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The functionality of surface hydroxyls on selective CH_4 generation from photoreduction of CO_2 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.[S1] 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 $°C\cdot min^{-1}$). 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 ^oC in air to remove residual carbon and the obtained sample was labeled as **SiC_700**. To remove the SiO_2 shell, the SiC_700 was then immersed into a 5% HF solution[S2] or 2M KOH solution[S3] 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. N_2 and CO_2 adsorption isotherms were performed on an ASAP2020M apparatus. The samples were thoroughly degassed in vacuum at 200 ^oC for 10 h, and then measured at 77 K and 273 K to determine N_2 and CO_2 adsorption, respectively. The BET surface area was evaluated from N_2 adsorption data.

Photocatalytic reduction of CO_2

Photocatalytic reduction of CO_2 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 ^oC, 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_2 (99.999%) was subsequently introduced into the reactor. The vacuum-filtration process was repeated 5 times. After that, 100 μL ultrapure H_2O was injected into the reactor *via* the silicone rubber septum and dispersed homogeneously on the bottom. A 300 W CEL-HXF300 Xe lamp was places 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)[S4] and with the PBE functional[S5] 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 the Brillouin zone. Moreover, the grimme-D2 correction[S6] 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..

Sample	Atomic %				Surface groups
	C	Si	O	F	
SiC_700	34.2	40.0	25.8	—	SiO_2
SiC_HF	48.03	41.26	9.26	1.46	Si-F, Si-H, C-H, -OH
SiC_KOH	44.19	43.55	12.26	—	Si-OH, C-OH

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.

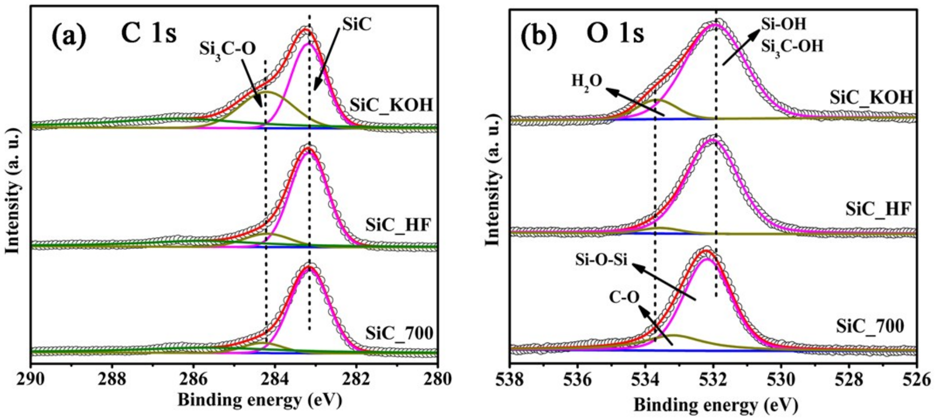

Fig. S1 (a) C1s and (b) O 1s XPS spectra of SiC_700, SiC_HF and SiC_KOH.

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_3C-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_2O) components. The coverage of -OH groups should influence the hydrophilicity and contribute to absorb H_2O molecules on SiC_KOH.

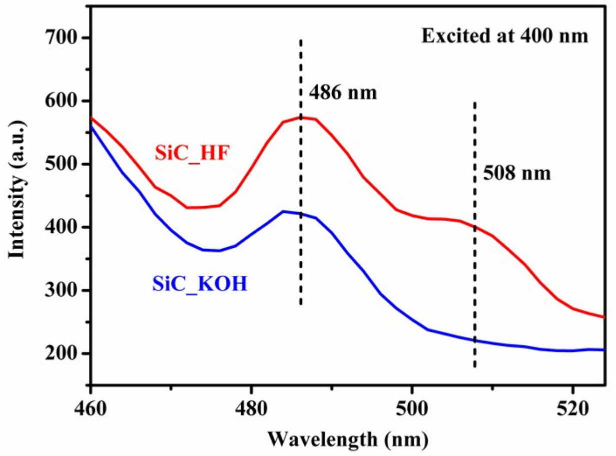

Fig. S2 PL spectra of SiC_KOH and SiC_HF in water suspensions with the excitation wavelength of 400 nm.

