Electronic Structure Engineering of Cu$_2$O Film/ZnO Nanorods Array All-Oxide p-n Heterostructure for Enhanced Photoelectrochemical Property and Self-powered Biosensing Application

Zhuo Kang, Xiaoqin Yan, Yunfei Wang, Zhiming Bai, Yichong Liu, Zheng Zhang, Pei Lin, Xiaohui Zhang, Haoge Yuan, Xueji Zhang, and Yue Zhang

1State Key Laboratory for Advanced Metals and Materials, School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, China, 2Research Center for Bioengineering and Sensing Technology, School of Chemistry and Biological Engineering, University of Science and Technology Beijing, Beijing 100083, China, 3Key Laboratory of New Energy Materials and Technologies, University of Science and Technology Beijing, Beijing 100083, China.

We have engineered the electronic structure at the interface between Cu$_2$O and ZnO nanorods (NRs) array, through adjusting the carrier concentration of Cu$_2$O. The electrodeposition of Cu$_2$O at pH 11 acquired the highest carrier concentration, resulting in the largest interfacial electric field between Cu$_2$O and ZnO, which finally led to the highest separation efficiency of photogenerated charge carriers. The optimized Cu$_2$O/ZnO NRs array p-n heterostructures exhibited enhanced PEC performance, such as elevated photocurrent and photoconversion efficiency, as well as excellent sensing performance for the sensitive detection of glutathione (GSH) in PBS buffer even at applied bias of 0 V which made the device self-powered. Besides, the favorable selectivity, high reproducibility and extremely wide detection range, make such heterostructure a promising candidate for PEC biosensing applications, probably for the extended field of PEC water splitting or other solar photovoltaic beacons.

As a newly emerged technique for the detection of biomolecules, photoelectrochemical (PEC) biosensor has rapidly become a research hotspot. Due to the complete separation of excitation source (light) and detection signal (PEC current), the PEC biosensors acquire efficient reduction of some undesired background noise and improved sensitivity. Nowadays, much related research is focused on the enhancement of PEC biosensor performance by incorporating numerous functional semiconductive nanomaterials. For examples, Graphene/CdSe multilayers and graphene/CdS nanocomposites were prepared for PEC analysis of thrombin and Glutathione (GSH), respectively. In addition, ZnO/graphene composite, as well as ZnO/ZIF-8 nanorods architecture were employed for construction of PEC sensors. Soon afterwards, IrO$_2$-Hemin-TiO$_2$ nanowire arrays were also developed for PEC detection of GSH with excellent selectivity and stability. More recently, bismuthoxyiodide nanoflakes/TiO$_2$ nanotubes array based p-n heterojunction was applied in the PEC biosensing of glucose. Even so, exploitation of novel semiconductor based photoanode is still urgent for advanced PEC biosensor fabrication.

The property of semiconductor heterostructure dominates the behavior of photoinduced charge carrier, which finally determines the photoelectrochemical response. As is known, a variety of Cu$_2$O/ZnO p-n junctions have been applied for enhanced photocatalytic performance and efficient photovoltaic cells due to their controllable electronic structure at interface and good energy band alignment. ZnO nanomaterials have been extensively studied because of their rather rich morphology world, large excitation binding energy (60 meV), deep level defects and high electron mobility. However, the large band gap of ZnO ($E_g = 3.37$ eV) greatly restricts its utility to UV region only. Hence, Cu$_2$O ($E_g = 1.9$ – $2.2$ eV) is a promising candidate to extend the photoresponse into the visible region during PEC process. Moreover, Cu$_2$O is normally synthesized as a p-type semiconductor due to the copper vacancies in the lattice, and its carrier concentration is determined by the pH value.
of electrolyte during the electrodeposition synthesis process. So this provides an approach to engineer the electronic structure at the interface of Cu2O/ZnO heterostructure. Besides, the non-toxicity, abundance and low cost of copper, as well as the long-term stability associated with oxides, allows for the feasibility of constructing PEC devices with environment-friendly Cu2O.

