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In-situ fabricated 2D/2D heterojunction of ultrathin SiC/RGO nanosheets for efficient CO₂ photoreduction with high CH₄ selectivity

Cheng Han,^[a] Yongpeng Lei,^[b] Bing Wang^[a] and Yingde Wang*^[a]

Abstract: Photoreduction of CO2 into fuel molecules like CH4 represents a rosy perspective in simultaneously exploring renewable energy and alleviating global warming. However, the implementation of such a process is hampered by low products yield and poor selectivity. Herein, a 2D/2D heterojunction of ultrathin SiC/RGO nanosheets was in-situ fabricated for efficient and selective photoreduction of CO2. Ultrathin SiC is preferred to suppress serious charge recombination in bulk phase, thus providing more energetic electrons. The robust 2D/2D heterojunction allows fast transfer of energetic electrons from SiC to RGO. Combining the vital role of RGO in facilitating CO2 activation, the optimized SiC/RGO exhibits an electrons-transfer-rate of 58.17 $\mu mol~h^{\text{-1}}~g^{\text{-1}}$ towards CO_2 reduction, 2.7-folder of that of pure SiC (20.25 $\mu mol~h^{\text{-1}}$ g^{\text{-1}}). More interestingly, about 92% of the transferred electrons from SiC are devoted to generating CH₄ (6.72 µmol h⁻¹ g⁻¹). Such high efficiency and selectivity are mainly contributed by the densely accumulated energetic electrons within RGO, which facilitates the eight-electrons process to produce CH4. Our work will inspire the design of catalystcocatalyst system for efficient and selective photoreduction of CO₂.

Introduction

The excessive consumption of fossil fuels brings increasing concerns on the energy deficiency and environmental problems. More and more carbon dioxide (CO₂) is released into the atmosphere, which becomes the main reason for climate change. Inspired by natural photosynthesis, photocatalytic reduction of CO₂ into hydrocarbon fuels like methane (CH₄) appears to be an ideal strategy to simultaneously develop renewable energy and alleviate global warming.^[1-5] Nevertheless, the state-of-the-art technology is far from practical implementation due to low overall efficiency. The exploration of low-cost, highly active and selective photocatalysts is urgently required to advance the application of CO₂ photoreduction.

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Currently, metal-free compound photocatalysts comprised of nonmetal elements, such as carbon, silicon, nitrogen and attentions.[6-11] boron. are attracting more and more Semiconductors of this type are less susceptible to erosion, have superior sustainability and cost effectiveness. As a representative, silicon carbide (SiC), with a proper band gap for visible-light absorption (~2.4 eV for 3C-SiC and ~3.0 eV for 6H-SiC), has been developed for wide photocatalytic application in synthesis,[12-14] splitting,^[15-21] organic water and CO_2 reduction.^[22,23] For example, in a pioneering study of photocatalytic CO₂ reduction in aqueous solution, Inoue and coworkers^[24] reported that the photoexcited electrons in more negative conduction band (CB) of SiC had much stronger reduction ability to reduce CO2. The high reduction potential of SiC also makes it promising for deep photoreduction of CO2 into CH₄.^[25] However, most of the reported SiC-based photocatalysts are in micro or sub-micro scale with poorly controlled nanostructure, thus suffering from serious charge recombination in the bulk phase. Recently, ultrathin semiconductors have been reported to shorten the diffusion length of photoexcited carriers, which helps to substantially suppress the bulk electron-hole recombination.^[26-28] To make full use of the above-mentioned potentials of SiC, ultrathin SiC is highly desired for efficient and selective photoreduction of CO₂.

