Supporting Information for

Atomic-Scale Tuning of Graphene/Cubic-SiC Schottky Junction for Stable Low-Bias Photoelectrochemical Solar-to-Fuel Conversion

Hao Li, a Yuchen Shi,a Huan Shang,b Weimin Wang,a,c Jun Lu,a Alexei A. Zakharov,c Lars Hultman,a Roger I. G. Uhrberg,a Mikael Syväjärvi,a Rositsa Yakimova,a Lizhi Zhangb and Jianwu Sun**

a Department of Physics, Chemistry and Biology (IFM), Linköping University, 58183, Linköping, Sweden

b Key Laboratory of Pesticide & Chemical Biology of Ministry of Education, Institute of Applied & Environmental Chemistry, College of Chemistry, Central China Normal University, Wuhan 430079, P. R. China

c MAX IV Laboratory, Fotongatan 2, SE-22484, Lund, Sweden

*Correspondence Author: Jianwu Sun, Email: jianwu.sun@liu.se
Supporting figures and text

1. XRD pattern of as-grown 3C-SiC(111) substrate

Supporting Figure 1. XRD pattern of as-grown single-crystal 3C-SiC(111) substrate with representative (111) and (222) diffraction peaks.
2. Raman spectra of the as-prepared graphene/3C-SiC samples

Supporting Figure 2. Raman spectra of the buffer layer (BL), monolayer (1 L), bilayer (2 L), and four-layer (4 L) graphene grown on 3C-SiC. The Raman signals of 3C-SiC were subtracted from the spectra.

The Raman spectra showed the good crystalline quality of the as-grown graphene on 3C-SiC substrate. In Supporting Figure 2, we observed the G and 2D peaks in all graphene/3C-SiC heterojunctions, which are characteristics of graphene. The G peak located around 1600 cm\(^{-1}\) is the first-order Raman scattering process in the first Brillouin zone, while the 2D band located from 2730 cm\(^{-1}\) to 2750 cm\(^{-1}\) originates from the second-order scattering.\(^1\) Besides these typical peaks, a double-band structure including two bands peaking around 1360 and 1600 cm\(^{-1}\) were observed, corresponding to the buffer layer underlying the graphene on hexagonal polytypes.\(^2,3\) The 2D peak of 1L/3C-SiC shows a single Lorentzian shape with a full width at half maximum (FWHM) of ~42 cm\(^{-1}\), suggesting the presence of monolayer graphene. As for 2L/3C-SiC and 4L/3C-SiC, their 2D peaks exhibited asymmetric shape, but was blueshifted along with an increase of FWHM to ~70 cm\(^{-1}\). This typical change of 2D peak is explained by the evolution of the electronic band with increasing the number of graphene layer.\(^4\) The position of Raman 2D peaks in the as-grown multilayer-graphene/3C-SiC samples correspond well to the 2D peaks of graphene grown on 4H- or 6H-SiC and measured with the same laser wavelength in other studies.\(^5\)
3. X-ray photoelectron spectroscopy depth profiling analysis

Supporting Figure 3. High resolution XPS spectra of the Si 2p region of 3C-SiC and BL/3C-SiC with (a) 10 s and (b) 100 s Ar$^+$ sputtering time.

The charge transfer density modulations at the interface could be possibly reflected from the XPS measurement. To this end, a sophisticated time-dependent XPS technique (also known as XPS depth profiling analysis) with continuous Ar$^+$ sputtering (0.02 nm/s) was adopted to investigate the chemical states of Si atoms both on the interface and in the bulk. With an Ar$^+$ sputtering time of 10 s, we were able to observe the Si 2p XPS spectra for Si atoms mainly on the surface (Supporting Figure 3a). As compared with 3C-SiC, the intense peak around 101.1 eV (typical of Si-C bonds) of BL/3C-SiC, shifted to higher binding energies. This is intriguing binding energy shifting after the growth of buffer layer on 3C-SiC was due to the localized charge decrease, agreeing well with the charge transfer from 3C-SiC to buffer layer as theoretically predicted (Figure 2a). When the Ar$^+$ sputtering time was lengthened to 100 s, corresponding to a bulk detection length of 10 nm, the XPS peak indexed to Si-C bonds of BL/3C-SiC remained almost unchanged as compared with that of 3C-SiC (Supporting Figure 3b). Intuitively, charge exchange mainly occurred at the interface, suggesting the electronic states of Si atoms within 3C-SiC were not possibly disturbed in the bulk.
4. Density of states of BL/3C-SiC and charge density of difference of 2L/3C-SiC