As described in a previous report,[S7] 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.[S7]

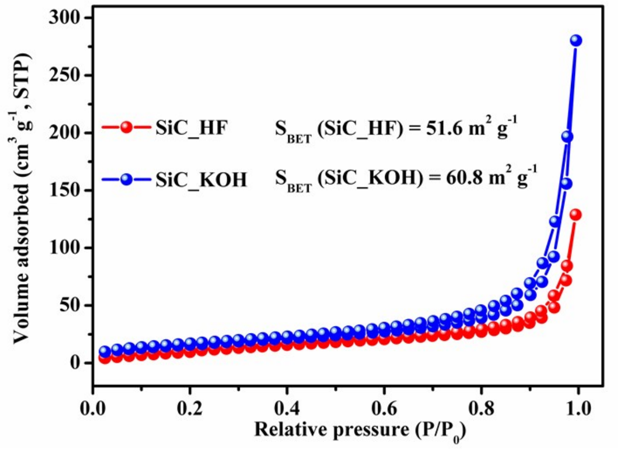

Fig. S3 Nitrogen adsorption-desorption isotherms of SiC_HF and SiC_KOH.

The BET surface area of SiC_KOH (60.8 m^2 g^{-1}) is close to that of SiC_HF (51.6 m^2 g^{-1}) (Fig. S2), so the much higher CO_2 uptake of SiC_KOH should be contributed by the abundant surface -OH groups, which serve as the active sites for strongly adsorbing and activating CO_2 molecules.

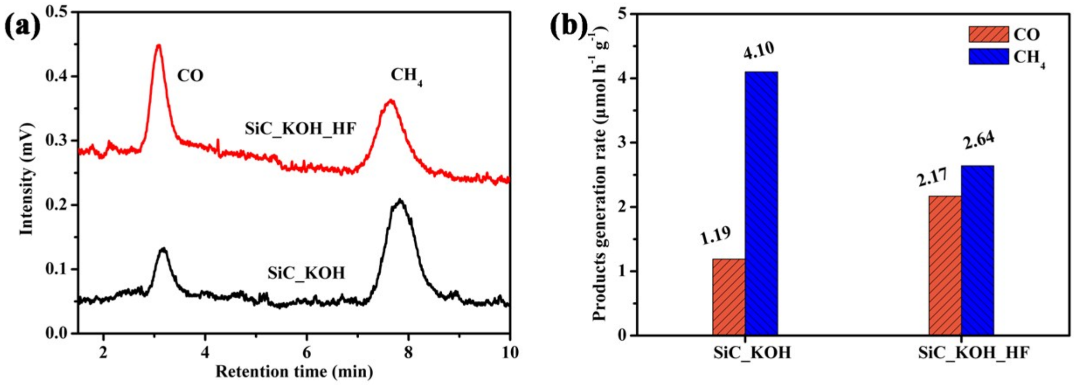

Fig. S4 (a) Original GC records and (b) corresponding generation rate of CO and CH4 products from photoreduction of CO_2 for 2 h.

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.

