermal synthesis of WSe$_2$ micro/nanorods and their application in supercapacitors. RSC Advances 5, 21700–21709, doi:10.1039/C4RA12599A (2015).
31. Bourlinos, A. B. et al. Graphite oxide: chemical reduction to graphite and surface modification with primary aliphatic amines and amino acids. Langmuir 19, 6050–6055, doi:10.1021/la0526525H (2003).
32. Kovtyukhova, N. I. et al. Layer-by-layer assembly of ultrathin composite films from micron-sized graphite oxide sheets and polycations. *Chemistry of Materials* 11, 771–778, doi:10.1021/cm981085a (1999).
33. Ai, W. et al. Nitrogen and sulfur codoped graphene: multifunctional electrode materials for high-performance Li-ion batteries and oxygen reduction reaction. *Advanced Materials* 26, 6168–6192, doi:10.1002/adma.201401427 (2014).
34. Shi, Y. et al. van der Waals epitaxy of MoS 2 layers using graphene as growth templates. *Nano letters* 12, 2784–2791, doi:10.1021/nl204562c (2012).
35. Wang, H., Robinson, J. T., Diankov, G. & Dai, H. Nanocrystal growth on graphene with various degrees of oxidation. *Journal of the American Chemical Society* 132, 3270–3271, doi:10.1021/ja103294d (2010).
36. Wang, H. et al. MnO 2–graphene hybrid as a high-capacity anode material for lithium ion batteries. *Journal of the American Chemical Society* 132, 13978–13980, doi:10.1021/ja105296a (2010).
37. Muscuso, L., Cravanzola, S., Cesano, F., Scarno, D. & Zecchina, A. Optical, Vibrational, and structural properties of MoS 2 nanoparticles obtained by exfoliation and fragmentation via ultrasound cavitation in isopropanol alcohol. *The Journal of Physical Chemistry C* 119, 3791–3801, doi:10.1021/jp511973k (2015).
38. Yu, J. H. et al. Vertical heterostructure of two-dimensional MoS 2 and WS 2 with vertically aligned layers. *Nano letters* 15, 1031–1035, doi:10.1021/acs.nanolett.4b04387 (2015).
39. Wang, R.-C., Chen, Y.-C., Chen, S.-J. & Chang, Y.-M. Unusual functionalization of reduced graphene oxide for excellent chemical surface-enhanced Raman scattering by coupling with ZnO. *Carbon* 79, 215–223, doi:10.1016/j.carbon.2013.12.110 (2014).
40. Dresselhaus, M. S., Jorio, A., Hofmann, M., Dresselhaus, G. & Saito, R. Perspectives on carbon nanotubes and graphene Raman spectroscopy. *Nano letters* 10, 751–758, doi:10.1021/nl904286e (2010).
41. Huang, T. et al. The effects of low power density CO 2 laser irradiation on graphene properties. *Applied Surface Science* 273, 502–506, doi:10.1016/j.apusc.2013.02.069 (2013).
42. Wang, Y. Y. et al. Raman studies of monolayer graphene: the substrate effect. *The Journal of Physical Chemistry C* 112, 10637–10640, doi:10.1021/jp8008404 (2008).
43. Ullah, K., Lei, Z., Ye, S., Ali, A. & Oh, W.-C. Microwave synthesis of a CoSe 2/graphene–TiO 2 core–shell structure. *Energy & Environment Science* 5, 7604–7609, doi:10.1039/c2ee20414e (2011).
44. Abbalah, W. A. & Nelson, A. Characterization of MoSe 2 (0001) and ion-sputtered MoSe 2 by XPS. *Journal of Materials Science* 46, 502–506, doi:10.1007/s10853-011-5648-5 (2011).
45. Abdallah, W. A. & Nelson, A. Evolution of surface functional groups in a series of progressively oxidized graphite oxides. *Chemistry of Materials* 18, 2740–2749, doi:10.1021/cm060258z (2006).
