Synergistic effects of 2D/2D ZnV$_2$O$_6$/RGO nanosheets heterojunction for stable and high performance photo-induced CO$_2$ reduction to solar fuels

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**GRAPHICAL ABSTRACT**

**ABSTRACT**

Highly photo-stable and efficient 2D/2D zinc vanadium oxide-reduced graphene oxide (ZnV$_2$O$_6$/RGO) nanosheets heterojunction was fabricated by the one-pot solvothermal method. The structures and properties of the catalysts were analyzed by XRD, FE-SEM, EDX, TEM, BET, UV–vis, Raman and PL spectroscopy. The 2D/2D ZnV$_2$O$_6$/RGO catalyst shows excellent performance towards CO$_2$ photo-reduction with H$_2$O to CH$_3$OH, CH$_3$COOH and HCOOH under visible light. The yield of the main product CH$_3$OH of 5154 μmol g-cat$^{-1}$, obtained over ZnV$_2$O$_6$/4%RGO, was 1.6 times the amount of CH$_3$OH produced over the pure ZnV$_2$O$_6$ (3254 μmol g-cat$^{-1}$) and a 5.5-fold higher than that of the ZnO/V$_2$O$_5$ composite (945 μmol g-cat$^{-1}$). In addition, CH$_3$OH selectivity of 39.96% achieved over the ZnO/V$_2$O$_5$ composite increased to 68.89% in ZnV$_2$O$_6$/4%RGO. The continuous and selective production of CH$_3$OH was detected over the entire irradiation time in ZnV$_2$O$_6$ and ZnV$_2$O$_6$/4%RGO samples, whereas the yield of products gradually decreased in ZnO/V$_2$O$_5$. The significant improvement in photoactivity over 2D ZnV$_2$O$_6$ structure was due to the hierarchical structure with enhanced charges separation. A combined 2D/2D ZnV$_2$O$_6$/RGO nanosheets prevailed as a promising strategy to ameliorate the photocatalytic performance of ZnV$_2$O$_6$ nanosheets due to efficient trapping and transport of electrons by RGO. The synergistic effects in ZnV$_2$O$_6$/RGO 2D/2D nanosheets exhibited excellent photocatalytic stability, which prevailed even after 32 h of operation time for selective and continuous CH$_3$OH production. A proposed photo-induced reaction mechanism, corroborated with the experimental data, was also deliberated.

1. Introduction

Due to global warming caused by a remarkable increase of carbon dioxide (CO$_2$) emission into the atmosphere, it is currently a great challenge to convert CO$_2$ into valuable fuels [1,2]. Artificial photosynthesis process to convert CO$_2$ into useful carbon sources such as CO, HCOOH, HCHO, CH$_3$OH, and CH$_4$ is an attractive alternatives because of the demand for methods to recycle CO$_2$ as a natural resource [3–8]. The solar photocatalytic conversion of CO$_2$ into industrially beneficial compounds offers one prospective path [9,10]. Sunlight is
one of the most attractive strategies to convert CO2 to value added fuels or chemical products [11–13]. Thus, many research efforts have been made to develop efficient photo-catalysts for the reduction of CO2 to fuels such as TiO2 [14–17], ZnO [18,19], CdS [20], Ta2O5 [21], InTaO4 [22]. Among all, ZnO has been a widely-studied semiconductor because of its strong oxidation and reduction abilities. In addition, it is environmentally friendly, relatively cheap and can be grown in various nanostructures via cost effective methods [23–25]. However, because of its wide direct band gap energy (∼3.2 eV), ZnO can only be activated by UV light, which cannot make full use of the incoming solar spectrum. Furthermore, it suffers through high rate of charges recombination, resulted in poor photocatalytic performance [26,27]. So, it is important to expand the absorption band of ZnO-based photo-catalyst towards visible light. To address these problems, many approaches have been made which include preparing quantized ZnO nano-crystallites [28], depositing noble metals [29–31], surface photo-sensitization [32], and forming carbon-based composites [33–36].

Graphene, as a new carbon material, is regarded as one of the most promising additive for hybrid materials, because of its large theoretical specific surface area, excellent electron mobility, and high transparency [37,38]. Thus, it is believed to be an attractive approach to modify ZnO with RGO to obtain a promising photo-catalyst for enhanced CO2 reduction. For example, graphene bonded with ZnO [39], TiO2 [40], WO3 [41], and CdS [13] composites have been widely investigated for the reduction of CO2 to various chemicals and fuels. In addition, coupling ZnO with visible light responsive semiconductors can extend optical absorption towards the visible part of the spectrum. In this perspective, vanadium oxide (V2O5), an important transition metal oxide semiconductor (band gap ∼2.3 eV), can be a good candidate for capturing visible light [42,43]. Furthermore, both zinc and vanadium are earth abundant, relatively economical, and can offer several oxidation states, which can render a broad range of redox reactions.