Supporting Figure 4. (a) Density of states (DOS) of BL/3C-SiC. TDOS represents for total DOS and PDOS represents for partial DOS. (b) Charge accumulation on the first and second layer of graphene in 2L/3C-SiC.

If we use the 3C-SiC as the reference substance and calculate the charge accumulation on as-grown graphene through \( \Delta \rho = \rho(2L/3C-SiC) - \rho(3C-SiC) - \rho(3\, L\, graphene) \), in which \( \rho(3C-SiC) \) is the charge density of 3C-SiC and \( \rho(3\, L\, graphene) \) the freestanding 3 L graphene, we can get the charge density difference as shown in Supporting Figure 4b. In Supporting Figure 4b, we are able to observe charge transfer from 3C-SiC/buffer layer interface to the first layer graphene and then the second layer graphene of 2L/3C-SiC.
Supporting Figure 5. (a) Energy band diagram for freestanding graphene and 3C-SiC. (b) Charge at the graphene/3C-SiC junction.

Supporting Figure 5a shows the energy band diagram for freestanding graphene and 3C-SiC. Work function ($\Phi_{3C-SiC}$) of 3C-SiC was calculated to be 4.11 eV. $\chi_{SiC}$ the electron affinity of 3C-SiC, which is calculated to be ~4.00 eV. In theory, difference between conduction potential ($E_{CB}$) and Fermi potential ($E_F$) should be around $E_{CB} - E_F = 0.11$ eV. To validate the theoretical value of the difference between $E_{CB}$ and $E_F$, we measured doping concentration ($N_D$) of the n-type 3C-SiC to be around $7.5 \times 10^{15}$ cm$^{-3}$. According to $E_{CB} - E_F = kT \times \ln(N_C/N_D)$, the experimental value of $E_{CB} - E_F$ is around 0.12 eV, close to the theoretical one. Here, the effective conduction band density of states ($N_C$) at room temperature for 3C-SiC is $1.54 \times 10^{19}$ cm$^{-3}$. 
6. Stacking of 4 L graphene on 3C-SiC

Supporting Figure 6. Band structure of a four layer graphene sample showing a flat-band at $E_F$ with a momentum width of $\sim 0.07 \text{ Å}^{-1}$.

Our previous DFT calculation of free standing four layer graphene revealed that the ABAB (Bernal) stacking has neither band degeneracy at the $K$ point below $E_F$ nor observable flat-band at $E_F$. As for the ABCA (Rhombohedral) stacking, the calculated band structure shows a prominent flat valence band near $E_F$. The other three valence bands coincide at a binding energy around -0.30 eV. Meanwhile, the flat-band width is calculated to be 0.06 Å$^{-1}$, close to the experimentally measured one. The formation of rhombohedral multilayer graphene can be a result of the ABC stacking order along the [111] direction of the 3C-SiC(111) substrate.
7. Work function of graphene with different layers

Supporting Figure 7. (a) Normalized ultraviolet photoemission spectra of the as-prepared graphene/3C-SiC samples. (b) Plot of the derived work function versus graphene layer numbers. Work function of freestanding graphene (4.52 eV) is taken from the DFT calculation.

8. DFT calculation of electrostatic potential energy

Supporting Figure 8. DFT calculation of electrostatic potential energy between (a) 3C-SiC and buffer layer, (b) buffer layer and 1 L graphene, (c) 1 L and 2 L graphene, (d) 3 L and 4 L graphene. (e) Schematic illustration of built-in electric field among graphene layers.
9. High-resolution TEM image of 4L/3C-SiC

Supporting Figure 9. Cross-sectional HRTEM image and lattice spacing of 4L/3C-SiC.