Very recently, the strategy of carbon template-deriving SiC has been developed to regulate the nanostructure of SiC by inheriting the morphology of carbon template.^[29-33] Using this method, it is possible to obtain ultrathin SiC on the 2D surface of graphene or reduced graphene oxide (RGO).^[34] Coincidentally, the coupling of graphene or RGO with various semiconductors such as $TiO_2,^{[35]}Cu_2O,^{[36]}g\text{-}C_3N_4,^{[37]}ZnV_2O_6,^{[38]}$ and CdS, $^{[39]}$ has been well proved as one of the most feasible ways to improve photosynthesis photocatalytic CO_2 artificial including reduction.[40-43] For instance, Yu et al.[39] reported that RGO-CdS composite exhibited an 10-folder enhancement of CH4 generation rate than that of pure CdS. Besides the facilitated charges separation contributed by RGO, they also concluded that the presence of RGO would promote the adsorption and activation of CO₂ due to the π - π conjugation interaction, thereby accelerating the photocatalytic reduction of CO2. Likewise, a heterojunction between ultrathin SiC and RGO nanosheets is specially anticipated which can fast transfer energetic electrons from SiC into active sites on RGO to participate in deep reduction of CO₂ into CH₄.

Herein, we realize the robust 2D/2D heterojunction of ultrathin SiC/RGO nanosheets by *in-situ* fabrication of ultrathin SiC on the 2D surface of RGO, which serves as both the carbon source and morphology template. The synergistic effects of ultrathin SiC and RGO nanosheets are integrated into SiC/RGO

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heterojunctions which can facilitate the separation of photogenerated charges,^[44] provide large surface area for CO₂ adsorption, and expose abundant catalytic sites for CO2 reduction. Accordingly, the optimal SiC/RGO heterojunctions exhibit outstanding photocatalytic performance for reducing CO2 into CH₄ and CO, with an electrons-transfer-rate of 58.17 µmol h ¹ g⁻¹, 2.7-folder of that of pure SiC (20.25 μmol h⁻¹ g⁻¹). Besides the improvements in photocatalytic activity, it is also of great significance to tune the selectivity of highly reduced hydrocarbons in the products.[45-47] Although different products have been obtained using carbon cocatalysts, such as CO,[48] $CH_{4}, ^{[49]}$ $CH_{3}OH, ^{[38]}$ $HCOOH^{[50]}$ even $C_{2}H_{4}, ^{[51]}$ fewer of these researches paid attention to the products selectivity and thus the understanding of the catalytic selectivity and mechanism remains unclear. In our case, we interestingly find that a higher CH₄ selectivity is achieved by less proportion of RGO. This is contributed by the densely accumulated energetic electrons within RGO cocatalyst, which facilitates the eight-electrons process to produce CH₄. Our work provides fresh insights into the design of catalyst-cocatalyst system, which will inspire more efficient and selective photocatalysts towards CO₂ reduction.

Results and Discussion

As schematically illustrated in **Figure 1a**, ultrathin SiC was *in-situ* grown on the surface of RGO to construct 2D/2D heterojunctions of SiC/RGO *via* a vapor-solid reaction,^[30-33] during which the RGO nanosheets acted as both the 2D

template and carbon source. The residual content of RGO was tuned by varying the holding time of step 2 from 30 to 180 min. Thereafter, thermal gravimetric analysis (TGA) was used to identify the real content of RGO in the prepared SiC/RGO-x samples, where x represented the mass ratio of RGO. Seen from **Figure 1b**, an abrupt mass loss occurs between 550 °C and 800 °C for all the samples with RGO component, indicating the burning of carbon in air. The mass fraction of residual RGO was estimated to be about 38.2, 25.0, 11.3 and 5.8%, corresponding to a holding time of 30, 60, 120 and 180 min, respectively. For comparison, pure SiC was prepared by eliminating the carbon component from SiC/RGO-5.8 (step 3 in **Figure 1a**) the TGA of which presents no obvious weight loss.

The X-ray diffraction (XRD) spectra were used to reveal the crystal structure of the synthesized samples and shown in Figure 1c. The broad peak of RGO at about 25.1° can be attributed to the (002) plane of the carbon structure. The SiC/RGO heterjunctions and pure SiC show obvious peaks at 35.6°, 41.2°, 60.2°, 72.1° and 75.5°, matching well with the (111), (200), (311) and (222) crystal planes of the cubic SiC phase (JCPDS, No. 29-1129), respectively, Moreover, with longer duration for SiC growth, the residual content of RGO decreases. Accordingly, the broad peak at 25.1° of the SiC/RGO-x samples emerges less clearly from SiC/RGO-38.2 to SiC/RGO-5.8, indicating that RGO was gradually consumed during the carbothermal reduction. Meanwhile, the intensity of SiC peaks rises correspondingly, indicating an increase of the crystal size by prolonging the reaction time. These results also indicate the integration of RGO and SiC in the SiC/RGO heterojunctions.