Lately, hierarchical nanostructures such as nanosheets, nanorods, or nanoplates have garnered enormous attention and demonstrated remarkable performances in energy storage, photovoltaic solar cells, photochemical, and other device applications [44,45]. Therefore, developing zinc-vanadium nanostructures could enhance both photo-activity and selectivity compared to ZnO/V2O5 composite. Recently, ZnV2O4 has gained attention because of its interesting structural changes at low temperatures [46]. Different nanostructures of ZnV2O4 have been reported like hollow spheres, clewlike hollow structures, nanosheets, and glomerulus nano/microspheres for various applications [46–49]. They have shown good charge–discharge performance in lithium ion batteries and a promising photo-catalyst. While keeping in view, the important role of spinel oxides in different applications, it is very crucial to improve new facile and cost effective routes for the fabrication of diverse morphologies of these nanostructures and to explore the potential as alternative energy storage materials for future applications. However, structured ZnV2O4 based photo-catalyst has never been reported for photo-induced CO2 reduction application. Therefore, it is appropriate to explore hierarchical ZnV2O4 semiconductor for photocatalytic CO2 reduction applications under solar energy. Furthermore, the construction of a semiconductor heterojunction has attracted a lot of attention because of its perfect effectiveness in developing the photocatalytic activity [50]. In this perspective, the graphene/Bi2WO6 composite has shown significantly enhanced photocatalytic activity compared with the bare semiconductors [51]. Similarly, enhanced photocatalytic has been reported over rGO@CuZnO@Fe3O4 composite catalyst for photocatalytic CO2 reduction to CH3OH [52]. Recently, g-C3N4 (2D)/CdS (1D)/rGO (2D) dual interface heterojunction for excellent and stable visible light photocatalytic hydrogen generation has been reported [53]. It is therefore, highly desirable to construct ZnV2O4/RGO composite heterojunction to enhance photocatalytic reduction of CO2 to solar fuels under visible light irradiation.

Herein, we successfully designed and synthesized novel 2D ZnV2O6 nanosheets and RGO modified ZnV2O6 2D/2D nanosheets heterojunction through a solvothermal process. The materials were investigated for photo-induced CO2 reduction by H2O to fuels under visible light irradiations. The 2D/2D ZnV2O6/RGO nanosheets demonstrated significantly enhanced photoactivity in comparison to pure ZnV2O6 nanosheets for converting CO2 to CH3OH, HCOOH and CH3COOH. The enhanced photocatalytic activity was attributed to hierarchical structure of ZnV2O6 with hindered charges recombination rate by RGO. The effect of the content of graphene on photocatalytic activity ZnV2O6 nanosheets were investigated. The stability test to determine the life of new materials and reaction pathways were also deliberated.

2. Experimental

2.1. Preparation of novel 2D ZnV2O6 nanosheets

The ZnV2O6 nanosheets were prepared using a solvothermal method. Typically, 2.052 mmole of ammonium metavanadate [NH4VO3] dispersed in 20 ml of N,N-dimethyl formamide (DMF) was added into zinc acetate [Zn(O2CCH3)2] and continuously stirred to obtain a homogenous solution. Oxalic acid dehydrated [H2C2O4·2H2O] with oxalic acid to NH4VO3 ratio of 1:3 was added afterward. After being stirred for 30 min, the obtained solution was transferred into a 50 ml Teflon lined autoclave, which was maintained at 200 °C for 24 h and then cooled to room temperature naturally to get black colour product. The precipitates collected were washed for several times with absolute ethanol, then dried in air flow oven at 80 °C for 12 h.

2.2. Synthesis of RGO-modified ZnV2O6 (ZnV2O6/RGO) nanosheets

In a typical synthesis, 2.052 mmole of ammonium metavanadate [NH4VO3] was added into 20 ml of N,N-dimethyl formamide (DMF). After stirring for 10 min, zinc acetate [Zn(O2CCH3)2] was added to above solution and suspension was stirred continuously to obtain a homogenous solution. Later, oxalic acid dehydrated [H2C2O4·2H2O] was added by adjusting ratio of oxalic acid to NH4VO3 of 1:3. Afterwards, a certain amount of graphene oxide was added into the solution and stirred for another 30 min. Finally, the obtained solution was transferred into a 50 ml Teflon lined autoclave, maintained at 200 °C for 24 h and then cooled to room temperature. The black precipitates collected were washed several times with absolute ethanol, and then dried in an oven at 80 °C for 12 h. A series of ZnV2O6-RGO nanosheets with different weight ratios of GO nanosheets (2%, 4%) were obtained using the same procedure.