In this work, we assembled Cu2O/ZnO NRs array all-oxide p-n heterostructure by directly electrodepositing p-type Cu2O film onto the vertically oriented n-type ZnO NRs array. As illustrated in Figure 1, the step-wise structure of energy levels constructed in the Cu2O/ZnO heterostructure was responsible for the mechanism of PEC biosensor. When Cu2O and ZnO came into contact, a p-n junction formed at their interface. There was a favorable energy band alignment for electrons transport from the conduction band (CB) of Cu2O to the CB of ZnO, and for holes transport from the valence band (VB) of ZnO to the VB of Cu2O. In the presence of illumination, the photoinduced electrons and holes were efficiently separated by the built-in interfacial electric field. The electrons transported through each individual ZnO NR and finally reached the FTO electrode to export the PEC electrical signals. While the holes migrated through Cu2O film and subsequently took part in the oxidation of GSH to GSSG at the surface of Cu2O. The quasi-1 D nature of ZnO NRs array significantly increased the interface area between ZnO and Cu2O crystal particles starting to form a film except for several points where ZnO was still exposed. By comparing the inset of Figure 2A and Figure 2C, the size of Cu2O crystal particles spread all over the top surface of ZnO NRs, and covered all over the ZnO NRs. By comparing Figure 2B, D and F, the thickness of Cu2O film increased from ~0.8 μm to ~1.1 μm along with the growth time. It is worth pointing out that the Cu2O crystal particles partially sank into the ZnO NRs array, so that the interface area between Cu2O and ZnO was significantly increased. In addition, the longer time ZnO was immersed in the alkaline electrodeposition solution, the more serious etching happened to ZnO NRs. Moreover, it is noticed that with the increase of size and amount of Cu2O particles, the vertical ZnO NRs suffered more stress and strain from Cu2O particles. However, taking all factors in terms of the PEC property into consideration, we still choose 30 min for electrodeposition of Cu2O film.

Figure 3A shows the X-ray diffraction (XRD) patterns of the ZnO NRs array and fabricated Cu2O/ZnO heterostructure. The diffraction peaks of the FTO substrate were marked with spades. For pristine ZnO NRs array, diffraction peaks were identified to the hexagonal ZnO crystalline phase with a wurtzite structure. After the deposition of Cu2O at pH 11 for 30 min, diffraction peaks from Cu2O were observed in addition to those from ZnO NRs array, which can be indexed to the cubic phase Cu2O (JCPDS 78-2076). No diffraction peaks of impurities were found in the XRD patterns.

X-ray photoelectron spectroscopy (XPS) (Figure 3B) was performed in order to identify the chemical state of the Cu element in the heterostructure. Since XPS is only capable for surface elemental analysis, the Zn element cannot be observed in the wide scan spectrum. In the Cu 2p core level spectrum, the Cu 2p3/2 and Cu 2p1/2 spin-orbital photo-electrons were located at binding energies of 932.6 eV and 952.5 eV, respectively. Such results are in good agreement with the reported values of Cu2O31,32, thus demonstrating the layer electrodeposited upon ZnO NR array was Cu2O rather than Cu or CuO.

Figure 4A shows the UV-vis diffuse reflectance spectra (DRS) of pristine ZnO NRs array and Cu2O/ZnO heterostructure with varied electrodeposition time of Cu2O at pH 11. The pristine ZnO resulted in an obvious absorption below 380 nm, which originated from the band edge of ZnO. And only a little absorption in the visible region can be observed, which might have resulted from the scattering effect of the NRs array structure. However, the absorption spectrum was significantly enhanced after subsequent electrodeposition of Cu2O. It is noteworthy that the visible light absorption difference between 10 min sample and 20 min sample was greater than that between 20 min sample and 30 min sample, which was corresponding to the isolated Cu2O nanocrystals for 10 min growth time, almost covering Cu2O film for 20 min growth time and the full covering Cu2O film for 30 min growth time. The strong absorption below 600 nm is attributed to the band edge absorption of the nanocrystalline Cu2O film. It suggests that the so-fabricated Cu2O/ZnO NRs array heterostructure has a quite broad absorption range from visible to ultraviolet, which well agrees with the solar irradiation. Consequently, good photoelectrochemical property of such nanostructure under white light irradiation is expected. The following PEC measurements were all based on the samples with electrodeposition of Cu2O for 30 min.

