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Supporting Information

High-Performance p-Cu₂O/n-TaON Heterojunction Nanorod Photoanodes Passivated with Ultrathin Carbon Sheath for Photoelectrochemical Water Splitting

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Figure S11. Raman spectra of carbon-Cu₂O/TaON nanorod array.



Figure S1. XRD pattern of F–Ta₂O₅ nanorod arrays on the Ta substrates.

The XRD patterns of as-prepared F–Ta₂O₅ nanorod array are shown in Figure S1. For F–Ta₂O₅ nanorod array without the nitridation, Figure S1 shows two strong diffraction peaks at $2\theta = 22.9^{\circ}$ and 46.3°, which respectively correspond to the (001) and (002) facets of orthorhombic Ta₂O₅ (JCPDS card No. 71-639).



Figure S2. Energy–dispersive X–ray spectroscopy of the elments Ta, O and F in the $F-Ta_2O_5$ nanorod sample.

The EDS patterns of as-prepared $F-Ta_2O_5$ nanorod array are shown in Figure S2. For $F-Ta_2O_5$ nanorod array without the nitridation, Figure S2 presents the relative peaks corresponding to the C, O, F, and Ta elements, indicating that this sample is composed of $F-Ta_2O_5$, which is in agreement with the XRD pattern (Figure S1).



Figure S3. Typical top–view scanning electron microscopy image of the Cu₂O nanoparticles/TaON nanorod array passivated with ultrathin carbon sheath.

To confirm the entire quality of carbon– $Cu_2O/TaON$ nanorods array, the surface view with the large magnification of SEM image was also presented in the Figure S3, indicating the whole carbon– $Cu_2O/TaON$ nanorods array maintained the homogeneous 1D morphology after the modification of the Cu_2O nanoparticles and the ultrathin carbon layer.



Figure S4. X–ray diffraction (XRD) patterns of the (a) TaON, (b) Cu(OH)₂/TaON and (c) glucose– Cu(OH)₂/TaON samples (A) and XRD pattern of carbon–Cu₂O/TaON sample after PEC test (B).

The XRD patterns of as-prepared TaON, Cu(OH)₂/TaON and glucose–Cu(OH)₂/TaON samples are shown in Figure 4. After the chemical bath deposition process, the Cu(OH)₂/TaON nanorod array was obtained. According to XRD patterns in Figure 4S, five main diffraction peaks near at $2\theta = 23.8, 34.1, 35.9, 39.8$ and 53.2° can be observed, corresponding to (021), (002), (111), (130) and (150) plane diffraction of Cu(OH)₂ [JCPDS No.12–420, Orthorhombic, space group: Cmc2₁], respectively, indicating that the Cu(OH)₂ phase was confirmed on the surface of the TaON nanorod (Figure S4). After the coating of glucose, there are no any changes upon the positions of Cu(OH)₂ and TaON phases in glucose-Cu(OH)₂/TaON sample in comparison of TaON, and Cu(OH)₂/TaON. Especially, the characteristic diffraction peaks of TaON/Ta phase (JCPDS No. 70-1193) are observed and there are no obvious changes of intensities and widths in all samples. In addition, the two strong peaks of (211) and (321) can be indexed to the phase of Ta for all samples. This implies that there is no significant change observed in phase structure of TaON while there is a little decrease upon the intensities due to the weak crystalline state and the low loading content during the whole modification of Cu(OH)₂ and glucose. Also no evident shift in the peak positions is observed in each of the as-prepared glucose-Cu(OH)₂/TaON samples, suggesting that the deposited Cu(OH)₂ and glucose species do not incorporate into the lattice of TaON, and are attached on the surface of TaON nanorod. After the PEC test in NaOH solution, the XRD pattern of C-Cu₂O/TaON sample was conducted, confirming that there is not the formation of copper hydroxide at the high pH value.



Figure S5. X–ray photoelectron spectra of the Cu₂O nanoparticles/TaON nanorod array passivated with ultrathin carbon sheath as integrated electrode.



Figure S6. X–ray photoelectron spectra of O, Ta and N elements from the Cu₂O nanoparticles/ TaON nanorod array passivated with ultrathin carbon sheath as integrated electrodes before the photoelectrochemical measurement.