2.3. Material characterization

The crystalline structure was determined using X-ray diffractometer (Rigaku Smart Lab) with Cu-Kα radiation (λ = 0.154178 nm) operated at 40 kV and 30 mA. The XRD patterns were obtained with a scanning rate of 0.02° min−1 and scanning range of 3–100° of 2θ. The morphology and EDX mapping analysis of the samples was examined by field emission scanning electron microscopy (FE-SEM, ZEISS Crossbeam 340). The high-resolution transmission electron microscope (HR-TEM) images were obtained in a transmission electron microscope (TEM, HITACHI HT7700). Nitrogen-adsorption–desorption isotherms were collected using Micromeritics ASAP 2020 at 77 K, after degassing the samples at 523 K for 4 h under vacuum and using the nitrogen flux. The BET surface area and pore diameters were calculated from the desorption branch of isotherms according to BJH method. Ultraviolet–visible (UV–vis) diffuse reflectance absorbance spectra were carried out on a Cary 100 Agilent UV–vis spectrophotometer equipped
Raman and photoluminescence (PL) spectra of the samples were recorded at room temperature using Raman Spectrometer (LabRAM HR Evolution, HORIBA), whereas, PL was conducted using 325 nm and Raman with a 532 nm emitting laser as an excitation source.

2.4. Photocatalytic activity

The schematic presentation of the slurry type photoreactor for CO₂ reduction is illustrated in Fig. 1. The CO₂ reduction reaction was performed using a quartz glass with a volume 100 ml. A 35 W HID Xe lamp was used as a visible light source with a light intensity of 20 mWcm⁻², measured using a reference solar cell (91150 V, Newport) [10]. First, 100 mg catalyst sample was added into 100 mL 0.1 M NaOH solution in a glass reactor under magnetic stirring. Then, compressed CO₂ regulated by mass flow controller (MFC) was bubbled through the solution for 30 min to remove the oxygen. The control experiments were conducted at room temperature, atmospheric pressure, and feed flow rate.
of 20 mL/min. The HID XENON lamp was turned on to start the photo-reaction. During the reaction process, the liquid products were taken out after 2 h interval, then were centrifuged using Syringe Filter with Nylon Membrane, pore size 0.45 µm and diameter 33 mm to remove catalyst particles. The concentration of methanol, formic acid and acetic acid were analyzed by a gas chromatograph (GC-7820A) equipped with a flame ionization detector (FID) and HP-5 capillary column. The calibration of the GC was conducted using standard solutions of methanol, formic acid and acetic acid. More importantly, methanol peaks areas obtained were consistent, yet peak areas for formic acid and acetic acid were different in different injections and their average values have been used for calibration curve. This happens because FID detector was not compatible for the analysis of these products. Control experiments were carried out in the dark or without catalyst under the same experimental conditions. The carbon containing products were not detected in the absence of light irradiation or catalysts.

3. Results and discussion

3.1. Characterization of catalysts

Fig. 2(a) shows XRD patterns of as synthesized and calcined ZnV$_2$O$_6$ samples. Clearly, the XRD pattern of the ZnV$_2$O$_6$ shows one pronounced diffraction peak located at around 2θ = 10.0°. Such a diffraction pattern can be attributed to the ZnV$_2$O$_6$ phase, which is a characteristic of metal alkoxides [54,55]. The ZnV$_2$O$_6$ nanosheets were converted to highly crystalline material after calcining at 550 °C for 3 h in air atmosphere. All the identified diffraction peaks can be assigned to ZnV$_2$O$_6$ with an orthorhombic structure (JCPDS Card No. 01-074-1262). Also, weak diffraction peaks of V$_2$O$_5$ appeared, which indicated that a small amount of V$_2$O$_5$ (JCPDS Card No. 01-072-0433) was generated and the resulting sample was a mixture of ZnV$_2$O$_6$ nanosheets and V$_2$O$_5$. Fig. 2(b) displays an obvious diffraction peak at 2θ = 25.0° appears in the XRD patterns of RGO corresponding to the (0 0 2) reflection of reduced phase of graphene oxide. The XRD patterns of the ZnV$_2$O$_6$/RGO samples show similar diffraction patterns as ZnV$_2$O$_6$. The RGO peak is not observed in the composite, probably due to its lesser content. These results indicate that the introduction of RGO do not affect the orientation and structure of ZnV$_2$O$_6$ nanosheets.