Figure 1. (a) The synthesis process for SiC/RGO heterojunctions and pure SiC. (b) TGA curves and (c) XRD spectra of SiC/RGO with various proportion of RGO. Inset image in (b) is given to show how to calculate the weight loss. The bottom pattern in (c) presents the crystal data of 3C-SiC from No. 29-1129 JCPDS card.

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Figure 2. TEM images of (a) RGO, (b) SiC/RGO-38.2 and (c, d) SiC/RGO-11.3. (e) EDS results from the selected two points marked with triangle and rectangle in (d). (f) HRTEM image and (g) AFM image with (h) corresponding height profile of SiC/RGO-11.3. (i) TEM image of pure SiC.

The morphology and microstructure of RGO, SiC/RGO heterojunctions, and pure SiC were investigated using transmission electron microscope (TEM) and atomic force microscope (AFM). Bare RGO in Figure 2a exhibits a 2D nanosheet morphology with micrometer long wrinkles. After short time reaction (30 min), the obtained SiC/RGO-38.2 presents an obvious islands-in-sea type morphology (Figure **2b**). We infer that the edged or defective structure on the RGO substrate would firstly react with Si atoms to obtain SiC. By prolonging the reaction duration, the obtained SiC/RGO-11.3 shows an obvious layered structure with an intimate and large area contact (Figure 2c and d). Furthermore, the composition of the heterojunctions was studied by Energy Dispersive X-Ray Spectroscopy (EDS) analyzed at the selected points from Figure 2d. The results in Figure 2e shows that Si and C peaks appear at the rectangle-marked area with an atom ratio of 0.59:1, while only C is observed at the triangle-marked area, directly proving the covering ultrathin layer to be SiC and the substrate nanosheets to be RGO. The partial conversion of 2D RGO into the heterojunction of ultrathin SiC/RGO nanosheets is much favorable to transfer the energetic electrons from SiC to RGO cocatalyst. The intimate junctions are also demonstrated by the high-resolution TEM (HRTEM) image in Figure 2f. The clear lattice fringes with a d-spacing of 0.25 nm are well observed corresponding to the (111) plane from the covering SiC layers. Fewer layers carbon with distance of 0.35 nm are also distinguished, contributed by the wrinkled RGO layers in the substrate. AFM was performed (Figure 2g) to analyse the height profile of SiC/RGO heterojunctions. Typically, the height values of 7.3 nm and 5.2 nm in Figure 2h can be ascribed to

SiC/RGO, demonstrating the ultrathin morphology of the whole heterojunctions. Their accompanied lower levels of 4.4 nm and 3.5 nm are considered as the height of RGO nanosheets. These results reveal that the 2D/2D heterojunctions of ultrathin SiC/RGO nanosheets are successfully fabricated. After eliminating the RGO substrate from SiC/RGO, we also acquire pure SiC for comparison. As can be expected, pure SiC exhibits a morphology of ultrathin and non-continuous pieces (**Figure 2i**), which further confirms the 2D/2D nanostructure of SiC/RGO from another side.

To examine the chemical composition and elemental status in the SiC/RGO heterojunctions, X-ray photoelectron spectroscopy (XPS) and Raman measurements were conducted (Figure 3). The XPS spectrum of C1s for RGO (Figure 3a) can be fitted into two main peaks at 284.4 and 285.1 eV, which can be ascribed to the sp² bonded carbon (C-C) and epoxy/hydroxyl (C-O), respectively. Another smaller peak is also distinguished at about 288.3 eV (inset image), attributed by the carbonyl (C=O) or carboxyl (O-C=O).[16,39] While for the C1s spectrum of SiC/RGO-11.3, the peaks inherited from residual RGO at 284.4 and 285.1 eV are well distinguished. Moreover, the peak at 283.2 eV is assigned to sp³ bonds of C-Si, which is also observed in pure SiC by comparison. The peak at 284.1 eV in pure SiC is attributed to Si₃C-O surface fragments, introduced by the HF/HNO₃ treatment.^[52] As for the Si 2p spectrum of SiC/RGO in Figure 3b, two main peaks at 101.1 and 101.9 eV should be ascribed to Si-C, and surface Si-OH, respectively. The presence of surface Si-OH bonds is beneficial for enhancing CO2 absorption.[53] For the Si2p spectrum of pure SiC, besides the

