Supplementary Information

The efficiency calculation

The incident photon to current efficiency (IPCE) was determined using monochromatic light irradiation with CEL-QPCE3000. IPCE was measured at 1.23 V_{RHE} in 1M KOH solution (pH=14) using the same three-electrode setup described in Experimental Section for photocurrent measurements. IPCE was calculated as follow:^{S1}

$$IPCE(\%) = \frac{1240 \times I(\frac{mA}{cm^2})}{Plight(\frac{mW}{cm^2}) \times \lambda(nm)} \times 100(\%)$$
(1)

where I am the measured photocurrent density at specific wavelength, λ is the wavelength of incident light, and Plight is the measured light power density at that wavelength.

The absorbed photon-to-current efficiency (APCE) was acquired based on the following formula:^{S2}

$$APCE = \frac{IPCE}{1 - 10^{-A(\lambda)}} \tag{2}$$

where $A(\lambda)$ is the absorbance at wavelength λ .

 H_2O_2 was added to the KOH solution as a hole-scavenger to speed up the kinetics of the reaction at the electrode/solution interface. Photocurrent density obtained in H_2O_2 -containing KOH was used to calculate charge injection efficiency (η_{sur}) and charge separation efficiency (η_{bulk}) using the formulas as following:^{S3, S4}

$$\eta_{sur} = \left(\frac{J_{H_20}}{J_{H_20_2}}\right) \times 100\%$$
(3)

$$\eta_{bulk} = \left(\frac{J_{H_2O_2}}{J_{abs}}\right) \times 100\% \tag{4}$$

$$J_{abs} = \frac{q}{hc} \int_{300}^{1240} \lambda * \phi(\lambda) * A(\lambda) * d\lambda$$
(5)

in which J_{H20} and J_{H202} are the photocurrent densities measured in 1 M KOH without and with the addition of H₂O₂, J_{abs} is the integrated current density (mA cm⁻²), q is elementary charge (1.6 x 10⁻¹⁹ C), h is planck's constant, c is the speed of light in vacuum, λ is the wavelength of photon, $\Phi(\lambda)$ is the AM 1.5G light spectrum and A(λ) is absorbance of photoelectrode.

The applied bias photon-to-current efficiency (ABPE) was calculated from the J-V

curves by assuming 100% Faradaic efficiency using the following equation,^{S2}

$$ABPE = \frac{J * (1.23 - V_{bias})}{P_{in}} \times 100\%$$
(6)

where J is the photocurrent density (mA cm⁻²), V_{bias} is the applied bias potential (V_{RHE}), and P_{in} is the incident light power density (AM 1.5G, 100 mW cm⁻²).

Transient photocurrent decay time

Transient photocurrent can be used to study the recombination behavior of charge on semiconductor electrodes, which can be compared by comparing the normalized D value of a single-period photocurrent to obtain the curve of ln D for time of different materials and find the transient time constant τ (τ takes the time value when ln D = -1). The larger transient time constant τ reflects a slower charge recombination process. The transient time constant τ is calculated as follows.^{S5}

$$lnD = \frac{-\tau}{t} \tag{7}$$

$$D = \frac{I_t - I_{st}}{I_{in} - I_{st}} \tag{8}$$

Mott-Schottky (MS) analysis in solution

The Mott-Schottky experiment was carried out at 500, 1000, and 1500 Hz, with an amplitude of 0.01 V and a potential range of -1.2 to 1.0 V (vs. SCE). The carrier density (N_D) and flat band potential (E_f) of photoanode can be obtained by fitting the straight-lined segment of M-S curve. The Mott-Schottky equation is shown as following:^{S7}

$$\frac{1}{C^2} = \frac{2}{e\varepsilon\varepsilon_0 N_D} \left[\left(E - E_{fb} \right) - \frac{KT}{e} \right]$$

$$N_D = \frac{2}{e\varepsilon\varepsilon_0} \left[\frac{d\left(\frac{1}{C^2}\right)}{dV} \right]^{-1}$$
(10)

where, C is the capacitance in space charge region, q is the charge of an electron $(1.6 \times 10^{-19} \text{ C})$, N_D is the donor concentration in the semiconductor, ε_0 is permittivity of vacuum, ε is the relative permittivity (9.66 for SiC),^{S8} E is the applied potential, E_f is the flat band potential, K is the Boltzmann's constant, and T is the temperature (K).