Fig. 2(c) shows the interesting crystal geometry of spinel oxide ZnV$_2$O$_6$. The ZnV$_2$O$_6$ is formed by ZnO$_2$, tetrahedra and VO$_6$ octahedra. It belongs to the FCC type crystal structure with Fd3m symmetry group. According to crystallographic studies, zinc atoms reside in the tetrahedral 8a position, whereas the vanadium atoms are on 16d position, whereas the vanadium atoms are on 16d position, the other hand, BET surface area of ZnV$_2$O$_6$ with 4 wt% RGO of 11.62 m$^2$/g is obtained, obviously higher than the BET surface of ZnV$_2$O$_4$ of 6.1 m$^2$/g [56]. This was perhaps due to their different hierarchical structures. On the other hand, BET surface area of ZnV$_2$O$_6$ with 4 wt% RGO of 11.62 m$^2$/g obtained, which revealed RGO has no effect on the BET surface area of ZnV$_2$O$_6$. Moreover, pore diameter decreased with RGO-combined with ZnV$_2$O$_6$. Thus, the reduced pore diameter was possibly due to controlled crystal growth in the RGO-combined with ZnV$_2$O$_6$ samples. Therefore, well-developed mesoporous structure with larger pore volume and smaller pore diameter could minimize mass transfer limitations to increase catalytic activity.

Fig. 3 portrays the field emission scanning electron micrographs (FE-SEM) recorded in order to measure the morphology of ZnV$_2$O$_6$ and RGO-combined with ZnV$_2$O$_6$ 2D/2D nanosheets. It can be seen in Fig. 3(a) that the ZnV$_2$O$_6$ sample prepared at 12 h reaction time composed of intermediate products which consist of many compact sheets. However, when the reaction time was increased to 24 h, large amounts of sheets were formed as shown in Fig. 3(b). Evidently, pure ZnV$_2$O$_6$ has 2D structure consisting of uniform size sheets with many wrinkles. Fig. 3(c and d) displays the micrograph of RGO sheets with a fold surface, the ZnV$_2$O$_6$ substrate is partly covered by the RGO nanosheets which reveals a good interaction between ZnV$_2$O$_6$ and RGO nanosheets. The EDX mapping analysis are presented in Fig. 4. The EDX mapping analysis in Fig. 4(a and b) revealed even distributed of RGO over ZnV$_2$O$_6$ nanosheets. Zinc, vanadium, oxygen and carbon were the elements found by EDX analysis as shown in Fig. 4(c). The atomic ratio was found to be 18.3, 54.0, 22.0 and 5.6%, respectively. No other atom/elements were detected indicating purity of the product. The observation have confirmed successful development of RGO/ZnV$_2$O$_6$ composite heterojunction, which could results in enhanced photocatalytic activity.

The growth mechanism of the ZnV$_2$O$_6$/RGO nanosheets heterojunction is presented in Fig. 5. Initially, ZnV$_2$O$_6$ sheet intermediate product with compact nanosheets were formed in large quantity, which might provide the reaction sites and sources for the impending next step [49]. Besides, GO sheets will be distributed uniformly over the ZnV$_2$O$_6$ structure during the growth of 2D sheets. Rising the reaction time, abundant ZnV$_2$O$_6$/RGO sheets were generated by in situ reduction and continuous dissolution of the sheets intermediate product, and simultaneously aggregated into nanosheets to reduce surface energy. As the reaction proceeded in longer time, the nanosheets completely aggregated to regular nanosheets with relatively smooth surface of 2D/2D ZnV$_2$O$_6$/RGO heterojunctions.

The morphology and microstructures of the ZnV$_2$O$_6$/RGO nanosheets was characterized using TEM as depicted in Fig. 6. Fig. 6(a) shows the ultrathin RGO sheet has a highly transparent 2D structure with obvious wrinkles and folds. The TEM images of ZnV$_2$O$_6$ sample prepared after 24 h reaction time is presented in Fig. 6(b), which shows ZnV$_2$O$_6$ structure composed of many compact nanosheets. From Fig. 6(cand d) the RGO nanosheets are observed on the surface of ZnV$_2$O$_6$ nanosheets, which reveals a good combination of RGO and ZnV$_2$O$_6$ to develop heterojunction. HRTEM image in Fig. 6(e) illustrates that the RGO nanosheets are successfully deposited on the surface of ZnV$_2$O$_6$ nanosheets developing 2D/2D structure. This revealed the formation of heterojunction structure of the RGO/ZnV$_2$O$_6$ nanosheets. The interplanar distance was found to be 0.48 nm and 0.25 nm, which corresponds to (1 1 1) and (3 1 1) planes of ZnV$_2$O$_6$ nanosheets. The SAED pattern of the composite in Fig. 6(f) shows an obvious polycrystalline ring due to good crystallization of ZnV$_2$O$_6$. The calculated “d” values corresponds to (1 1 1) and (3 1 1) Miller indices of ZnV$_2$O$_6$.

