ABSTRACT: The ultimate goal of photocatalytic CO$_2$ reduction is to achieve high selectivity for a single product with high efficiency. One of the most significant challenges is that expensive catalysts prepared through complex processes are usually used. Herein, gram-scale cubic silicon carbide (3C-SiC) nanoparticles are prepared through a top-down ball-milling approach from low-priced 3C-SiC powders. This facile mechanical milling strategy ensures large-scale production of 3C-SiC nanoparticles with an amorphous silicon oxide (SiO$_x$) shell and simultaneously induces abundant surface states. The surface states are demonstrated to trap the photogenerated carriers, thus remarkably enhancing the charge separation, while the thin SiO$_x$ shell prevents 3C-SiC from corrosion under visible light. The unique electronic structure of 3C-SiC tackles the challenge associated with low selectivity of photocatalytic CO$_2$ reduction to C$_1$ compounds. In conjugation with efficient water oxidation, 3C-SiC nanoparticles can reduce CO$_2$ into CH$_4$ with selectivity over 90%.

KEYWORDS: photocatalysis, CO$_2$ reduction, 3C-SiC, selectivity, CH$_4$
The influence of the surface states and the SiOx shell on the charge-carrier dynamics and photocatalytic CO2 reduction under visible light is comprehensively discussed.

2. RESULTS AND DISCUSSION

Ball milling is a typical top-down technique for the large-scale production of nanomaterials.19,20 This process is associated with breaking and reducing the bulk solid materials into nanoscale particles through high-energy balls (Figure 1a).

According to the scanning electron microscope (SEM) images, the as-grown 3C-SiC crystalline powder we adopted contained micron-sized particles. After the ball-milling process, the 3C-SiC powder was transformed into nanosized particles (Figures 1b,c and S1). The phase structure of the as-prepared 3C-SiC nanoparticles was then investigated by X-ray diffraction (XRD), whose diffraction peaks at 35.6°, 41.4°, and 60.0° corresponded well with the crystal faces (111), (200), and (220) of the cubic SiC structure, also called ascorresponded well with the crystal faces (111), (200), and (XRD), whose diffraction peaks at 35.6°, 41.4°, and 60.0° corresponded well with the crystal faces (111), (200), and (220) of the cubic SiC structure, also called ascorresponded well with the crystal faces (111), (200), and (XRD), whose di

3C-SiC nanoparticles showed additional Raman modes between 300 and 700 cm−1, due to the presence of the surface Si–O species (Figure 2a).21 This result was confirmed by the X-ray photoelectron spectroscopy (XPS) measurement. According to the high-resolution XPS Si 2p spectra, the as-grown 3C-SiC powder displayed a dominant peak at around 100.4 eV corresponding to the Si–C bond (Figure 2b). In contrast, 3C-SiC nanoparticles showed a remarkable shoulder peak at around 102.0 eV (Figure 2b). We believe that the new shoulder peak should be indexed to the surface amorphous Si–O species, rather than crystallized SiO2, whose Si–O bond will appear at around 103.0 eV in the XPS spectra.23–25 This assumption was consistent with the XRD result, as no diffraction peaks were detected for SiO2. Moreover, compared to that of the 3C-SiC powder, the intense peaks at 100.28 eV (typical of Si–C bond) of 3C-SiC nanoparticles shifted to lower binding energies (Figure 2b). The intriguing binding-energy shift was due to the localized charge decrease, possibly due to newly formed surface states, including the surface defects and dangling groups.26–28 This is clear, as the high-energy ball-milling process could result in surface defects while the surface layer might also be oxidized due to the high temperature during the process. The amorphous SiO2 was directly visualized through high-resolution transmission electron microscopy (TEM). The interplanar distance of 0.25 nm matches with the (111) plane of 3C-SiC, and an amorphous thin SiO2 shell was formed on the 3C-SiC surface (Figures 2c and S2). These results demonstrated that along with the ball-milling process, an amorphous Si–O shell was in situ formed on the nanosized 3C-SiC (inset of Figure 2c). The optical absorption of the as-prepared 3C-SiC nanoparticles was then evaluated through UV–vis absorption spectra. In contrast to commercial P25-TiO2 with a band-edge absorption at around 390 nm, 3C-SiC nanoparticles showed broader absorption with an edge at around 520 nm and an absorption tail extending to 800 nm (Figure S3). The extended absorption tail is also an evidence of the new surface states. The Tauc plot shown in the inset of Figure S3 reveals the band gap of 3C-SiC...
nanoparticles is at around 2.36 eV. The schematic illustration of the band structure of the 3C-SiC nanoparticles is shown in Figure 2d. Based on CO2 reduction and redox potentials of water oxidation, 3C-SiC nanoparticles can energetically reduce CO2 into CH4 or CH3OH in conjugation with O2 evolution reaction under visible light.6,18,29

