The functionality of surface hydroxyls on selective CH₄ generation from photoreduction of CO₂ over SiC nanosheets

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1. Experimental details

Synthesis of ultrathin SiC nanosheets with different surface component (SiC_700, SiC_HF and SiC_KOH)

SiC nanosheets were synthesized via a template-assisted carbonthermal process as described in our previous reports. Typically, graphite oxide (GO) solution with a concentration of 5 mg mL⁻¹ was hydro-thermally treated and then freeze-dried to obtain reduced GO (rGO) monoliths, which was thereby loaded on a graphite sieve in a corundum crucible, at the bottom of which excessive Si powder was added previously. Subsequently the crucible was heated at 1400 °C for 3 hours under Ar atmosphere (with a heating rate of 5 °C·min⁻¹). During this process, rGO nanosheets severed as both the carbon source and the morphology template for the growth of SiC. The products were further calcinated at 700 °C in air to remove residual carbon and the obtained sample was labeled as SiC_700. To remove the SiO₂ shell, the SiC_700 was then immersed into a 5% HF solution or 2M KOH solution and stirred for 30 min. After thoroughly washing with deionized water, the final samples were labeled as SiC_HF and SiC_KOH, respectively.

Characterization

The microstructure were observed using a Titan G2 60-300 TEM machine. FT-IR spectra were collected on a Nicolet Nexus 6700 spectrometer in transmittance mode (pellets with KBr). XPS was conducted on a Thermo Scientific ESCALAB 250Xi machine with an Al Kα source. N₂ and CO₂ 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 BET surface area was evaluated from N₂ adsorption data.

Photocatalytic reduction of CO₂

Photocatalytic reduction of CO₂ was carried out in a home-made cylinder reactor (60 mL) with a quartz cover involving a gas-solid heterogeneous reaction. For a typical test, 10 mg sample was dispersed into deionized water under sonication to get a homogeneous ink, which was then poured into a petri dish. After evaporation at 120 °C, the catalyst was deposited as a thin film, which was then placed into the reactor supported by a glass holder. After sealing, the
photoreactor was vacuumed at -0.1 MPa (relative pressure) for 20 min, and CO\textsubscript{2} (99.999\%) was subsequently introduced into the reactor. The vacuum-filtration process was repeated 5 times. After that, 100 μL ultrapure H\textsubscript{2}O was injected into the reactor \textit{via} the silicone rubber septum and dispersed homogeneously on the bottom. A 300 W CEL-HXF300 Xe lamp was placed 10 cm away from the reactor and used as the source of UV-visible light. Each test was typically performed under 4 h irradiation. During the test, the temperature in reactor was kept constant by cooling water. Certain amount of gases mixture would be taken and analyzed by a gas chromatography (SP6890) equipped with a flame ionized detector (FID) and methanizer. The produced gases were calibrated with a standard gas mixture and the identity was determined by the retention time.

**Computational details**

In this work the absorption of molecules and relative chemical processes on SiC (111) surface were investigated. The SiC was cut from bulk along the [111] direction and then constructed a 4×4×1 supercell including 4 layers of SiC sheets and each layer had 16 Si and 16 C atoms. The vacuum was added in Z-direction and translation invariances in X & Y directions were kept in order to simulate a surface. The cell and atomic coordinates were then fully relaxed with the density functional theory method implemented in the Vienna Ab-initio Simulation Package (VASP)\textsuperscript{84} and with the PBE functional\textsuperscript{85} until the residual forces was less than 0.01 eV/Å. The convergence of electronic energy was set to be less than 1E-6 eV. The energy cutoff was adopted as 550 eV and a 3×3×1 Gamma centered k mesh is used to sample the Brillouin zone. Moreover, thegrimme-D2 correction\textsuperscript{86} was involved to taken into account the possible hydrogen bonding and Van der Waals forces.
Table S1 Elemental compositions of SiC_700, SiC_HF and SiC_KOH from XPS results.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Atomic %</th>
<th>Surface groups</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>Si</td>
</tr>
<tr>
<td>SiC_700</td>
<td>34.2</td>
<td>40.0</td>
</tr>
<tr>
<td>SiC_HF</td>
<td>48.03</td>
<td>41.26</td>
</tr>
<tr>
<td>SiC_KOH</td>
<td>44.19</td>
<td>43.55</td>
</tr>
</tbody>
</table>