10. UV-VIS absorption, Tauc plot of the absorption spectrum and band position of 3C-SiC

Supporting Figure 10. (a) UV-VIS absorption spectra of the as-prepared 3C-SiC substrate. Note that the absorption was saturated above 4 a.u. due to the large thickness (~300 µm) of 3C-SiC. (b) The optical bandgap plot (Tauc plot) of \((\alpha h\nu)^{1/2}\) vs photo energy \(h\nu\). (c) Band position of 3C-SiC.
(d) Schematic illustration of space charge region, carrier diffusion length, and light penetration depth in the 3C-SiC photoanode.

3C-SiC is an indirect bandgap ($E_g = 2.36$ eV) semiconductor, which results in a relatively larger light penetration depth. For instance, it is reported that the absorption coefficient ($\alpha$) of 3C-SiC is around $\sim 100$ cm$^{-1}$ at 2.4 eV, which gives rise to the light penetration depth ($1/\alpha$) of $\sim 100$ µm.$^9$ However, the width of space charge region $W = \sqrt{2\varepsilon_s \varepsilon_0 V_b/(eN_D)}$ and carrier diffusion length $L_D = \sqrt{\mu \tau k_B T/q}$ are much smaller than the light penetration depth. Here, $\mu$ is the carrier mobility, $\tau$ is the carrier lifetime, $k_B T/q$ is the product of the Boltzmann constant and the temperature divided by the electron charge, $\varepsilon_s$ is the dielectric constant of the semiconductor, $\varepsilon_0$ is the permittivity in vacuum, $V_b$ is the built-in potential and $N_D$ is the donor concentration.

Using the $N_D$ of $7.5 \times 10^{15}$ cm$^{-3}$, the width of space charge region $W$ is smaller than 0.3 µm if we assume $V_b < 1$ V. Using the highest carrier lifetime ($\tau = 8.6$ µs) reported in our previous work,$^{10}$ we estimate that the value of $L_D$ is smaller than 10 µm if assuming $\mu < 5$ cm$^2$/Vs (We determined this mobility value of $\sim 5$ cm$^2$/Vs by the Hall-effect measurement). Therefore, the maximum value of $(W + L_D)$ is $\sim 10.3$ µm, which is much smaller than the light penetration depth ($\sim 100$ µm at 2.4 eV). This indicates that most of photogenerated carriers are distributed within the neutral region and recombine there. And only a small part of photogenerated carriers within the region of $(W + L_D)$ can contribute to the photocurrent. This explains the smaller photocurrent compared to the theoretical value from the bandgap of 3C-SiC.
11. I-V curves of Au (200 nm)/Ti (5 nm) contact on graphene side of the graphene/3C-SiC photoanodes

Supporting Figure 11. Representative linear I-V curves of Au (200 nm)/Ti (5 nm) on backside of the graphene/3C-SiC photoanodes showing good Ohmic contact.

The use of Al as the Ohmic contact on the backside of 3C-SiC has been successfully demonstrated in our previous work.\textsuperscript{11} It is to be noticed that during the growth of graphene on 3C-SiC (annealing process), the backside the 3C-SiC samples was simultaneously graphitized. Unfortunately, Al was found to be inappropriate as the Ohmic contact on the backside of multilayer graphene/3C-SiC junctions. In this light of this fact, we chose Au (200 nm)/Ti (5nm) to deposit on backside of graphene/3C-SiC samples and found that it showed very good Ohmic behaviour. The use Au/Ti layer for making the Ohmic contact with graphene has been reported early.\textsuperscript{12} Supporting Figure S11 shows three representative linear I-V curves on the backside of three graphene/3C-SiC photoanodes, demonstrating the formation of the reliable Ohmic contact on the backside of these graphene/3C-SiC photoanodes. The voltage was set in the range of -0.5 V to 0.5 V. Among different graphene/3C-SiC photoanodes, the measured current did not differ remarkably and the absolute current density was in the range of 0.15 to 0.40 mA in our case. It should be pointed out that the crystalline quality of the 3C-SiC can be varied from sample to sample.
12. Mott-Schottky plot of the as-prepared anodes