We then collected and analyzed the CO2 reduction products through gas chromatography (GC) to test our hypothesis. P25 was used as the reference sample, which selectively reduces CO2 into CO with 63% selectivity (Table 1). As for both as-grown 3C-SiC powder and nanosized 3C-SiC, CH4 became the dominant product; however, the nanosized 3C-SiC showed over four times an enhanced linear CH4 generation rate (4.9 μmol g−1 h−1) than that of the as-grown 3C-SiC powder (Figure 3a). Compared with other single-component and sacrificial reagent-free photocatalytic CO2 reduction systems, 3C-SiC nanoparticles display either comparable or much higher CH4 generation rates (Table S1). The low cost and large yield for synthesizing 3C-SiC nanoparticles are promising for practical visible-light-driven CO2 reduction (Table S1).

Meanwhile, along with CH4 generation, O2 simultaneously evolved, suggesting that CO2 would react with H2O through two half-reactions with photoinduced electrons and holes, respectively, reducing CO2 and oxidizing H2O. Moreover, the evolved O2 amount from 3C-SiC nanoparticles was almost 2.1 times that of CH4 close to the theoretical value of 2.0 (CO2 + 2H2O → CH4 + 2O2), exhibiting the high selectivity of 3C-SiC nanoparticles for CO2 reduction (Figure 3b). To confirm that the reduced CO2 was not from 3C-SiC decomposition, we then adopted isotopic 13CO2 as the carbon source. It was found that 13CH4 with a mass/charge ratio (m/z) of 17 was the only product, indicating the high stability of 3C-SiC nanoparticles (Figures 3c and S4). As shown in 3C-SiC nanoparticles, the unexpected high selectivity could be explained by its unique band structure, as shown in Figure 2d, which demonstrates that CH4 is the most likely and thermodynamically possible CO2 reduction product. To evaluate the stability and charge separation efficiency of the as-prepared 3C-SiC, we monitored the photocurrent response of the as-prepared 3C-SiC photoanodes under visible-light irradiation. Nanosized 3C-SiC showed a much higher photocurrent density than that of the as-grown 3C-SiC powder, consistent with its higher reactivity for CO2 reduction (Figure 3d). Moreover, the transient decay of the 3C-SiC powder shows a large spike in the initial stage, followed by a multieponential decrease. However, the spike was suppressed in 3C-SiC nanoparticles, exhibiting more efficient charge-carrier separation and transfer within the 3C-SiC nanoparticles, as well as higher stability (Figure 3d).15,30 The efficient charge-carrier separation and transfer can be further supported by electrochemical impedance spectroscopy, which revealed that the 3C-SiC nanoparticles had a much smaller impedance arc radius than that of the 3C-SiC powder (Figure 3e).

Enlightened by the above results and discussion, it is reasonable to propose that surface states are responsible for the enhanced activity of the photocatalytic CO2 reduction. At the same time, the amorphous SiO2 shell prevents 3C-SiC from oxidation. Room-temperature photoluminescence (PL) spectroscopy was conducted to determine the possible surface states and charge-carrier dynamics of 3C-SiC nanoparticles. For the 3C-SiC powder, it displayed a negligible near-band-edge emission (∼520 nm) due to the nature of its indirect band gap (Figure 4a). However, after the high-energy ball-milling process, the 3C-SiC nanopowders exhibited a much broader (from 450 to 700 nm) and more substantial emission peak centered at 550 nm, which was located at the lower energy side of the band gap of 3C-SiC and thus could not be related to the quantum confinement. This broad emission band was thus attributed to the radiative recombination through surface states.11 In particular, given that the high-energy ball-milling process could result in many surface defects, the significantly increased emission band compared to the low photoluminescence emission of the as-grown 3C-SiC powder. We proposed that the photogenerated electrons could be easily trapped in the surface states below the conduction band, whose recombination with the photogenerated holes in the valence band was responsible for the defect emission (Figure 4b). To further confirm these assignments, we measured the time-resolved PL. The decaying of the PL emission band at 550 nm of 3C-SiC nanoparticles was apparently much slower than that of the 3C-SiC powder (Figure 4c). Both of the decaying curves can be fitted by a double-exponential model as illustrated in Table 2, including a fast decay component (τ1) and a much slower component (τ2), which are attributed to the radiative recombination from the conduction band to the valence band and the radiative recombination through the surface states, respectively.32,33 The band-to-band recombination dominated the decaying curve of the as-grown 3C-SiC powder, based on the higher proportion of the fast decay component (τ1).