**Results**

**Characterization of Cu2O/ZnO heterostructure.** Figure 2 shows the morphology of Cu2O/ZnO NRs array heterostructure prepared by electrodeposition of Cu2O at pH 11 for different durations. Independent ZnO NRs, with average length of ~1.8 μm and diameter of ~150 nm, were vertically grown on the FTO surface. For the electrodeposition of Cu2O for 10 min (Fig 1A and B), the individual Cu2O crystal particles spread all over the top surface of ZnO NRs array, and covered almost half of the surface area. When the electrodeposition time was increased to 20 min (Fig 1C and D), the Cu2O crystal particles started to form a film except for several points where ZnO was still exposed. By comparing the inset of Figure 2A and Figure 2C, the size of Cu2O crystal particles obviously increased. For the samples of 30 min (Figure 2E and F), the Cu2O particles further expand their size, and the Cu2O film covered all over the ZnO NRs. By comparing Figure 2B, D and F, the thickness of Cu2O film increased from ~0.8 μm to ~1.1 μm.

**Electronic structure engineering of Cu2O/ZnO heterostructure.** Figure 4B shows the current density of pristine ZnO NRs array and Cu2O/ZnO heterostructures electrodeposited at various pH values without and with illumination as the function of applied bias potential. For pristine ZnO, the dark current density is on the order of 10-10 mA/cm², and the photocurrent density has a slight increment. While all samples with Cu2O/ZnO heterostructure showed pronounced photoreponse under illumination, which can be attributed to the improved visible light absorption and efficient interfacial charge transport of Cu2O/ZnO heterostructure. Noticeably, the photoreponse was gradually improved along with the increase of the electrodeposition pH value from 9 to 11. The saturated photocurrent density of Cu2O (pH 11)/ZnO was approximately 13.5 times that of pristine ZnO NRs array, 2.3 times...
that of Cu$_2$O (pH 9)/ZnO, and 1.7 times that of Cu$_2$O (pH 10)/ZnO at 0 V bias. Such results can be explained by the different carrier concentrations of Cu$_2$O in the samples, which is demonstrated by Mott-Schottky plots (Figure S2). During the liquid electrodeposition of Cu$_2$O, the carrier concentration of Cu$_2$O was adjusted by changing the pH value of precursor solutions$^{31,32}$, which in turn led to the alteration of the built-in potential in Cu$_2$O/ZnO heterostructure$^{14,15}$. As illustrated in Figure 5, the built-in potential $V_{bi}$ is equal to the difference between the Fermi levels of ZnO and Cu$_2$O. Consequently, the samples with higher electrodeposition pH value, that is with higher carrier concentration of Cu$_2$O, possess larger built-in potential. When the illumination was applied, the photoinduced electron-hole pairs were separated under the effect of the interfacial electric field. Therefore, Cu$_2$O (pH 11)/ZnO got the highest charge separation efficiency, which resulted in the best photoresponse at bias potential of 0V.

Based on the discussion above, Cu$_2$O/ZnO heterostructure electrodeposited at pH value of 12 or 13 should perform better photoresponse. However, in such strong alkaline electrodeposition electrolytes, the dissolution and etching of ZnO NRs array is very serious, which would certainly introduce a high concentration of interface states at the Cu$_2$O/ZnO heterostructure, thus to a large extent affecting the quality of the heterostructure$^{10,11}$. Moreover, considering the stability of the fabricated devices, pH 11 is the optimal parameter for construction of Cu$_2$O/ZnO heterostructure based PEC biosensor with ideal performance. So the following PEC measurements were based on the samples acquired at pH 11.