Supporting Figure S12. (a) Mott-Schottky plot of the as-prepared 3C-SiC and graphene/3C-SiC junctions measured at a frequency of 1 kHz. (b) Mott-Schottky plot of the as-prepared 3C-SiC and graphene/3C-SiC junctions measured at a frequency of 5 kHz. (c) Mott-Schottky plot of the as-prepared 1L/3C-SiC and FeOOH/1L/3C-SiC photoanodes measured at a frequency of 1 kHz.

13. Electrochemical impedance spectroscopy plots of the graphene/3C-SiC photoanodes

Supporting Figure 13. Electrochemical impedance spectroscopy plots of the graphene/3C-SiC photoanodes in 0.5 M pH 7.5 KHCO₃ solution. The plots were measured under AM1.5G 100 mW cm² illumination in the frequency range of 10–10⁵ Hz under open-circuit conditions. Inset shows the equivalent circuits for the fitting of the impedance data. Rₛ is the series resistance. Rₜₐₜ is the charge transfer resistance from the bulk to the photoanode surface and CPEₛₐₜ is the constant phase element of the space-charge capacitance. Rₑₜ,ₜrap represents the charge-transfer resistance from the photoanode to the electrolyte and CPEₜrap is corresponding capacitance.
Supporting Figure 14. (a) Top-view SEM image of the as-prepared FeOOH/1L/3C-SiC photoanode (inset shows the side-view). (b, c) TEM images of the FeOOH nanorods, and (d) XRD pattern of the as-prepared FeOOH/1L/3C-SiC photoanode. High-resolution XPS spectra of (e) the Fe 2p region and (f) the C 1s region of FeOOH/1L/3C-SiC.

SEM image shows the as-grown vertical FeOOH nanorods on 1L/3C-SiC photoanode (Supporting Figure S14a). Thickness of the as-grown FeOOH nanorods is around 200 nm and diameter of the FeOOH nanorods is around 20 nm (inset of Supporting Figure S14a). Supporting Figure S14b and S14c show the TEM images of the FeOOH nanorods. According to the XRD measurement, besides two diffraction peaks of single-crystalline 3C-SiC, 1L/3C-SiC contained a diffraction peak at 27° indexed to the (310) peak of β-FeOOH due to the nano-crystalline nature of the FeOOH nanorods (Supporting Figure S14d). High-resolution XPS spectra of the Fe 2p region of FeOOH/1L/3C-SiC showed two major peaks, ~711.18 eV for Fe 2p$_{3/2}$ and ~725.0 eV for Fe 2p$_{1/2}$ (Supporting Figure S14e). Binding energies of these peaks matched well with the characteristics of Fe$^{3+}$ in FeOOH.$^{13-15}$ Moreover, the Fe 2p XPS spectrum also showed two small satellite peaks (sat) located at higher binding energies, ~719.0 eV for Fe 2p$_{3/2}$, and ~733.2 eV for Fe 2p$_{1/2}$, which were
due to the charge-transfer or shakeup processes associated with Fe$^{3+}$. These features of the Fe 2p XPS peaks suggested that the oxidation state of Fe in the as-deposited iron oxide was 3+ and Fe$^{3+}$ ions existed in the form of FeOOH. The C 1s XPS spectrum showed three components at 283.4, 284.4, and 285.7 eV in binding energy (Supporting Figure S14f). The two important components at 283.4 eV and 284.4 eV were respectively corresponded to C atoms of 3C-SiC and 1 L graphene in FeOOH/1L/3C-SiC. Meanwhile, the third peak at 285.7 eV was detected, which was due to the presence of interface or buffer layer.$^{17,18}$