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Table 1. Distribution of H2 and CO2 Reduction Products

| Photocatalyst       | H2 (%) | CH4 (%) | CO (%) | CH3OH (%) |
|---------------------|--------|---------|--------|-----------|
| P25                 | 13     | 16      | 63     | 8         |
| 3C-SiC/powder       | 3      | 91      | 6      | 94        |
| 3C-SiC/nanoparticle | 94     | 5       |        |           |

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Figure 3. Photocatalytic performance of the as-prepared 3C-SiC photocatalysts. (a) Photocatalytic CH4 evolution over the as-prepared photocatalysts. (b) Photocatalytic CH4/O2 evolution over 3C-SiC nanoparticles. (c) GC-mass spectra of 13CH4 evolved from photocatalytic isotopic 13CO2 over 3C-SiC nanoparticles. (d) Photocurrent decay and (e) electrochemical impedance spectroscopy plots of the as-prepared 3C-SiC nanoparticle photoanodes.
Figure 4. Charge-carrier kinetics and photocatalytic CO2 reduction mechanisms of 3C-SiC nanoparticles. (a) Room-temperature steady-state PL spectra of the as-prepared 3C-SiC photocatalysts. (b) Schematic illustration of the charge-carrier dynamics in 3C-SiC nanoparticles. (c) Time-resolved PL decaying curve at 550 nm of the as-prepared 3C-SiC photocatalysts. (d) CO2 adsorption isotherms and (e) CO2-temperature-programmed desorption (TPD) profiles of the 3C-SiC powder and nanoparticles. (f) In situ Fourier transform infrared (FTIR) spectra of 3C-SiC nanoparticles during photocatalytic CO2 reduction.

Table 2. Parameters of the Time-Resolved PL Decaying Curves Based on a Biexponential Decay**

| catalyst          | τ1 (ns) | B1 (%) | τ2 (ns) | B2 (%) | τaverage (ns) |
|-------------------|---------|--------|---------|--------|---------------|
| 3C-SiC/powder     | 1.12    | 68.33  | 6.69    | 31.67  | 2.88          |
| 3C-SiC/nanoparticle| 1.25    | 36.85  | 38.9    | 63.15  | 25.02         |

**The data in the decaying curve could be correctly fitted by a double-exponential function of I(t) = A1exp(-t/τ1) + A2exp(-t/τ2). I(t) is the intensity of the PL signal, A1 are the pre-exponential factors, and τ1 are the characteristic lifetimes. We calculated the average lifetime (τaverage) through τaverage = B1×τ1 + B2×τ2. The B1 is the relative concentration in the double-exponential decay (B1 = A1/(A1 + A2)).

As for the 3C-SiC nanoparticles, the high proportion of long-living surface defects (∼63.15%) suggested the efficient trapping of electrons on the surface states, resulting in a much longer τ2 than that of as-grown 3C-SiC. As a result, 3C-SiC nanopowders show an average lifetime of 25.02 ns, almost nine times longer than that of the as-grown 3C-SiC powder (Table 2). The surface states of 3C-SiC nanoparticles act as a trapping center of the photogenerated electrons, thus suppressing the charge recombination from the conduction band to the valence band and enhancing the charge separation (Figure 4b). These results agree well with the transient photocurrent response and electrochemical impedance spectroscopy results. The stability test for multiple CH4 generations revealed that the photocactivity of 3C-SiC nanoparticles did not decay, while the 3C-SiC powder gradually lost 60% of its original photocactivity (Figure S5). Photocorrosion is a common phenomenon for conventional SiC due to the surface oxidation (SiC + 4H2O + 8H+ → SiO2 + CO2 + 8H2)16,18,34. The corrosion was directly reflected by rapidly decreased photocorrosion and photocurrent response (Figures 3d and S5). Our previous studies pointed out that only if its surface was protected by cocatalysts or graphene would 3C-SiC achieve high stability for photocatalytic applications.16,18,34 Here, the high stability of 3C-SiC nanoparticles was due to the protection of the in situ formed SiO2 layer because the nanosized 3C-SiC was inclined to suffer from self-corrosion under light irradiation (Figure 4e). 3C-SiC nanoparticles maintained their original phase structure after multicycle CO2 photoreduction according to the XRD pattern and Raman spectra (Figure S6a,b). Meanwhile, the SiO2 shell still remained amorphous (Figure S6c).

To further clarify the photocatalytic mechanism, we first evaluated the CO2 adsorption capacity of the 3C-SiC powder and nanoparticles. According to CO2 adsorption isotherms, 3C-SiC nanoparticles showed a much better ability to capture CO2 than the 3C-SiC powder (Figure 4d). The enhanced CO2 adsorption was not only due to the increased surface area but also related to the surface states that served the CO2 binding sites, as evidenced by the CO2-temperature-programmed desorption (TPD) profiles. As compared with the 3C-SiC powder, 3C-SiC nanoparticles displayed two prominent CO2 desorption peaks at 326 and 336 °C, indicating that the surface defects served as the chemical CO2 adsorption and activation sites (Figure 4e).