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two peaks of Si-C (101.1 eV) and surface Si-OH (101.9 eV), another peak at about 102.5 eV belongs to silicon oxocarbide (C_2SiO_2 fragments), contributed by the absorbed oxygen, which is usually observed in SiC nanomaterials.^[52,54]

Raman spectra were further employed to analyse the residual carbon in the prepared SiC/RGO heterojunctions. As presented in Figure 3c, two peaks at 791 cm⁻¹ and 943 cm⁻¹ are recorded in both the samples of SiC/RGO and pure SiC, which can be attributed to the TO and LO phonon of β -SiC, respectively.^[55,56] The spectra of bare RGO exhibits three carbon-related peaks at 1335, 1571 and 2674 cm⁻¹, respectively. The 1335 cm⁻¹ (D band) one is commonly associated with disordered sp² carbon and the 1571 cm⁻¹ (G band) one is resulted from the in-plane vibration of sp² carbon atoms. The 2D band caused by the double resonant Raman scattering with two-phonon emissions is also observed.[31] All the typical peaks of pure SiC and RGO are observed in the spectra of SiC/RGO, further proving the existence of SiC and RGO. Moreover, the D band and 2D band peaks in SiC/RGO have slight blue shift compared with RGO, indicating the interfacial charge transfer between the intimate heteroiunction. Generally, the relative intensity ratio of D and G band (I_D/I_G) can be used to evaluate the degree of defects in carbon materials.^[39,57] In Figure 3c, the I_D/I_G value of RGO and SiC/RGO-11.3 is 0.68 and 0.76, respectively, which implied a good quality of sp² domains upon reduction at 1400 °C. The increase of I_D/I_G from RGO to SiC/RGO reveals that the defect sites were consumed during the SiC growth process. It is reported that graphene with relatively fewer basal plane defects possesses higher electrical conductivity and mobility, and thus contribute to a more superior photocatalytic CO₂ reduction activity when used as cocatalyst.^[58]

The light absorption property of the prepared photocatalysts is evaluated by UV-Vis diffuse reflectance spectra (DRS) and presented in Figure 3d. Bare RGO absorbs a wide range from UV to visible-light, determined by the black nature of carbon nanomaterials (see inset the photography). For pure SiC, its spectrum exhibits an absorption edge at about 480 nm, attributed by its bandgap absorption. As presented in Figure S1, the calculated bandgap (2.59 eV) here is a bit larger than the reported 3C-SiC (2.4 eV) in bulk phase, originated from the ultrathin layered structure with quantum confinement effect. Compared with pure SiC, the SiC/RGO-x samples show significant enhancement of absorption in the visible light region, which is in accordance with the color change from bright green to grevish-green (insets of Figure 3d). The absorption improvement attributed by the residual RGO is favored for utilization of incident light. Moreover, there may exist some black body heating around the layered heterojunctions, which will speed up the diffusion of reactants and products, and help to enhance the photocatalytic performance.[49,59]



Figure 3. XPS spectra of (a) C 1s, (b) Si 2p and (c) Raman spectra for RGO, SiC/RGO-11.3 or pure SiC.(d) UV-vis diffuse reflectance spectra of RGO, various SiC/RGO-*x* heterojunctions and pure SiC. Inset in (d) shows digital photographs of typical samples.



Figure 4. (a) Nitrogen adsorption-desorption isotherms with corresponding pore size distribution curves and (b) CO₂ adsorption isotherms for the sample of SiC/RGO-11.3 and pure SiC.