15. Characterizations of CoOOH/1L/3C-SiC

CoOOH nanoparticles were in situ grown on the 3C-SiC and graphene/3C-SiC photoanodes through a facile photoelectrochemical method.$^{19}$ It should be pointed out that for this comparison, we cut the same 3C-SiC substrate into two pieces, one for the deposition of CoOOH and the other one

Supporting Figure 15. SEM images of as-prepared (a) 3C-SiC photoanode and (b) CoOOH/1L/3C-SiC (d) XRD pattern of the as-prepared CoOOH/1L/3C-SiC photoanode. (d) High-resolution XPS spectra of the Co 2p region of CoOOH/1L/3C-SiC. (e) $J$-$V$ curves of the graphene/3C-SiC photoanodes loaded with CoOOH cocatalyst under illumination. Light source: simulated solar light (AM1.5G, 100 mW/cm$^2$). The electrolyte: 0.5 M pH 7.5 KHCO$_3$ solution. (f) $J$-$t$ behavior of the CoOOH/1L/3C-SiC photoanode at a bias of 0.6 V$_{\text{RHE}}$.
for growth of monolayer graphene and subsequent deposition of CoOOH. In a typical three electrode cell, 3C-SiC was used as the working electrode, Ag/AgCl as the reference electrode, and Pt mesh as the counter electrode. 0.6 V<sub>RHE</sub> was applied in 0.01 mol/L CoCl<sub>2</sub> aqueous solution under simulated solar light irradiation (AM1.5G, 100 mW/cm<sup>2</sup>) with a deposition time of 30 min. The accumulated charge passing through 3C-SiC photoanode was in situ recorded. Since photocurrent of 1L/3C-SiC photoanode was over 2 times higher than that of 3C-SiC. Therefore, in order to make sure similar amount of CoOOH was deposited on 3C-SiC and 1L/3C-SiC photoanodes, we shortened the photoelectrochemical deposition time to ~13 min, ensuring that comparable charges passed through the 1L/3C-SiC photoanode. Meanwhile, during the photodeposition process, traces of O<sub>2</sub> was concurrently generated, suggesting most of the photo-generated holes were used to oxidize CoCl<sub>2</sub> to CoOOH. We then specifically characterized the CoOOH on 1L/3C-SiC photoanode. SEM images clearly show the CoOOH was mainly composed of a layer of small nanoparticles (Supporting Figure 15a and 15b). As revealed by XRD pattern, CoOOH/1L/3C-SiC displays an additional diffraction peak corresponded to the (012) peak of rhombohedral CoOOH (JCPDS Card No. 78-11213) (Supporting Figure 15c).<sup>20</sup> High-resolution XPS spectra of the Co 2p region of CoOOH/1L/3C-SiC showed two main peaks around 780.4 eV and 781.7 eV, as well as two satellite peaks located at higher binding energies of 784.1 eV and 789.8 eV (Supporting Figure 15d). Features of the Co 2p XPS peaks suggested that the oxidation state of Co in the as-deposited cobalt oxide was 3+ and Co<sup>3+</sup> ions existed in the form of CoOOH (Supporting Figure 15d).<sup>19,21</sup> For photoelectrochemical water oxidation, loading of CoOOH on 3C-SiC photoanode (CoOOH/3C-SiC) did not remarkably improve the photocurrent density. As for 1L/3C-SiC with CoOOH (CoOOH/1L/3C-SiC), an over one-fold increase of the photocurrent was also observed (Supporting Figure 15e). Meanwhile, CoOOH/1L/3C-SiC displayed high photostability according to the long-term J-t curve (Supporting Figure 15f). These results further highlight the indispensable role of the graphene layer that promotes hole transfer to the cocatalyst for water oxidation reaction.
16. H$_2$ and CH$_4$ evolution in PEC system with different photoanodes

Supporting Figure S16. (a) Electrochemical impedance spectroscopy plots and (b) open-circuit potentials of the graphene/3C-SiC photoanodes. H$_2$ and CH$_4$ evolution from the cathode compartment of the PEC system with (c) 3C-SiC as the photoanode, (d) 1L/3C-SiC as the photoanode, and (e) FeOOH/1L/3C-SiC as the photoanode. Cu was used as the cathode in these PEC systems.