Electrochemical Active Surface area

Cyclic voltammetry (CV) curves were measured in the potential range of 1.05 to -1.15 V_{RHE} at scan rates from 0.01 to 0.1 V s⁻¹ with an increment of 0.01 V. To obtain the electrochemical active surface area (ECSA), the double-layer capacitance (C_{dl}) was calculated from the CV curves according to the following equation:^{S8}

$$C_{dl} = \frac{I}{v} \tag{11}$$

$$ECSA = \frac{C_{dl}}{C_s} \tag{12}$$

where *I* is the current density (mA cm⁻²) measured at 1.10 V_{RHE} and *v* is the scan rate (V s⁻¹). C_s is the specific capacitance of the corresponding surface-smoothed sample under the same conditions.



Fig. S1 EDX mapping (a-d) and spectrum (e) of the CC.



Fig. S2 FEDX mapping (a-e) and spectrum (f) of the SiC@CC.



Fig. S3 EDX mapping (a-f) and spectrum (g) of the N,V_c-SiC@CC.



Fig. S4 Low-magnification TEM image of SiC nanowires



Fig. S5 Selected area electronic diffraction pattern of $N_{\rm 2}$ plasma-treated SiC nanowire



Fig. S6 XRD patterns of the CC, SiC@CC, and N,Vc-SiC@CC





Fig. S8 BET adsorption-desorption curves of the CC, SiC@CC and N,V_c-SiC@CC. The BET specific surface areas were 11.18, 26.63, and 79.81 m⁻² g⁻¹ for the CC, SiC@CC and N,V_c-SiC@CC, respectively.



Fig. S9 Electrochemical surface areas of the (a) CC, (b) SiC@CC, and (c) N,V_c-SiC@CC. (d-f) Relative electrochemical surface areas for the linear relationship between the capacitive current and scan rate.



Fig. S10 (a) XPS survey spectra of the Ar-SiC@CC, NH₃-SiC@CC, and N,V_c-SiC@CC. (b) XPS N 1s spectrum of the NH₃-SiC@CC.



Fig. S11 EPR spectra of the NH₃-SiC@CC, SiC@CC and N,V_c-SiC@CC.



Fig. S12 (a) J-V curves of the Ar-SiC@CC, NH₃-SiC@CC, and N,V_c-SiC@CC in 1M KOH solutions. (b) Transient photocurrent responses of the Ar-SiC@CC, NH₃-SiC@CC, and N,V_c-SiC@CC under AM1.5 100 mA cm⁻² illumination.



Fig. S13 XPS survey spectra of the N,V_c-SiC@CC, N,V_c-SiC@CC (4 sccm), and N,V_c-SiC@CC (8sccm).



Fig. S14 (a) J-V curves of the N,V_c-SiC@CC, N,V_c-SiC@CC (4 sccm), and N,V_c-SiC@CC (8 sccm) in 1M KOH solution. (b) Transient photocurrent responses of the N,V_c-SiC@CC, N,V_c-SiC@CC (4 sccm), and N,V_c-SiC@CC (8 sccm) under AM1.5 100 mA cm⁻² illumination.



Fig. S15 EPR spectrum detected from the photoanode of N,V_c-SiC@CC under AM 1.5G (100 mW cm⁻²) illumination in H₂O containing DMPO as spin-trapping agent.



Fig. S16 Gas productions of N,V_c-SiC@CC.