Fig. 7 shows UV–vis diffuse reflectance absorbance spectra of the ZnO/V$_2$O$_5$ composite, pure ZnV$_2$O$_6$ and ZnV$_2$O$_6$/RGO nanosheets. The combined RGO with ZnV$_2$O$_6$ nanosheets can obviously enhance the absorbance of ZnV$_2$O$_6$ towards visible light irradiations. The energy band gaps (Ebg) of all the samples were obtained from the extrapolation of Tauc plot to the abscissa of photon energy (eV) and results are presented in Table 1. The wavelengths of the ZnO/V$_2$O$_5$, ZnV$_2$O$_6$ and ZnV$_2$O$_6$/RGO samples are 447 nm, 613 nm and 630 nm corresponding to the band gap energy of 2.77 eV, 2.02 eV, and 1.97 eV, respectively. Obviously, ZnV$_2$O$_6$ nanosheets displays higher absorption intensities than ZnO/V$_2$O$_5$ composite in the visible light region. Similarly, ZnV$_2$O$_6$/RGO nanosheets show slightly higher absorption intensities

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area S$_{BET}$ (m$^2$/g)</th>
<th>BJH surface area S$_{BJH}$ (m$^2$/g)</th>
<th>Pore volume (cm$^3$/g)</th>
<th>Pore width (nm)</th>
<th>Crystal size d$_{XRD}$ (nm)</th>
<th>Band gap (Ebg, eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnV$_2$O$_6$</td>
<td>11.57</td>
<td>3.80</td>
<td>0.0045</td>
<td>17.30</td>
<td>1.355</td>
<td>2.02</td>
</tr>
<tr>
<td>ZnV$_2$O$_6$/ RGO (4%)</td>
<td>11.62</td>
<td>10.48</td>
<td>0.0037</td>
<td>5.46</td>
<td>1.035</td>
<td>1.97</td>
</tr>
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than that of ZnV₂O₆ in the visible light region. The enhanced light absorption by RGO can be ascribed to the introduction of the black-body properties of graphene-like materials [51].

Raman spectra of the pure ZnV₂O₆ and RGO-combined with ZnV₂O₆ samples are depicted in Fig. 8(a). The Raman spectrum of the blank RGO contains both D (the symmetry A₁g k-point phonon) and G (the E₂g phonon of sp² carbon atoms) bands at 1323 and 1581 cm⁻¹, respectively. The peaks in the range of 100–1100 cm⁻¹ were observed in the pure ZnV₂O₆ sample. All the characteristic bands of the pure ZnV₂O₆ are found in the Raman spectrum of the ZnV₂O₆/RGO nanosheets, while, both the D and G bands disappeared due to its lesser content. However, the changes are obvious in the position and width of the combined ZnV₂O₆ sample peaks. With the RGO combined, the width of the Raman bands, in particular the peaks increase and the slight position shift towards higher wavenumber, attributed to the reduction of particle size of the combined ZnV₂O₆ samples with higher mobility of charges.

Fig. 8(b) shows photoluminescence (PL) spectra of the pure ZnV₂O₆ and RGO combined with ZnV₂O₆ samples. ZnV₂O₆ displays a broad PL emission peak at around 510 nm. The PL intensity of the pure ZnV₂O₆ exhibits the strongest emission due to the highest recombination of the photo generated charge carriers on the pure ZnV₂O₆ surface. After the RGO was introduced, the ZnV₂O₆/RGO nanosheets show lower PL emission intensity compared with the pure ZnV₂O₆. The weaker intensity of the peak represents the lower recombination probability of free charges [57]. This indicates that RGO can effectively mitigate the recombination of photo-generated electron hole pairs of ZnV₂O₆ nanosheets.

3.2. Photocatalytic CO₂ reduction with H₂O reductant

The control experiments were conducted in the presence of catalysts without CO₂ flow under visible light irradiation at room temperature, atmospheric pressure, and N₂ feed flow rate of 20 mL/min. In all the cases, carbon containing compounds were not detected, thus, any carbon based products would be produced during CO₂ reduction process only.