Supporting Figure S16a shows the Nyquist plot of the FeOOH/1L/3C-SiC photoanode in comparison with that of 1L/3C-SiC and SiC photoanode. The loading of FeOOH remarkably enhanced charge transfer from 3C-SiC towards the electrolyte for water oxidation. Supporting Figure S16b shows open-circuit potentials of FeOOH/1L/3C-SiC and 1L/3C-SiC photoanode, which are much larger than that of 3C-SiC photoanode. Supporting Figure S16c-e reveal the trend of CH$_4$ and H$_2$ evolution, which show high dependency on the photoanodes used in distinct PEC systems. Apparently, high photovoltage benefited the multi-electron CO$_2$ reduction and suppressed the two-electron proton reduction reaction.
3. Supporting Table

Supporting Table 1. EIS fitting results of R\textsubscript{ct} and R\textsubscript{ct, trap} for as-prepared 3C-SiC and graphene/3C-SiC junctions as shown in Figure 3d.

| Photoanode      | 3C-SiC | BL/3C-SiC | 1L/3C-SiC | 2L/3C-SiC | 4L/3C-SiC | FeOOH/1L/3C-SiC |
|-----------------|--------|-----------|-----------|-----------|-----------|-----------------|
| R\textsubscript{ct} (\Omega cm\textsuperscript{2}) | 177    | 174       | 115       | 270       | 254       | 51              |
| R\textsubscript{ct, trap} (\Omega cm\textsuperscript{2}) | 1719   | 1431      | 649       | 1863      | 1908      | 179             |

Supporting Table 2. Distribution of the CO\textsubscript{2} reduction products and the corresponding Faradaic efficiency

| Photoanode||cathode | Faradaic efficiency (%) |
|------------|----------|-------------------------|
|            | H\textsubscript{2} | CO | CH\textsubscript{4} | HCOOH | Total |
| 3C-SiC||Cu | 63.0 | 15.8 | 13.6 | 5.0 | 97.4 |
| 1L/3C-SiC||Cu | 26.1 | 3.3 | 60.5 | 8.3 | 98.2 |
| FeOOH/1L/3C-SiC||Cu | 9.3 | 2.1 | 82.8 | 2.0 | 96.2 |
| FeOOH/1L/3C-SiC||Pt | 91.2 | 7.5 | - | - | 98.7 |
| FeOOH/1L/3C-SiC||Zn | 11.1 | 76.6 | 6.1 | 3.1 | 96.9 |
| FeOOH/1L/3C-SiC||Bi | 13.3 | 2.6 | 7.7 | 75.0 | 98.6 |

* All photoanode-driven PEC CO\textsubscript{2} reduction under simulated solar light under a bias of 0.60 V\textsubscript{RHE}. The Faradaic efficiency was calculated based on the reduction reactions happened on the metal cathode.
### Supporting Table 3. Literature reports of photoelectrochemical reduction of CO₂ to CH₄