The porous structure of catalysts, determining the number of active sites and the transport pathways for reactant and product molecules, plays important roles in the photocatalysis reaction. Therefor, the pores structure and surface area were investigated using nitrogen adsorption-desorption measurements for the sample SiC/RGO-11.3 and pure SiC. Similar shape of the two isotherms in Figure 4a demonstrates that the SiC/RGO heterojunctions have inherited the nanosheets structure of RGO template. The pore size distributions (inset in Figure 4a) indicate that the samples have wide pore size distributions from 2 to over 100 nm, confirming the existence of large mesopores and some macropores. The SiC/RGO heterjunctions have larger specific surface area (90.1 cm^2 g⁻¹) than that of pure SiC (71.1 cm^2 g⁻¹) due to the presence of some RGO whose theoretical specific surface area is 2600 m² g⁻¹. A photocatalyst with high specific surface area can accommodate more surface active sites and facilitate the transport of charge carriers, which is beneficial for enhancing the photocatalytic CO₂ reduction.^[60] It is believed that the π - π conjugation interaction between CO2 and RGO would promote the adsorption and subsequent activation of CO₂ molecules.^[43] Actually, we proved such an important role of RGO using the CO₂ adsorption profiles in Figure 4b, which exhibit that the SiC/RGO heterojunctions have higher CO₂ adsorption capacity compared with that of SiC.

Photocatalytic CO₂ reduction performance was evaluated in the presence of H₂O vapor, involving a gas-solid heterogeneous reaction. CO and CH4 were detected as the main products in our reaction system (Figure S2), in line with previous reports using similar method.^[25,61-63] The generation rates of CO, CH₄, and active electrons are summarized in Figure 5a. The active electrons' rate represents the rate of photogenerated electrons that participate in CO2 reductions (details see Table S1), reflecting the real charge transfer efficiency of a specified photocatalysts.[47] Pure SiC exhibits an average CH₄ evolution rate of 2.25 µmol h⁻¹g⁻¹ and CO evolution rate of 1.13 µmol h⁻¹ g⁻¹, respectively. Its active electrons' rate is 20.25 µmol h⁻¹g⁻¹. Surprisingly, by remaining certain amount of RGO, the active electrons' rate increases obviously from SiC to SiC/RGO, achieving a maximum of 58.17 µmol h⁻¹ g⁻¹ with 11.3 wt% of RGO. To make it clear that if some

carbonaceous residues contributed to the yields of CO or CH₄,^[64] a contrast test in Ar instead of CO₂ was performed under identical conditions using the optimized sample. As shown in Figure S2, no CO or CH4 was detected under Ar atmosphere, implying that there was negligible interference from the carbonaceous residues. This is reasonable, considering the synthesis of SiC/RGO involved a hightemperature carbothermal process and the subsequent sample treating did not use any organics. Control experiments were also carried out under CO₂ or Ar without adding H₂O (Table S2). The obviously decreased or negligible CO or CH₄ yield confirmed the vital role of H₂O by providing protons for CH₄ or CO generation (Figure S3 and S4). These contrast results demonstrated that the carbon products of CO and CH4 originated from the CO₂ and H₂O. The photocatalysis stability of the optimized SiC/RGO sample was also investigated. As shown in Figure S5, there is no obvious loss of the CH4 and CO generation rates in three successive cycles. Moreover, the XRD spectra in Figure S6 reveal that the composition and structure of SiC/RGO-11.3 did not change after three cycles test in comparison with the fresh sample. Therefore, it is proved that the optimized SiC/RGO have a good stability in both the structure and performance for photocatalytic reduction of CO2 under UV-visible irradiation.

Of note, bare RGO is not active for the conversion of CO_2 to CH_4 under the photocatalysis conditions employed (**Figure S7**). Therefor in the SiC/RGO heterojunctions, the SiC phase serves as the source of photogenerated electrons while the RGO helps to fast transfer energetic electrons for subsequent CO_2 reduction. A lower RGO content in the SiC/RGO will not provide adequate electrons trapping sites to suppress the recombination of charge carriers; or otherwise, a higher RGO content means a relatively low content of SiC, which will definitely result in a decreased number of photogenerated electrons. Thus it is reasonable that a suitable ratio of SiC with RGO is crucial for optimizing photocatalytic CO_2 reduction, which is a similar observation to previous studies of graphene-based photocatalysts.^[35-39]

From **Figure 5a**, it is also noticeable that the proportion of RGO has important effects on both the activity and selectivity. A higher CH_4 selectivity is achieved by a less proportion of RGO.