As presented in Table S1, a significant fraction of oxygen in the SiC_700 is due to the presence of oxide layer, while for the SiC_KOH or SiC_HF it relates to surface hydroxyls. The presence of fluorine in SiC_HF clearly indicates the existence of fluorinated surface species. The listed surface groups will be discussed in the following XPS spectra.
The C 1s spectrum of SiC_700 presents a main peak of 283.1 eV originating from the C-Si bonds of SiC. In its O 1s spectrum, the main component at 532.3 eV is ascribed to Si-O-Si fragments in SiO\(_2\) and silicon oxocarbide, while another peak corresponds to C-O fragments (533.2 eV). Treatment of oxidized sample with HF or KOH does not significantly affect the peak positions of C 1s spectrum but the relative intensity of 284.2 eV is enhanced. Probably, the oxide removal resulted in some surface relaxation as well as formation of interfacial Si\(_3\)C-OH groups, described in Ref S2. Especially, the removal of the oxide layer by KOH solution resulted in the surface covered with more abundant -OH groups than HF treating. The O 1s spectrum of SiC_HF or SiC_KOH is deconvoluted into 531.9 eV (surface hydroxyls) and 534.8 eV (H\(_2\)O) components. The coverage of -OH groups should influence the hydrophilicity and contribute to absorb H\(_2\)O molecules on SiC_KOH.
As described in a previous report\textsuperscript{57}, the surface/water-molecule states caused by the OH$^-$ and H$^+$ bonding processes play an essential role in the emergence of an additional PL band at \(~510\) nm in the water suspension of SiC nanocrystals. Inspired by this work, we measured the PL spectra of SiC\_HF and SiC\_KOH to analyse the differences in their surface states. The samples were dispersed in pure water and sonicated for about 3 hours. After quietly standing overnight, the supernatant was taken out for analysis. As shown in Fig. S2, under the excitation wavelength of 400 nm, both SiC\_HF and SiC\_KOH presented a blue band at 486 nm corresponding to the band-gap recombination. A green band at \(~508\) nm was observed using SiC\_HF, which was related to the complex consisting of the rearranged surface together with -OH and -H groups. While for SiC\_KOH, the absence of green band implied that a large portion of surface terminations was occupied by abundant -OH groups, since the introduction of excess -OH can easily damage the surface luminescent centers.\textsuperscript{57}
The BET surface area of SiC_KOH (60.8 m² g⁻¹) is close to that of SiC_HF (51.6 m² g⁻¹) (Fig. S2), so the much higher CO₂ uptake of SiC_KOH should be contributed by the abundant surface -OH groups, which serve as the active sites for strongly adsorbing and activating CO₂ molecules.
**Fig. S4** (a) Original GC records and (b) corresponding generation rate of CO and CH4 products from photoreduction of CO$_2$ for 2 h.

We tried removing surface -OH groups on SiC_KOH by further treating with HF solution. The obtained sample, denoted as SiC_KOH_HF, exhibited inferior performance in photocatalytic activity and CH$_4$ selectivity as that of SiC_KOH. That was to say, the abundant -OH groups on SiC_KOH could selectively improve the yield of CH$_4$, a more desired product from photocatalytic CO$_2$ reduction.
Fig. S5 (a) Original GC records of the products from photoreduction of CO\textsubscript{2} with or without the addition of H\textsubscript{2}O into the photoreactor, (b) time course evolution of CH\textsubscript{4} or CO production over 10 mg SiC\_KOH under solar light irradiation for 4 h.

Photocatalytic reduction of CO\textsubscript{2} was operated in a gas-solid reaction mode with the participation of H\textsubscript{2}O vapor. CO and CH\textsubscript{4} were detected in the products. A contrast experiment was also performed under CO\textsubscript{2} without additional H\textsubscript{2}O (Fig. S3). CO and CH\textsubscript{4} could also be detected although with low yields, which could be contributed by the surface -OH species. We inferred that the surface -OH species on SiC nanosheets could serve as local protons source directly participating in CO\textsubscript{2} reduction reaction. The decreased supply of H\textsubscript{2}O vapor had less influence on the generation of CO because it required less hydrogen protons than CH\textsubscript{4}. The products evolution over SiC\_KOH exhibited linear growth, indicating a stable reactivity of CO\textsubscript{2} reduction.
Fig. S6 (a) Original GC records of the CH$_4$ product from photoreduction of CO$_2$ in three successive cycles and (b) FTIR spectra of SiC_KOH before and after cycles test.

The hydroxylated SiC nanosheets (SiC_KOH) presented good stability in photocatalytic performance of CH$_4$ generation from CO$_2$ reduction. As has been demonstrated that the surface -OH groups on SiC nanoparticles would easily recover in H$_2$O atmosphere once they were removed or consumed by CO$_2$ hydrogenation reaction.$^{58}$ It also meant that the surface Si-O-Si bridge bonds would easily turn to be two Si-OH bonds. In our case, the FTIR spectrum after cycles test confirmed the recovery of surface -OH groups.
Fig. S7 Comparative configurations of absorbed CO$_2$ on SiC(111) surface. The absorption energy is obtained with the definition $\Delta E = E_{(\text{SiC}+\text{CO}_2)} - E_{(\text{SiC})} - E_{(\text{CO}_2)}$. 

(a) $\Delta E_{\text{absorb}} = -2.893$ eV  

(b) $\Delta E_{\text{absorb}} = -2.629$ eV
References