| Electrode | Conditions | Overpotential (vs. RHE) | Faradaic efficiency of CH₄ | Ref. |
|-----------|------------|-------------------------|---------------------------|------|
| Cathode: Cu<br>Photoanode: FeOOH/1L/3C-SiC | 0.5 M KHCO₃<br>AM 1.5 (100 mW cm⁻²) | +0.60 V | **82.8%**<br>This work |
| Cathode: Cu₂O<br>Photoanode: TiO₂ | 0.1 M KHCO₃<br>AM 1.5 (100 mW cm⁻²) | +0.75 V | 54.6%<br>18 |
| Cathode: Cu<br>Photoanode: WO₃ | 0.5 M KHCO₃<br>AM 1.5 (100 mW cm⁻²) | +0.75 V | 67.0%<br>19 |
| Cathode: Cu<br>Photoanode: Co-Ci/BiVO₄/WO₃ | 0.5 M KHCO₃<br>AM 1.5 (100 mW cm⁻²) | +0.40 V | 46.8%<br>20 |
| Cathode: Cu<br>Photoanode: Nitrogen-doped TiO₂ | 0.5 M NaCl<br>100 W Xe lamp (3.12 mW cm⁻²) | +2.65 V | 7.8%<br>21 |
| Photocathode: CdSeTe/TiO₂<br>Anode: Pt | 0.1 M KHCO₃<br>500 W Xenon lamp (λ ≥ 420 nm, 100 mW cm⁻²) | -0.99 V | 40.8%<br>22 |
| Photocathode: GaN/Si<br>Anode: Pt | 0.5 M KHCO₃<br>300 W Xenon lamp (~8 suns) | -0.73 V | 18.3%<br>23 |
| Photocathode: Cu/p-Si<br>Anode: Pt | 0.5 M KHCO₃<br>AM 1.5 (100 mW cm⁻²) | -0.52 V | 25.0%<br>24 |

*Reported potentials in the table were converted to RHE values using the pH of the electrolyte*
References:

(1) Ferrari, A. C.; Meyer, J. C.; Scardaci, V.; Casiraghi, C.; Lazzeri, M.; Mauri, F.; Piscanec, S.; Jiang, D.; Novoselov, K. S.; Roth, S.; Geim, A. K. Raman Spectrum of Graphene and Graphene Layers. Phys. Rev. Lett. 2006, 97, 187401.

(2) Fromm, F.; Oliveira Jr, M. H.; Molina-Sánchez, A.; Hundhausen, M.; Lopes, J. M. J.; Riechert, H.; Wirtz, L.; Seyller, T. Contribution of the Buffer Layer to the Raman Spectrum of Epitaxial Graphene on SiC(0001). New J. Phys. 2013, 15, 043031.

(3) Shi, Y.; Zakharov, A. A.; Ivanov, I. G.; Yazdi, G. R.; Jokubavicius, V.; Syväjärvi, M.; Yakimova, R.; Sun, J. Elimination of Step Bunching in the Growth of Large-Area Monolayer and Multilayer Graphene on Off-Axis 3C SiC (111). Carbon 2018, 140, 533–542.

(4) Ferrari, A. C.; Basko, D. M. Raman Spectroscopy as a Versatile Tool for Studying the Properties of Graphene. Nat. Nanotechnol. 2013, 8, 235–246.

(5) Ide, T.; Kawai, Y.; Handa, H.; Fukidome, H.; Kotsugi, M.; Ohkochi, T.; Enta, Y.; Kinoshita, T.; Yoshigoe, A.; Teraoka, Y.; Suemitsu, M. Epitaxy of Graphene on 3C-SiC(111) Thin Films on Microfabricated Si(111) Substrates. Jpn. J. Appl. Phys. 2012, 51, 06FD02.

(6) Davydov, S. Y. On the Electron Affinity of Silicon Carbide Polytypes. Semiconductors 2007, 41, 696–698.

(7) Wang, W.; Shi, Y.; Zakharov, A. A.; Syväjärvi, M.; Yakimova, R.; Uhrberg, R. I. G.; Sun, J. Flat-Band Electronic Structure and Interlayer Spacing Influence in
Rhombohedral Four-Layer Graphene. *Nano Lett.* **2018**, *18*, 5862–5866.

(8) Coletti, C.; Forti, S.; Principi, A.; Emtsev, K. V.; Zakharov, A. A.; Daniels, K. M.; Daas, B. K.; Chandrashekhar, M. V. S.; Ouisse, T.; Chaussende, D.; MacDonald, A. H.; Polini, M.; Starke, U. Revealing the Electronic Band Structure of Trilayer Graphene on SiC: An Angle-Resolved Photoemission Study. *Phys. Rev. B* **2013**, *88*, 155439.