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Figure 5. (a) Photocatalytic generation rate of CH₄, CO and active electrons with various samples.(b) ratio of CH₄ in products depending on the relative electrons density on RGO. (c, d) illustrated mechanism of the electrons density-dependant CH₄ selectivity in SiC/RGO heterojunctions with (c) low electrons density and (d) high electrons density on RGO. The active electrons' rate in (a) represents the rate of photogenerated electrons that participate in CO₂ reductions and is calculated by the equation: r(active electrons) = $8*r(CH_4) + 2*r(CO)$.

Thermodynamically speaking, CH₄ generation from CO₂ photoreduction should be easier than CO formation because the reduction potential for CH₄/CO₂ (-0.24 V vs. NHE) is less negative than that for CO/CO2 (-0.52 V vs. NHE). But the generation of one CH4 molecule involves the participation of eight electrons (CO₂ + 8e⁻ + 8H⁺ \rightarrow CH₄ + 2H₂O), while for one CO generation it needs only two electrons (CO₂ + 2e⁻ + 2H⁺ \rightarrow $CO + H_2O$). In our case, the energetic electrons in all the samples come from the same CB band of SiC, thus they should have a same reduction potential. Accordingly, a sufficient supply of energetic electrons should be considered as the main parameter that determines CH₄ selectivity in this context. To make this point clear, we calculate the relative electrons density on RGO cocatalyst by using the active electrons' rate to divide the mass ratio of RGO in SiC/RGO-x (Table S1). Consequently, a positive correlation is found between the CH₄ ratio selectivity and the relative electrons density on RGO, plotted in Figure 5b. In other words, a high proportion of RGO in SiC/RGO heterojunctions will share sparse energetic electrons on RGO, facilitating the two electrons process for CO generation; otherwise, a low proportion of RGO will accumulate dense energetic electrons, promoting the eight electrons process for

 CH_4 generation, as schematically illustrated in **Figure 5c** and **d**, respectively. We expect our understanding of electrons densitydependent CH_4 selectivity here may instruct the development of efficient and selective CO_2 reduction photocatalysts especially when 2D nanosheets are used as cocatalysts, such as graphene, MXene, or transition metal disulfides.

The Mott-Schottky plots, transient photocurrent responses, electrochemical impedance spectra (EIS) and photoluminescence (PL) emission spectra were further characterized to gain insights into the charge transfer dynamics in the typical samples. The CB potential of pure SiC and SiC/RGO heterojunction is measured to be about -1.58 V and -1.41 V using Ag/AgCl reference electrode (Figure 6a), corresponding to -1.38 V and -1.21 V vs NHE (pH = 7.0, the same below), respectively. Both of them are far more negative than the reduction potential of CO₂/CH₄ (-0.24 V) and CO₂/CO (-0.58 V). Combining the bandgap result of pure SiC (2.59 V), its valance band (VB) potential is estimated to be 1.01 V (-1.58 V + 2.59 V), more positive than the oxidation potential of O₂/H₂O (0.82 V). Hence, the photogenerated electrons from SiC with strong reduction potential is energetically favorable to trigger the conversion of CO₂ into CO and CH₄, especially the

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Figure 6. (a) Mott-Schottky plots, (b) transient photocurrent responses, (c) Nyquist plots measured in $0.5 \text{ M} \text{ Na}_2\text{SO}_4$ (pH = 7.0) solution and (d) room-temperature PL spectra for the sample of SiC and SiC/RGO-11.3.