Fig. 9(a) displays the effect of different photo-catalysts such as ZnO, V₂O₅, ZnO/V₂O₅, ZnV₂O₆, and ZnV₂O₆ calcined on the photocatalytic performance for dynamic CO₂ conversion with H₂O under visible light irradiation. The effectiveness of the catalyst samples were analysed based on the yield of CH₃OH, HCOOH and CH₃COOH which were the three products from the process. Pure ZnO, V₂O₅ and ZnO/V₂O₅ nanocatalyst synthesized by the sol–gel method scarcely reduced CO₂ and showed very poor activity.
for CH$_3$OH formation. However, the production of CH$_3$OH was significantly enhanced using novel 2D ZnV$_2$O$_6$ nanosheets due to efficient visible light absorption, efficient charge transfer property and higher electron mobility with hindered recombination rate by some amount of V$_2$O$_5$ in the sample as evidenced by XRD analysis \[58\]. More importantly, ZnV$_2$O$_6$ calcined at 550 °C for 3 h showed very poor activity under the same operating conditions. Recently, Zhang et al. \[55\] reported similar observations while investigating hydrogen evolution from water over BiFeO$_3$, Bi$_2$Fe$_4$O$_9$ and BiFeO$_3$/Bi$_2$Fe$_4$O$_9$ heterojunction nanofibers under visible light irradiation. Therefore, lower photoactivity of calcined ZnV$_2$O$_6$ sample was possibly due to change in morphology at elevated temperature. According to results, the production of CH$_3$OH in bare ZnV$_2$O$_6$ was much closer to calcined sample, yet it has an impact on the production of HCOOH and CH$_3$COOH. Therefore, further investigations would be required on understanding the possible reasons in lowering the photocatalytic activity of calcined samples.

Fig. 9(b) shows the effect of different exposure times of heating for 12 h, 24 h, 48 h and 72 h for prepared ZnV$_2$O$_6$ catalyst for CO$_2$ photoreduction with H$_2$O under visible light irradiation (Room temperature, atmospheric pressure, feed flow rate 20 mL/min and irradiation time = 2 h). The results show that the effect of exposure time of heating for 24 h for prepared ZnV$_2$O$_6$ sample exhibits much higher CH$_3$OH, HCOOH and CH$_3$COOH evolution rate than heating time for 12 h. In particular, the evolution rate of products firstly increased with the exposure times of heating until 24 h, afterwards, there is not significant effect of exposure times of heating on ZnV$_2$O$_6$ catalyst photo-activity.

Further investigations were carried out to study the effect of irradiation time on dynamic photocatalytic CO$_2$ reduction in a slurry photoreactor. The production of CH$_3$OH and CH$_3$COOH gradually increased with increasing the time up to an optimum, whereas the HCOOH was decreased and then remained constant as shown in Fig. 10. Fig. 10(a) shows the yield of CH$_3$OH on ZnO/V$_2$O$_5$, ZnV$_2$O$_6$ and ZnV$_2$O$_6$/RGO catalysts under visible light irradiation. It can be seen that without RGO, pure ZnO/V$_2$O$_5$ and ZnV$_2$O$_6$ samples have a lower activity for CH$_3$OH production in the photocatalytic reduction of CO$_2$ compared with ZnV$_2$O$_6$/RGO composite catalyst. After irradiation time of 10 h, CH$_3$OH yield of ZnV$_2$O$_6$/4% RGO (5153.97 μmol g-cat$^{-1}$) was about 5.5 times higher than that of pure ZnO/V$_2$O$_5$ (945.28 μmol g-cat$^{-1}$) and 1.6 times higher than that of pure ZnV$_2$O$_6$ (3253.84 μmol g-cat$^{-1}$). From the above results, graphene has a positive impact on the photocatalytic performance of ZnV$_2$O$_6$, which can be attributed to the synergetic effects between ZnV$_2$O$_6$ nanosheets and graphene nanosheets. This synergetic effect can improve the charge separation and the photocatalytic activity \[59,60\].

Fig. 10(b) presents HCOOH production over ZnO/V$_2$O$_5$, ZnV$_2$O$_6$ and ZnV$_2$O$_6$/RGO catalysts at different irradiation time. Obviously, HCOOH formation over ZnO/V$_2$O$_5$, ZnV$_2$O$_6$ and ZnV$_2$O$_6$/RGO catalysts at different irradiation time. Obviously, HCOOH formation over ZnO/V$_2$O$_5$, ZnV$_2$O$_6$ and ZnV$_2$O$_6$/RGO presented a different behaviour, initially reaching maximum concentration, then gradually decreased. This declined in HCOOH production over the
Fig. 5. Schematic illustration for the formation process of 2D/2D ZnV$_2$O$_6$/RGO nanosheets.