In order to determine the surface composition and chemical nature of carbon-Cu₂O/TaON composites. the chemical state of each element in the samples were carefully checked by X-ray photoelectron spectroscopy (XPS). XPS characterization was performed, from which survey spectrum, Ta, O, N, C and Cu elements were observed (Figure S5-6). The binding energies were calibrated by using the contaminating carbon C1s peak at 284.5 eV as a standard. In Figure S5, XPS signals of Ta 4f in the carbon-Cu₂O/TaON composites are observed at binding energies at around 26.0 eV (Ta $4f_{7/2}$) and 27.6 eV (Ta $4f_{5/2}$) ascribed to Ta^{5+, 1-7} Figure 4b displays the Cu 2p level spectrum. The Cu $2p_{3/2}$ and Cu $2p_{1/2}$ spin–orbital photoelectrons were located at binding energies of 932.5 eV and 952.4 eV, respectively, which are in good agreement with the reported values of Cu₂O.⁸ Obviously, the deposited nanoparticles were Cu₂O rather than Cu or CuO. Especially, after the combination of the ultrathin carbon on the surface of Cu₂O/TaON, the strong C-C peak at 285.0 eV implies the formation of a carbon layer on on the surface of Cu₂O/TaON, as shown in Figure 4c. Furthermore, a notable decrease in oxygen content is clearly visible and the peak corresponding to the C–O bond has disappeared in Figure 4c, compared with the extensive results of carbon.^{8,9} The oxygen loss mainly results from the loss of C–O and O–C=O, indicating the partial removal of the oxygen-containing functional groups. As shown in Figure S6, the N1s peak in the XPS spectrum of the N is fitted, indicating that the lowest energy peak is near 396.4 eV, which can be indexed to N 1s from TaON.¹⁻ ⁷ Furthermore, in order to confirm the composition of carbon-Cu₂O/TaON sample with the depositon of Cu²⁺ ions for 40 s and the 0.1 M glucose according to XPS results, the atomic ratio of Ta/N and Ta/Cu was about 1 : 0.96 and 20 : 1, repectively, indicating that TaON possesses the stoichiometric component and the Cu species is lying on the surface of TaON sample passivated with ultrathin carbon sheath. Combined with TEM and STEM images as well as XPS spetra, the

carbon layer is lying on the surface of $Cu_2O/TaON$, confirming the formation of the Cu_2O nanoparticles/TaON nanorod array passivated with ultrathin carbon sheath as integrated electrodes.



Figure S7. The Cu LMM Auger spectra for the Cu₂O on FTO substrate, Cu₂O/TaON and carbon– $Cu_2O/TaON$ nanorods array on Ta substrate as the photoanodes after PEC measurement.

In order to determine whether the photocorrosion of the Cu₂O/TaON and carbon–Cu₂O/TaON photoanodes were existed during the photoelectrochemical test, the Cu LMM Auger spectra of the as-prepared Cu₂O/TaON and carbon–Cu₂O/TaON nanorods array on Ta substrate as the photoanodes was performed after the photoelectrochemical measurement, as shown in Figure S7. It is very interesting that there is no any peaks for the Cu LMM Auger spectra of the Cu₂O/TaON and carbon–Cu₂O/TaON photoanodes. In comparison to that of different photoanodes, the Cu₂O nanoparticles were deposited on FTO substrate. A peak of kinetic energy at 918.5 eV, which corresponds to the Cu(0) state, appeared after the test for the Cu₂O photoanode, confirming that the surface of the bare Cu₂O was reduced to Cu, which is in agreement with the previous work.¹¹ Combined with the previous works about poor stability of Cu₂O,^{12,13} the limited enhancement of photostability for the Cu₃O/TaON photoanode is ascribed to the phase conversion because the

accumlated surface holes lead to the oxidation of Cu₂O and a certain of photocorrosion of TaON because Cu₂O nanoparticles doesn't fully cover TaON nanorods. Especially, there is no any peak for the Cu LMM Auger spectra of the stable carbon–Cu₂O/TaON photoanode. The combined results from the Cu LMM Auger spectra and the photostability indicate that the photocorrosion and the phase conversion did not occur on the carbon–Cu₂O/TaON photoanode after the PEC test. Therefore, this modified approach using the Cu₂O nanoparticles and ultrathin carbon layer has almost resolved the above-mentioned limitations of the TaON based photoanodes due to a high built-in potential in the protective p–n heterojunction device encapsulated in an ultrathin graphitic carbon sheath from the electrolyte.



Figure S8. X–ray photoelectron spectra of Ta, N and Cu elements from the Cu_2O nanoparticles/TaON nanorod array passivated with ultrathin carbon sheath as integrated electrodes after the Faradaic efficiency test.

As surface nitrogen contents are important parameters for evaluating the photoelectrochemical properties of carbon-Cu₂O/TaON photoelectrode, surface nitrogen contents after the Faradaic efficiency test were monitored by XPS analysis on the carbon-Cu₂O/TaON photoanodes. After

photostability measurement in NaOH, there is no obvious change for the N 1s peak of carbon- $Cu_2O/TaON$ photoanodes in comparison to that before PEC measurement. The high-resolution Cu 2p XPS spectra of carbon- $Cu_2O/TaON$ photoanode was shown in Figure S8b. The peaks at 932.4 and 952.2 eV correspond to the binding energy of Cu $2p_{3/2}$ and Cu $2p_{1/2}$ of Cu₂O, and those at 934.3 and 953.8 eV are attributed to CuO,^{14,15} confirming the coexistence of a trace amount of CuO. Thus, there is still a certain decrease of the photocurrent in the carbon–Cu₂O/TaON photoanode, which may be ascribed to the little oxidation of Cu₂O and the charge recombination or other mechanisms, such as photon exchange, tunneling through the electric potential barrier near the interface, or thermionic emission. The in-depth research about these mechanisms is beyond the scope of our present work, but efforts will be conducted in the future.