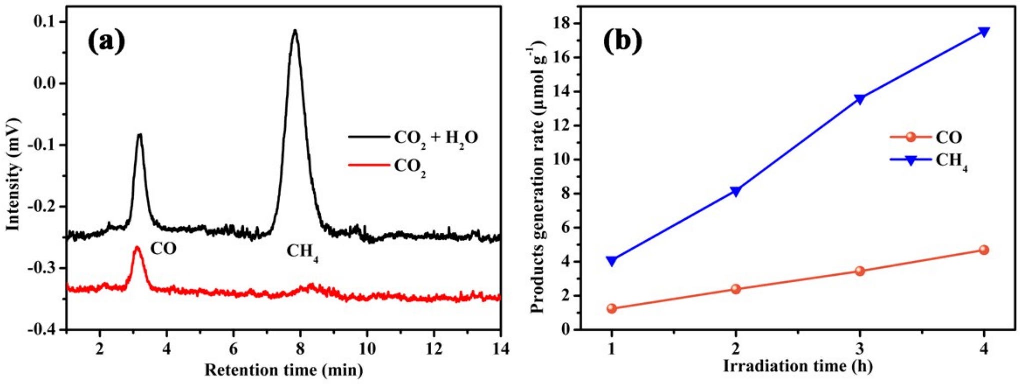

Fig. S5 (a) Original GC records of the products from photoreduction of CO_2 with or without the addition of H_2O into the photoreactor, (b) time course evolution of CH_4 or CO production over 10 mg SiC_KOH under solar light irradiation for 4 h.

Photocatalytic reduction of CO_2 was operated in a gas-solid reaction mode with the participation of H_2O vapor. CO and CH_4 were detected in the products. A contrast experiment was also performed under CO_2 without additional H_2O (Fig. S3). CO and CH_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_2 reduction reaction. The decreased supply of H_2O vapor had less influence on the generation of CO because it required less hydrogen protons than CH_4. The products evolution over SiC_KOH exhibited linear growth, indicating a stable reactivity of CO_2 reduction.

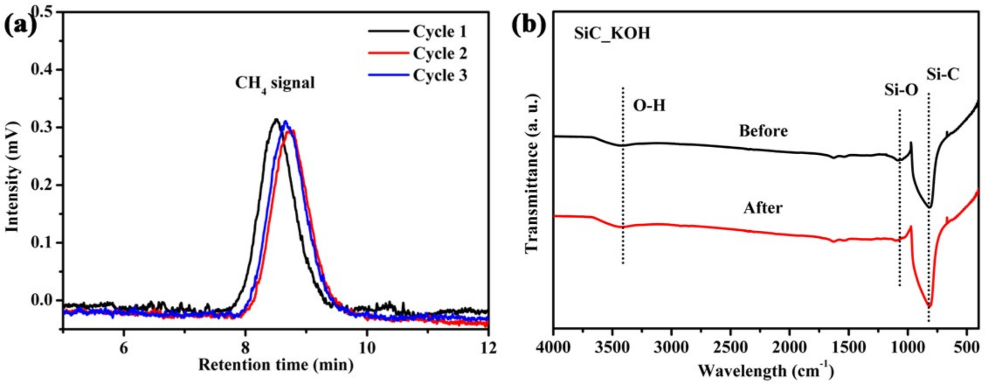

Fig. S6 (a) Original GC records of the CH_4 product from photoreduction of CO_2 in three successive cycles and (b) FTIR spectra of SiC_KOH before and after cycles test.

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_2O atmosphere once they were removed or consumed by CO_2 hydrogenation reaction.[S8] 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.

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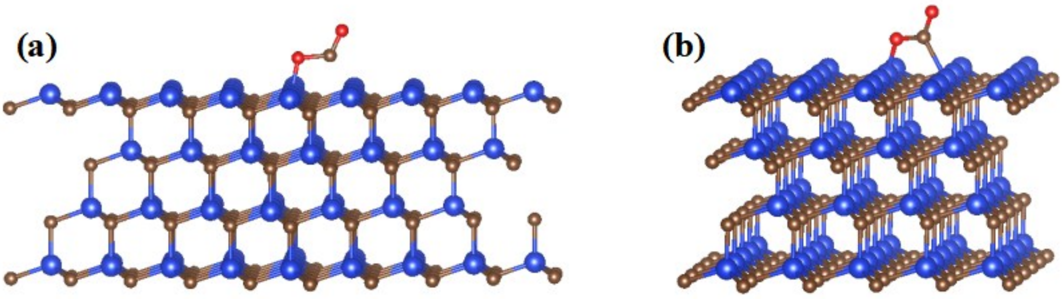

ΔE_{absorb}= -2.893 eV **ΔE_{absorb}= -2.629 eV**

Fig. S7 Comparative configurations of absorbed CO_2 on SiC(111) surface. The absorption energy is obtained with the definition $\Delta E = E(SiC+CO_2)-E(SiC)-E(CO_2)$.

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