Fig. 6. (a) TEM image of RGO; (b) TEM image of 2D ZnV$_2$O$_6$ nanosheets; (c, d) TEM image of 2D/2D ZnV$_2$O$_6$/RGO (4%) nanosheets; (e) d-spacing of ZnV$_2$O$_6$/RGO sample; (f) SAED pattern of the corresponding sample.
irradiation time was probably due to some amounts of CH₃OH that was initially converted to HCOOH, when there was more production of electrons at the start of the reaction [6]. In general, significantly enhanced photoactivity of RGO combined with ZnV₂O₆ nanosheets towards CO₂ reduction was evidently due to the effects of RGO for efficient separation of charges and more production of electrons over hierarchical ZnV₂O₆ nanosheets.

Fig. 10(c) shows that initially the yield of CH₃COOH production is gradually increased and then remained constant after 6 h of irradiation time. However, the amount of CH₃COOH over ZnO/V₂O₅ catalyst was significantly higher than ZnV₂O₆/RGO and ZnV₂O₆ samples. This confirms that ZnV₂O₆ nanosheets are less favourable for CH₃COOH production but has potential for selective CO₂ reduction with H₂O to CH₃OH.

The performance of ZnV₂O₆/RGO 2D/2D nanosheets was further compared with the results reported by previous researchers. CO₂ was converted to CH₃OH using ZnO modified reduced graphene oxide nanocomposites (ZnO-rGO) and a yield of 263.1 μmol g-cat⁻¹ obtained after 3 h reaction time [39]. ZnS/MMT was used for CO₂ photo-reduction with the maximum CH₃OH yield of 3.2 μmol g-cat⁻¹ after 2 h [61]. Similarly, lamellar BiVO₄ gave CH₃OH yield of 35 μmol g-cat⁻¹ after 6 h during CO₂ photo-reduction with H₂O [62]. CdS(Bi₂S₃)/TiO₂ hetero-structure nanotubes were used to convert CO₂ to CH₃OH and reported optimum yield of 224.6 μmol g-cat⁻¹ after 5 h [63]. Although, appreciable amount of CH₃OH production has been detected over different type of photo-catalysts, yet, superior yield of CH₃OH obtained in the present study using ZnV₂O₆/RGO 2D/2D nanosheets can be attributed to the hierarchical structure with visible light absorption property and hindered charges recombination rate by RGO in 2D/2D
ZnV$_2$O$_6$/RGO hetero-structure system.

In order to check the stability of the ZnV$_2$O$_6$ and ZnV$_2$O$_6$/RGO (4%) nanosheets, a photo-stability test was performed with a cumulative of 32 h irradiation time. The effects of RGO-combined with ZnV$_2$O$_6$ for photocatalytic CO$_2$ reduction to CH$_3$OH, HCOOH and CH$_3$COOH using different irradiation times at room temperature, atmospheric pressure, and feed flow rate 20 mL/min are presented in Fig. 12. Evidently, over ZnV$_2$O$_6$ and ZnV$_2$O$_6$/RGO (4%), CH$_3$OH was observed as the main product during CO$_2$ photo-reduction over the entire irradiation time. The production of CH$_3$OH and CH$_3$COOH concentrations gradually increased until reached to steady state, while the yield of HCOOH was decreased significantly. At the start of the reaction, the photocatalytic CO$_2$ reduction into HCOOH was significantly higher in all ZnV$_2$O$_6$ and ZnV$_2$O$_6$/RGO (4%) catalysts, possibly due to initially some amount of...
CH$_3$OH was converted to HCOOH, when there were more production of electrons. More importantly, catalyst sustained photo-stability even after 32 h of irradiation for selective production of CH$_3$OH. Therefore, novel 2D ZnV$_2$O$_6$ nano-sheets provide higher photoactivity and stability for enhanced CO$_2$ reduction to fuels. The addition of RGO further improved the photo-activity due to higher mobility of charges over hierarchical ZnV$_2$O$_6$ structure with hindered charges recombination rate due to their synergistic effects.