46. Wang, H. et al. MoSe 2 and WS 2 nanofilms with vertically aligned molecular layers on curved and rough surfaces. *Nano letters* 13, 3426–3433, doi:10.1021/nl401944f (2013).
47. Zhao, L. et al. Microwave-assisted hydrothermal synthesis of ito 4–microcrystalline diamond/graphene hybrid as a high-capacity anode material for lithium ion batteries. *Nanoscale* 4, 7628–7632, doi:10.1039/c2nr25163c (2012).
48. Wang, H. et al. MnO 2–graphene hybrid as a high-capacity anode material for lithium ion batteries. *Journal of the American Chemical Society* 132, 13978–13980, doi:10.1021/ja105296a (2010).
49. Jeong, H.-K. et al. Microwave-assisted hydrothermal synthesis of ito 4–microcrystalline diamond/graphene hybrid as a high-capacity anode material for lithium ion batteries. *Journal of the American Chemical Society* 132, 13978–13980, doi:10.1021/ja105296a (2010).
50. Dreyer, D. R., Park, S., Bielawski, C. W. & Ruoff, R. S. The chemistry of graphene oxide. *Chemical Society Reviews* 41, 307–351, doi:10.1039/c1cs15005d (2012).
51. Zhang, L.-f & Zhang, C.-y Multifunctional Co 0.85 Se/graphene hybrid nanosheets: controlled synthesis and enhanced performances for the oxygen reduction reaction and decomposition of hydrazine hydrate. *Nanoscale* 6, 1782–1789, doi:10.1039/c3nr05509d (2014).
52. Wan, D. et al. Low-temperature aluminum reduction of graphene oxide, electrical properties, surface wettability, and energy storage applications. *ACS nano* 6, 9068–9078, doi:10.1021/nn504704h (2016).
53. Jeong, H.-K. et al. Microwave-assisted hydrothermal synthesis of ito 4–microcrystalline diamond/graphene hybrid as a high-capacity anode material for lithium ion batteries. *Journal of the American Chemical Society* 132, 13978–13980, doi:10.1021/ja105296a (2010).
54. Bonaccorso, F. et al. Graphene photonics and optoelectronics. *Nature Photonics* 4(9), 611–622, doi:10.1038/nphoton.2010.186 (2010).
55. Xiang, X. et al. One-pot synthesis of reduced graphene oxide–CdS/methylene blue composite and its photocatalytic hydrogen production. *Physical Chemistry Chemical Physics* 13, 21496–21502 (2011).
56. Ai, A. & Oh, W.-C. Catalytic reduction of CO 2 to alcohol with Cu 2Se-combined graphene binary nanocomposites. *Fullerenes, Nanotubes and Carbon Nanostructures* 24, 555–563, doi:10.1080/1536383X.2016.1205036 (2016).
57. Wang, R. et al. Characterization of MoSe 2 (0001) and ion-sputtered MoSe 2 by XPS. *Journal of Materials Science* 46, 502–506, doi:10.1007/s10853-011-5648-5 (2011).
58. Chen, M.-L., Park, C.-Y., Choi, J.-G. & Oh, W.-C. Synthesis and characterization of metal (Pt, Pd and Fe)–graphene composites. *Journal of the Korean Ceramic Society* 48, 147–151, doi:10.4191/KCERS.2011.48.2.147 (2011).
59. Zhai, Q. et al. Photocatalytic conversion of carbon dioxide with water into methane: platinum and copper (I) oxide co-catalysts with a core–shell structure. *Angewandte Chemie* 125, 5888–5891, doi:10.1002/ange.201301473 (2013).

**Author Contributions**
W.C. Oh proposed and supervised the project; Asghar Ali designed and performed the experiments. Asghar Ali analyzed the data and wrote the manuscript. All authors participated in the discussions and provided input on the manuscript.

**Additional Information**

**Competing Interests**: The authors declare that they have no competing interests.

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