deeply-reduced product of CH₄.^[25] Seen from the transient photocurrent results in Figure 6b, SiC/RGO-11.3 exhibits a much higher current than pure SiC under irradiation, confirming the better charge transfer within the heterojunctions. Specifically, the curve of pure SiC witnesses a saltatory sharp at the beginning of each irradiation, induced by the immediately excited carriers and their subsequent fast recombination. While for SiC/RGO-11.3, the photocurrent is firstly generated by the stored electrons from RGO rather than directly from SiC, resulting in a gradual increase (decrease) when the light is on (off).^[39,49] As evidenced by the EIS Nyquist plots in Figure 6c, SiC/RGO-11.3 shows a lower electrochemical impedance compared to that of pure SiC, which is preferred for the transport of photogenerated electrons.^[59] Accordingly, under irradiation, the electrochemical impedance of SiC/RGO-11.3 further diminished due to the excitation of abundant free carriers. Furthermore, room-temperature PL spectroscopy were performed to reveal the separation-recombination fate of photoexcited charges.^[27,65] As depicted in Figure 6d, the PL emission intensity of SiC/RGO heterojunctions decreased dramatically in comparison with pure SiC, suggesting that the carrier recombination rate was hindered effectively. These photoelectrochemical observations and PL results credibly demonstrate that the electron-hole separation efficiency is dramatically enhanced in the robust 2D/2D heterojunction of ultrathin SiC/RGO nanosheets, which certainly contributes to the improved photocatalytic CO₂ reduction. Particularly, the

densely accumulated energetic electrons on RGO cocatalyst would facilitate the eight-electrons process to produce CH₄.

Conclusions

To sum up, the heterojunctions of ultrathin SiC/RGO nanosheets with intimate 2D/2D contact have been in-situ fabricated by using RGO nanosheets as both the carbon source and morphology template. Ultrathin SiC is much preferred to provide energetic electrons with strong reduction potential. The robust 2D/2D heterojunction allows fast transfer of energetic electrons from SiC to RGO. The content of residual RGO was easily tuned in the synthesis process, which had vital roles in promoting both the activity and selectivity of SiC in photocatalytic CO₂ reduction. A higher CH₄ selectivity was achieved by a less proportion of RGO with densely accumulated energetic electrons, which facilitates the eightelectrons process to produce CH₄. Our findings provide fresh insights into the design of catalyst-cocatalyst system, which will inspire more efficient and selective photocatalysts towards CO2 reduction.

Experimental Section

Synthesis of 2D/2D heterojunctions of SiC/RGO



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GO was prepared in our laboratory from natural graphite flakes (>99.8%, Alfa Aesar) using a modified Hummers method (details see Supporting information).^[66] All other reagents were analytical grade and purchased from Sinopharm Chemical Co., Ltd. (Shanghai, China). The in-situ fabrication process of SiC/RGO heterojunction is graphically shown in Figure 1a with the setup illustrated in Figure S8. In a typical procedure, 50 mL GO solution (5 mg mL⁻¹) was heated to 180 °C for 12 h in a Teflon-lined stainless steel autoclave. After the hydrogel was freeze-dried overnight, the obtained RGO monoliths was directly loaded on a porous graphite sieve in a corundum crucible, at the bottom of which excessive Si (3-fold mass of RGO) powder was added previously. Then, the crucible was heated to 1,400 °C (5 °C·min-1) under Ar atmosphere with a holding time of 30-180 min. The SiC was in-situ grown on the surface of RGO via a vapor-solid reaction between Si atoms and solid carbon template. Thereafter, the products were treated with 1:3 HF/HNO₃ aqueous solutions to remove the unreacted Si, washed repeatedly with water and then dried at 70 °C. The finally obtained samples were remarked as SiC/RGO-x, where x represents the mass ratio of RGO in the SiC/RGO heterjunctions and could be measured by subsequent thermal gravimetric analysis (TGA). To prepare pure SiC as comparison, SiC/RGO (obtained after 180 min reaction) was calcined in air at 700°C for 1 h to remove the RGO substrate and then treated with HNO₃/HF to remove surface SiO_x. Bare RGO was also treated with identical conditions to compare with SiC/RGO heterjunctions when characterized.