Meanwhile, we performed in situ Fourier transform infrared (FTIR) spectroscopy to explore the intermediates associated with CO2 reduction to CH4 (Figure 4f). Once the light was turned on, we were able to detect a dominant peak at 1622 cm⁻¹ ascribed to the *COOH species in the presence of saturated CO2. *COOH is widely accepted as a critical intermediate for CO2-to-CH4 reduction, formed through a proton-coupled electron transfer process (CO2 + e⁻ + H⁺ → *COOH).35,36 Another two absorption bands at 1042 and 1166 cm⁻¹ were the feature bands of *CHO, while the absorption band at 1089 cm⁻¹ was the characteristic band of *CHO. Both *CHO and *COOH are the important intermediate products of CO2-to-CH4 reduction.13,37,38 A shoulder peak next to *COOH at 1683 cm⁻¹ was the asymmetric stretching of *HCOO.33 Based on the in situ FTIR analysis, the selective CO2 reduction to CH4 was likely to proceed via the following steps:

\[ \text{CO}_2 + e^- + H^+ \rightarrow *\text{COOH} \]
\[ *\text{COOH} + 2e^- + 2H^+ \rightarrow *\text{CHO} + \text{H}_2\text{O} \]
\[ *\text{CHO} + 2e^- + 2H^+ \rightarrow *\text{CH}_3\text{O} \]
*CH$_3$OH + e$^-$ + H$^+$ $\rightarrow$ CH$_4$ + *O

It is still ambiguous why CH$_4$OH was not the primary product despite its low reduction potential. It is known that the formation of CH$_4$OH is dependent on formic acid (HCOOH) as the critical intermediate via *HCOOH + 4H$^+$ + 4e$^-$ $\rightarrow$ CH$_4$OH + H$_2$O. Unfortunately, HCOOH is also thermodynamically unaccessible for 3C-SiC (Figure 2d). Therefore, CH$_3$OH is unlikely the selective CO$_2$ reduction product of 3C-SiC. For a better understanding of the selectivity of 3C-SiC for photocatalytic CO$_2$ reduction, preparation of 3C-SiC nanoparticles with distinct exposed facets coupled with the density functional theory calculation is highly desirable, which is one of our research goals in the future.

3. CONCLUSIONS

In conclusion, gram-scale 3C-SiC nanoparticles were prepared through a top-down ball-milling approach from low-priced 3C-SiC crystalline powder. This facile mechanical milling strategy ensures large-scale production of 3C-SiC nanoparticles and simultaneously induces the formation of abundant surface states and an amorphous SiO$_2$ shell. The surface states are shown to remarkably trap the photogenerated electrons and thus suppress the electron–hole recombination, while the SiO$_2$ shell prevents 3C-SiC from corrosion under visible light. Due to the unique electronic structure of 3C-SiC, it is capable of reducing CO$_2$ into CH$_4$ with a high selectivity of over 90% in conjugation with efficient water oxidation. We believe this work provides a new strategy to synthesize nanosized SiC and other nonmetallic carbides with good chemical stability and high catalytic efficiency for practical photocatalytic applications.

4. EXPERIMENTAL SECTION

4.1. Catalyst Preparation. 3C-SiC nanoparticles were prepared through a ball-milling process from 3C-SiC crystalline powders grown by chemical vapor deposition in a typical high-energy ball-milling machine. The whole milling process was carried out under ambient conditions for 5 h at a speed of 500 rpm. Then, the 3C-SiC nanoparticles were carefully collected and thoroughly washed with water and ethanol, and finally dried at 120 °C in the air.

4.2. Photocatalytic CO$_2$ Reduction. We adopted a 300 W Xenon lamp with a 420 nm filter as the light source to simulate visible light. For CO$_2$ reduction, we uniformly dispersed 0.05 g of 3C-SiC into a gas reactor (volume: 200 mL). The reaction setup was vacuum-treated six times before high-purity CO$_2$ was pumped to achieve ambient pressure. Then, we injected 1 mL of Milli-Q water into the reaction setup and simulated a gas–solid heterogeneous reaction condition. In the end, the visible light was turned on. During CO$_2$ reduction, we took 1 mL of gas each time using a silicon rubber septum for gas chromatography (GC: Agilent HP 6890) analysis. For an isotopic labeling experiment, $^{13}$CH$_4$ was collected and analyzed via a gas chromatography-mass spectrometer (Pfeiffer OmniStar) with $^{13}$CO$_2$ ($^{13}$C 99%, Sigma-Aldrich) as the carbon source.

**ASSOCIATED CONTENT**

1. Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c19945.

Experimental details, supplementary figures and table (PDF).
Photocatalytic Activity for Reduction of CO2 with H2O.

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