Fig. S17 Transient photocurrent response of N,V_c-SiC@CC after 33 h cycling under AM1.5 100 mA cm⁻² illumination.



Fig. S18 J-V curves of the SiC@CC (a) and N,V_c-SiC@CC (b) photoanodes measured in 1 M KOH with or without 0.2 M H_2O_2 as a hole scavenger.



Fig. S19 APCE curve of the N,V_c-SiC@CC



Fig. S20 TR-PL spectra of the SiC@CC and N,V_c-SiC@CC and their corresponding fittings



Fig. S21 Nyquist plots of the (a) CC, (b) SiC@CC, (c) N,V_c-SiC@CC photocathodes with different applied potentials in 1M KOH aqueous solution



Fig. S22 Charge transfer resistance (R_{ct}) vs. potential curves of the SiC-based photocathodes. (a) The data were extracted from EIS experiments of the SiC@CC, and N,V_c-SiC@CC photocathodes. R_{ct} was followed by the order of SiC@CC> N,V_c-SiC@CC. Bode plots from electrochemical impedance spectroscopy (EIS) measurement. (b) Phase angles and (c) resistances plots vs. frequency of the SiC@CC and N,V_c-SiC@CC photocathodes at 1.0 V_{RHE} in 1M KOH (pH=14.0).



Fig. S23 (a) UV-vis diffuse reflection spectra of the CC, SiC, and N,V_c -SiC; (b) Tauc plot of high-quality CC, SiC, and N,V_c -SiC.

Catalyst	C Atomic (%)	O Atomic (%)	Si Atomic (%)	N Atomic (%)
CC	96.99	3.11	/	/
SiC@CC	52.89	20.53	26.58	/
N,V _c -SiC@CC	30.47	39.29	24.43	5.82
N,V _c -SiC@CC (4 sccm)	32.64	33.41	25.11	8.84

Table S1 Contents of Si, C, O and N calculated from the XPS survey analysis.

N,V _c -SiC@CC (8 sccm)	35.88	29.00	21.59	13.53
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Table S2 A comparison of the photocurrent densities of SiC-based photoanodes for PECwater splitting reported recently.

Photoanode	J@1.23 V _{RHE}	PEC experimental conditions	Ref.	
3C-SiC	~0.11 mA cm ⁻²	400 mW cm ⁻² Xe light;0.1 M Na ₂ SO ₄	S9	
3C-SiC ([N]=1.0×10 ¹⁶ cm ⁻³)	0.20 mA cm ⁻² at 1.0 V vs. Ag/AgCl			
3C-SiC ([N]=3.6×10 ¹⁸ cm ⁻³)	0.13 mA cm ⁻² at 1.0 V vs. Ag/AgCl	994 mW cm ⁻² Solar-light lamp;0.1 M HCl	S10	
3C-SiC/Pt	2.03 mA cm ⁻² at 1.0 V vs. Ag/AgCl			
3C-SiC	0.70 mA cm ⁻² at 1.0 V vs. Ag/AgCl	100 mW cm ⁻² Xe lamp;0.1 M KHCO ₃	S 11	
3C-SiC(111)	0.12 mA cm ⁻²	100 mW cm ⁻² AM1.5G;1.0M NaOH	S12	
3C-SiC(111)/NiO	1.18 mA cm ⁻²	100 mW cm ⁻² AM1.5G;1.0M NaOH	S13	
3C- SiC(111)/FeOOH	0.73 mA cm ⁻²	$100 \text{ mW} \text{ cm}^{-2} \text{ AM1 5C} \cdot 1.0 \text{ M}$	4 _{S14}	
3C- SiC(111)/Ni:FeOO H	1.15 mA cm ⁻²	NaOH		
3C- SiC(111)/monolaye r-graphene	0.67 mA cm ⁻²	100 mW cm ⁻² AM1.5G;1.0M	015	
3C- SiC(111)/monolaye r-graphene/FeOOH	1.14 mA cm ⁻²	KHCO ₃	815	
Nanoporous p3C(001)5M/NiFe	1.50 mA cm ⁻²	100 mW cm ⁻² AM1.5G;1.0M	S16	
Nanoporous p3C(111)5M/NiFe	2.31 mA cm ⁻²	NaOH		
N-4H-SiC NHAs	4.39 mA cm ⁻² at 1.4 V <i>vs</i> . Ag/AgCl	vicible light: 0.5 No. 50	C 17	
N-4H-SiC sheet	1.58 mA cm ⁻² at 1.4 V vs. Ag/AgCl	visible light; $0.5 \operatorname{Na}_2 \mathrm{SO}_4$	51/	
	0.36 mA cm ⁻²	visible light; 0.1 M Na ₂ SO ₄		
SiCN	0.05 mA cm ⁻²	visible light; 0.1 M KOH	S18	
	0.12 mA cm ⁻²	visible light; 0.1 M NaOH		
N,V _c -SiC@CC	2.50 mA cm ⁻²	100 mW cm ⁻² AM1.5G;1.0M KOH	This work	