Characterization

The residual mass ratio of RGO in SiC/RGO heterojunctions was measured by TGA in a PerkinElmer Pyris 1 machine with a heating rate of 10 °C min⁻¹ in air from room temperature to 1000 °C. The crystal structure was firstly characterized by X-ray diffraction (XRD) spectra, recorded on a Bruker AXS D8 Advance device using Cu-Ka radiation (λ = 1.5418 Å). The morphology of prepared samples was observed using Titan G2 60-300 high resolution transmission electron microscope (HR-TEM) equipped with Energy Dispersive X-Ray Spectroscopy (EDS) analyzer. The thickness was further measured by atomic force microscope (AFM) observation on a Bruker Multimode 8 machine. The elemental status were analyzed by X-ray photoelectron spectroscopy (XPS), conducted on a Thermo Scientific ESCALAB 250Xi machine with an Al K α source. Ultraviolet-visible (UV-vis) light diffuse reflectance spectra were collected on a U-4100 Hitachi spectrophotometer. N_2 and CO_2 adsorption isotherms were performed on an ASAP2020M apparatus. The samples were thoroughly degassed in vacuum at 200 °C for 10 h, and then measured at 77 K and 273 K to determine N₂ and CO₂ adsorption, respectively. The Brunauer-Emmett-Teller (BET) surface area was evaluated from N2 adsorption data. Barrett-Joyner-Halenda (BJH) method was chosen to determine the pore size distributions. Raman measurements were conducted on Bruker RAM II with a laser wavelength of 514 nm. Photoluminescence (PL) emission spectra were obtained on a Hitachi F-7000 fluorescence spectrometer under excitation of 300 nm.

All of the the electrochemical experiments were performed in a standard three-electrode system using an

electrochemical workstation (CHI660e, Shanghai). The working electrode was fabricated on fluorine-doped tin oxide coated (FTO) substrates by a facile drop-casting method (0.4 mg cm⁻²). Insulate epoxy resin was used to protect the boundary of the FTO glass and leave a fixed area of 1*1 cm². After air drying, the working electrode was further dried at 100 °C for 2 h to improve adhesion. A Pt wire and a Ag/AgCl electrode was used as the counter electrode and reference electrode, respectively. For the measurement of transient photocurrent responses, a 300 W Xe lamp (CEL-HXF300, Beijing Aulight Co.,) was used as the source of simulated solar light to provide chopped irradiation from a horizontal quartz window in the cell. The electrochemical impedance spectra (EIS) measurement was carried out in the same system and recorded over a frequency from 100 mHz to 1 MHz with an amplitude of 5 mV at 0.5 V bias potential. The Mott-Schottky (MS) plots were measured with a frequency of 1000 Hz and amplitude of 10 mV in 0.5 M Na₂SO₄ aqueous solution (details see Supporting information).

Photocatalytic CO₂ reduction experiment

Photocatalytic reduction of CO₂ in the presence of H₂O vapor was carried out as a gas-solid heterogeneous reaction in a home-made cylinder reactor with a guartz plate cover (Figure S9). Typically, for each test, 30 mg of the powdered sample was dispersed into some deionized water with 10 min sonication to get a homogeneous suspension, which was then transferred into a petri dish. After evaporation at 120 °C, the catalyst was deposited as a thin film. The petri dish with catalyst was then placed in the reactor (60 mL), in which there is a glass holder to support the the petri dish. After sealing the cover of quartz plate, the photoreactor was vacuumed at -0.1 MPa (relative pressure) for 20 min, and CO₂ (99.995%) was subsequently introduced into the reactor. The vacuum-filtration process was repeated 5 times. After that, 100 µL ultrapure H₂O was injected into the reactor via the silicone rubber septum and dispersed homogeneously on the bottom. A 300 W Xe arc lamp (CEL-HXF300, Beijing Aulight Co., Ltd.) was used as the irradiation source (10 cm away from the reactor) to provide UVvisible light with intensity of 0.86 W cm⁻² measured by a CEL-NP2000 optical power meter.Each test was typically performed under 4 h irradiation. Certain amount of gases mixture would be taken and analyzed by a gas chromatography (SP6890) equipped with a flame ionized detector (FID) and a thermal conductivity detector (TCD). The produced gases were calibrated with a standard gas mixture and the identity was determined by the retention time.

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Keywords: photocatalysis • CO₂ reduction • heterojunction • silicon carbide • CH₄ selectivity

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In the described 2D/2D heterojunction of SiC/RGO, energetic electrons would be fast transferred from ultrathin SiC and densely accumulate on RGO for efficient and selective CH₄ generation from CO₂ photoreduction.



Cheng Han, Yongpeng Lei, Bing Wang, Yingde Wang*

Page No. – Page No.

In-situ fabricated 2D/2D heterojunction of ultrathin SiC/RGO nanosheets for efficient CO₂ photoreduction with high CH₄ selectivity