Figure S9. Photocurrent densities at 1.23 V vs. RHE and photostability of the $Cu_2O/TaON$ photoelectrodes as a function of deposition time of Cu^{2+} ions during the chemical bath deposition process at 1.0 V vs. RHE under AM 1.5G 100 mW cm⁻² simulated sunlight.

To explore the influence of the content of Cu₂O nanoparticles upon the photocurrent densities at 1.23 V vs. RHE and photostability of the Cu₂O/TaON photoelectrode as a function of deposition time of Cu²⁺ ions from 0 to 80 s during the chemical bath deposition process at 1.0 V vs. RHE under AM 1.5G 100 mW cm⁻² simulated sunlight were also investigated in this work, as shown in Figure S9. Under the deposition time of 40 s for Cu ions, the Cu₂O/TaON photoelectrode showed the highest photocurrent densities of 2.94 mA cm⁻² at 1.23 V vs. V_{RHE} under AM 1.5G solar light and the best photostability of 47% at 1.0 V vs. V_{RHE} under AM 1.5G solar light in comparison of that of TaON photoelectrode with the photocurrent densities of 0.93 mA cm⁻² and the photostability of 6%. However, the other Cu₂O/TaON photoelectrode under the deposition time of 0, 10, 20, 60 and 80 s for Cu ions presented the relative decrease of the photocurrent densities and photostability.

Especially, the low photostability, less than 47% of the Cu₂O/TaON photoelectrode is ascribed to the unstable state of Cu₂O phase. Further increase of Cu₂O on the nanostructured TaON array; likely reduce the contact area between the sample and the electrolyte, thereby increasing charge recombination in the Cu₂O due to its short exciton diffusion length.¹⁶ Therefore, if the Cu₂O content exceeds a critical amount, the photocurrent density of the composite will decrease.



Figure S10. Photocurrent densities at 1.23 V vs. RHE and photostability of the carbon– $Cu_2O/TaON$ photoelectrodes as a function of glucose concentration at 1.0 V vs. RHE under AM 1.5G 100 mW cm⁻² simulated sunlight.

To further explore the effect of the content of carbon upon the photocurrent densities at 1.23 V vs. RHE and photostability of the carbon–Cu₂O/TaON photoelectrode as a function of glucose concentration from 0 to 0.2 M after solution-based carbon precursor coating (i.e., glucose solution) combined with subsequent carbonization strategy at 1.0 V vs. RHE under AM 1.5G 100 mW cm⁻² simulated sunlight were also investigated in this work, as shown in Figure S10. Since most previous works has confirmed that the thickness of carbon layer in the carbon–Cu₂O/TaON photoelectrode is determined by the concentration of glucose, it is necessary to assure the content of carbon sheath. The as-prepared Cu₂O/TaON photoelectrode passivated with ultrathin carbon sheath (carbon–Cu₂O/TaON using 0.1 M glucose) as a surface protection layer exhibited the highest photocurrent densities of 4.36 mA cm⁻² at 1.23 V vs. V_{RHE} under AM 1.5G solar light and the best photostability

of 87.3% at 1.0 V vs. V_{RHE} under AM 1.5G solar light, which are ~4.69 times in the photocurrent density and ~14.55 times in the photostability higher than that of bare TaON photoanode. However, the other Cu₂O/TaON photoelectrode with the various concentration of glucose of 0.01, 0.05, 0.15 and 0.2 M, presented the relative decrease of the photocurrent densities and photostability. A carbon layer with more content may reduce the inherent optical absorption of Cu₂O/TaON sample and result in a rapid decrease in photogenerated charges, ultimately reducing the photocatalytic activity.^{17,18} Thus, the above-mentioned results indicate that the carbon sheath with the appropriate content is indeed an effective strategy for combating the photocorrosion problem of this unstable photoanode.



Figure S11. Raman spectra of carbon-Cu₂O/TaON nanorod array.

In order to confirm the carbon sheath as the graphitic carbon layer, the nature of the carbon present in the carbon-Cu₂O/TaON samples was investigated by Raman spectroscopy, as shown in Figure S11. The spectra of carbon-Cu₂O/TaON shows two peaks around 1341 and 1596 cm⁻¹. The Raman-active E_{2g} mode at 1596 cm⁻¹ is characteristic for graphitic carbon. The above-mentioned result has been confirmed the presence of sp² carbon-type structures within the carbonaceous wall of the carbon-Cu₂O/TaON samples.^{19,20} The D-band at around 1341 cm⁻¹ can be attributed to the presence of defects within the hexagonal graphitic structure.

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