(9) Solangi, A.; Chaudhry, M. I. Absorption Coefficient of β–SiC Grown by Chemical Vapor Deposition. *J. Mater. Res.* **1992**, *7*, 539–541.

(10) Sun, J. W.; Ivanov, I. G.; Liljedahl, R.; Yakimova, R.; Syväjärvi, M. Considerably Long Carrier Lifetimes in High-Quality 3C-SiC(111). *Appl. Phys. Lett.* **2012**, *100*, 252101.

(11) Jian, J.; Shi, Y.; Ekeroth, S.; Keraudy, J.; Syväjärvi, M.; Yakimova, R.; Helmersson, U.; Sun, J. A Nanostructured NiO/Cubic SiC p–n Heterojunction Photoanode for Enhanced Solar Water Splitting. *J. Mater. Chem. A* **2019**, *7*, 4721–4728.

(12) Robinson, J. A.; LaBella, M.; Zhu, M.; Hollander, M.; Kasarda, R.; Hughes, Z.; Trumbull, K.; Cavalero, R.; Snyder, D. Contacting Graphene. *Appl. Phys. Lett.* **2011**, *98*, 053103.

(13) Cai, L.; Zhao, J.; Li, H.; Park, J.; Cho, I. S.; Han, H. S.; Zheng, X. One-Step Hydrothermal Deposition of Ni:FeOOH onto Photoanodes for Enhanced Water Oxidation. *ACS Energy Lett.* **2016**, *1*, 624–632.

(14) Long, C.; Jiang, L.; Wei, T.; Yan, J.; Fan, Z. High-Performance Asymmetric Supercapacitors with Lithium Intercalation Reaction Using Metal Oxide-Based Composites as Electrode Materials. *J. Mater. Chem. A* **2014**, *2*, 16678–16686.
(15) Baltrusaitis, J.; Cwiertny, D. M.; Grassian, V. H. Adsorption of Sulfur Dioxide on Hematite and Goethite Particle Surfaces. *Phys. Chem. Chem. Phys.* **2007**, *9*, 5542.

(16) Yin, L.; Adler, I.; Tsang, T.; Matienzo, L. J.; Grim, S. O. Paramagnetism and Shake-Up Satellites in X-Ray Photoelectron Spectra. *Chem. Phys. Lett.* **1974**, *24*, 81–84.

(17) Pallecchi, E.; Lafont, F.; Cavaliere, V.; Schopfer, F.; Mailly, D.; Poirier, W.; Ouerghi, A. High Electron Mobility in Epitaxial Graphene on 4H-SiC(0001) *via* Post-Growth Annealing under Hydrogen. *Sci. Rep.* **2015**, *4*, 4558.

(18) Emtsev, K. V.; Bostwick, A.; Horn, K.; Jobst, J.; Kellogg, G. L.; Ley, L.; McChesney, J. L.; Ohta, T.; Reshanov, S. A.; Röhrl, J.; Rotenberg, E.; Schmid, A. K.; Waldmann, D.; Weber, H. B.; Seyller, T. Towards Wafer-Size Graphene Layers by Atmospheric Pressure Graphitization of Silicon Carbide. *Nat. Mater.* **2009**, *8*, 203–207.

(19) Xu, Z.; Li, X.; Li, J.; Wu, L.; Zeng, Q.; Zhou, Z. Effect of CoOOH Loading on the Photoelectrocatalytic Performance of WO$_3$ Nanorod Array Film. *Appl. Surf. Sci.* **2013**, *284*, 285–290.

(20) Pauporté, T.; Mendoza, L.; Cassir, M.; Bernard, M. C.; Chivot, J. Direct Low-Temperature Deposition of Crystallized CoOOH Films by Potentiostatic Electrolysis. *J. Electrochem. Soc.* **2005**, *152*, C49.

(21) Yang, J.; Liu, H.; Martens, W. N.; Frost, R. L. Synthesis and Characterization of Cobalt Hydroxide, Cobalt Oxyhydroxide, and Cobalt Oxide Nanodiscs. *J. Phys. Chem. C* **2010**, *114*, 111–119.