Time-resolved photoluminescence (TR-PL) curve of photoanode and fitting results of its twoexponential model. According to the literature,^{S9} it can be interpreted that τ_1 and τ_2 represent the rapid decay life and slow decay life of photocatalysts, respectively, which are related to radiation recombination from CB to VB, radiation recombination through surface state, and shallow capture of electron-hole recombination, respectively.

The fitting equation is presented as follows:^{S10}

$$I(t) = A_1 \cdot e^{(-t/\tau 1)} + A_2 \cdot e^{(-t/\tau 2)}$$
(13)
$$\tau_{ave} = \frac{(A_1 \tau_1^2 + A_2 \tau_2^2)}{A_1 \tau_1 + A_2 \tau_2}$$
(14)

Table S3 The fitted parameters obtained from the decay curves of TR-PL.

Catalyst	\mathbf{A}_{1}	τ_1 (ns)	A_2	τ_2 (ns)	τ _{ave} (ns)
SiC@CC	124692.8964	1.5938	18.6435	2.8567	2.70
N,V _c - SiC@CC	38435.7447	1.9275	21.0965	23.0464	2.07

Catalyst	R _s (ohm cm ⁻²)	R _{ct} (ohm cm ⁻²)	CPE _{sc} -T (F cm ⁻²)	CPE _{sc} -P (F cm ⁻²)
SiC@CC	2.84	4128	0.0011	0.93736
N,V _c -SiC@CC	3.56	738.1	0.0026	0.94287

Table S4 Summarized parameters of EIS for the SiC based photoanodes at $1.23V_{RHE}$.

 $\label{eq:table_stable_stable_stable} \textbf{Table S5} \ DFT\mbox{-calculated bond length} \ (\text{\AA}) \ of \ SiC@CC, \ V_c\mbox{-SiC}@CC \ and \ N\mbox{-SiC}@CC.$

Materials	Bond	Length (Å)
	C-Si	1.776
SiC@CC	C-Si	1.776
	C-Si	1.844
	C-Si(-vacancy)	1.769
V _c -SiC@CC	C-Si(-vacancy)	1.769
	C-Si(-vacancy)	1.824
	N-Si	1.751
N-SiC@CC	N-Si	1.751
	N-Si	1.822

Materials	Atom	Charge (e)
	Si(-C)	1.24
SiC@CC	Si(-C)	1.37
	Si(-C)	1.37
	Si(-vacancy)	0.81
V _c -SiC@CC	Si(-vacancy)	0.77
	Si(-vacancy)	0.77
	Si(-N)	1.34
N-SiC@CC	Si(-N)	1.39
	Si(-N)	1.39

Table S6 DFT-calculated atom Mulliken charges of SiC@CC, V_c -SiC@CC and N-SiC@CC.Parentheses indicate connection to the atom or to the C vacancy.

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