### 3.3. Mechanism of reaction

Pure 2D ZnV$_2$O$_6$ and ZnV$_2$O$_6$/RGO 2D/2D nanosheets are used as photocatalysts to evaluate the photocatalytic activity for photocatalytic reduction of CO$_2$ into CH$_3$OH, HCOOH and CH$_3$COOH. During the reduction process, the major reaction steps are described briefly in Eqs. (1)–(7).

\[
\begin{align*}
\text{ZnV}_2\text{O}_6 + \text{hv} & \rightarrow \text{h}^+ + e^- \\
\text{RGO} + e^- & \rightarrow \text{RGO} \\
\text{H}_2\text{O} + \text{h}^+ & \rightarrow \cdot\text{OH} + \text{H}^+ \\
\text{CO}_2 + \text{e}^- & \rightarrow \text{CO}_2^{\cdot^-} \\
\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- & \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \\
2\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- & \rightarrow \text{CH}_3\text{COOH} + 2\text{H}_2\text{O}
\end{align*}
\]

The production of photo-excited electron-hole pairs over ZnV$_2$O$_6$ under visible light and electron trapping by RGO are listed in Eqs. (1) and (2). This leads to an increase in lifetime of charges and fosters redox reaction at the surfaces. Reduction of CO$_2$ occurs at the CB by the activity of electrons and H$_2$O is oxidized by holes at the VB and this is kinetically explained in Eqs. (3) and (4). The production of HCOOH, CH$_3$OH and CH$_3$COOH through the photo-reduction of CO$_2$ is shown in Eqs. (5)–(7). Based on the photoactivity and reaction pathway, insights for the reaction mechanism were obtained as shown in Fig. 13. Under visible light irradiation, the excited electrons jump from the valence band (VB) of ZnV$_2$O$_6$ nanosheet to its conduction band (CB), but these electrons can combine with holes quickly. In ZnV$_2$O$_6$/RGO nanosheets, due to the interaction between ZnV$_2$O$_6$ nanosheet and graphene nanosheet, the electrons from ZnV$_2$O$_6$ can easily transfer to the surface of graphene and delay the combination of electron and hole. Holes in the VB of ZnV$_2$O$_6$ react with water producing O$_2$ and H$^+$. Absorbed CO$_2$ molecules are reduced to CH$_3$OH, HCOOH and CH$_3$COOH by enriched electrons on the graphene surface.Using ZnV$_2$O$_6$, poor photoactivity is registered attributed to higher electron-hole pairs recombination rate over the ZnV$_2$O$_6$ surface. However, production of CH$_3$OH was significantly enhanced using novel ZnV$_2$O$_6$/RGO.
2D/2D nanosheets due to synergistic effects, efficient visible light absorption, appropriate band structure and higher electron mobility with hindered recombination rate.

4. Conclusions

The novel 2D ZnV$_2$O$_6$ nanosheets combining with 2D RGO successfully synthesized to get 2D/2D nanosheets heterojunction with hindered charges recombination rate and enhanced photocatalytic CO$_2$ reduction with H$_2$O to CH$_3$OH, HCOOH and CH$_3$COOH. More importantly, hierarchical structure of ZnV$_2$O$_6$ favoured selective CH$_3$OH production under visible light irradiation. Yield rate of CH$_3$OH as the main product over ZnV$_2$O$_6$/4.0 wt% RGO catalyst was 5154 μmol g$^{-1}$cat$^{-1}$, significantly higher than using ZnV$_2$O$_6$ and ZnO/V$_2$O$_5$ under visible light irradiation. The observed CH$_3$OH selectivity of 39.96% significantly higher than using ZnV$_2$O$_6$ and ZnO/V$_2$O$_5$ under visible light irradiation. The observed CH$_3$OH selectivity of 39.96% higher than using ZnV$_2$O$_6$ and ZnO/V$_2$O$_5$ under visible light irradiation. The observed CH$_3$OH selectivity of 39.96% higher than using ZnV$_2$O$_6$ and ZnO/V$_2$O$_5$ under visible light irradiation. The observed CH$_3$OH selectivity of 39.96% higher than using ZnV$_2$O$_6$ and ZnO/V$_2$O$_5$ under visible light irradiation. The observed CH$_3$OH selectivity of 39.96% higher than using ZnV$_2$O$_6$ and ZnO/V$_2$O$_5$ under visible light irradiation. The observed CH$_3$OH selectivity of 39.96% higher than using ZnV$_2$O$_6$ and ZnO/V$_2$O$_5$ under visible light irradiation. The observed CH$_3$OH selectivity of 39.96% higher than using ZnV$_2$O$_6$ and ZnO/V$_2$O$_5$ under visible light irradiation. The observed CH$_3$OH selectivity of 39.96% higher than using ZnV$_2$O$_6$ and ZnO/V$_2$O$_5$ under visible light irradiation.

The finding of this work could be useful to develop an efficient solar system for selective photo-catalytic CO$_2$ reduction to valuable chemicals and fuels.

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