**PEC property of Cu$_2$O/ZnO heterostructure photoanode.** Electrochemical impedance spectroscopy (EIS) was carried out both in the dark and under illumination at bias potential of 0 V vs. Ag/AgCl. It is known that the semicircle in the Nyquist plot at high frequencies is the characteristic of the charge transfer process, and the diameter of the semicircle is equal to the charge transfer resistance ($R_{ct}$). As shown in Figure 6A, the $R_{ct}$ of Cu$_2$O/ZnO heterostructure was apparently much smaller than that of the pristine ZnO NRs array under illumination. Such result indicates that the formation of Cu$_2$O/ZnO heterostructure dramatically promoted the interfacial charge transport and the separation efficiency of photoinduced charges under illumination, thus demonstrating the enhanced PEC performance for Cu$_2$O/ZnO NRs array heterostructure.

PEC behaviors of pristine ZnO NRs array and Cu$_2$O/ZnO heterostructure with and without addition of GSH at bias potential of 0V were also characterized in Figure 6B. No photocurrent was observed in the dark. Upon photoexcitation, the photocurrent composed of three steps: (a) the photocurrent climbed promptly; (b) the photocurrent decreased sharply; (c) the photocurrent gradually reached a stable state. These three stages are corresponding with the photoin-
duced electrons under illumination, the recombination of photoinduced electron-hole pairs, and the balance of generation and recombination process, respectively. The pristine ZnO NRs array photoanode performed an average photocurrent density of 0.097 mA/cm² (curve a), whereas the Cu₂O/ZnO heterostructure showed an average photocurrent density of 1.35 mA/cm² (curve b), demonstrating the remarkable improvement of photoelectric conversion efficiency. The formed p-n heterojunction between Cu₂O and ZnO provided an interfacial electric field, which subsequently contributed to the charge separation efficiency, and finally led to the significantly enhanced photoresponse. Moreover, the elevated photocurrent could be further strengthened with the presence of sacrificial reagent who served as the hole scavenger.

Since GSH plays an important role in many biological functions, it was adopted as a model molecule to demonstrate the feasibility of fabricating Cu₂O/ZnO heterostructure based PEC biosensor. When GSH was added in the blank PBS (200 μM), the average photocurrent density reached 2.91 mA/cm² (curve c). The great photocurrent change indicated the fabricated Cu₂O/ZnO heterostructure is suitable for detecting GSH based on PEC method.

There is no doubt that when a positive bias potential is applied, the photocurrent density will apparently increase due to the more efficient charge separation and longer lifetime of photoinduced electron-hole pairs. Nevertheless, in order to realize the self-powered function, plus taking energy conservation and the selectivity of PEC biosensors into consideration, 0 V was selected as bias potential in this work.

Self-powered PEC biosensing of GSH. In order to further verify the sensitive sensing of GSH based on Cu₂O/ZnO heterostructure, Figure 7 displays the photocurrent response in the presence of GSH with various concentrations at applied bias potential of 0 V (vs. Ag/AgCl). The photocurrent density performed a fine linear relationship with the concentration of GSH from 10 to 1000 μM (R² = 0.991), which is much wider than that of porous TiO₂-Pt nanowhisker, flower-like Cu₂O/ZnO, and IrO₂-Hemin-TiO₂ photoanodes based on PEC method, as well as Au nanoparticles@Si nanowires, Hg/Pd and ordered mesoporous carbon photoanodes based on electrochemical method. The detection limit was estimated as low as 0.42 μM through 3σ. The detailed performance comparisons with previously reported literatures are listed in Table S1. Obviously, the proposed Cu₂O/ZnO NRs array heterostructure based PEC biosensor shows great promise for applications in the monitoring of GSH with high sensitivity and wide linear range.

Figure 4 | (A) UV-vis diffuse reflectance spectra of pristine ZnO NRs array and fabricated Cu₂O/ZnO heterostructure with various electrodeposition time of Cu₂O. (B) Linear sweep voltammograms of pristine ZnO NRs array photoanodes without and with illumination, Cu₂O/ZnO heterostructure electrodeposited at pH values of 9, 10 and 11 for 30 min with illumination at a scan rate of 50 mV/s under bias potentials from −0.4 to +0.1 V vs. Ag/AgCl.

Figure 5 | Energy band diagrams for isolated ZnO and Cu₂O electrodeposited at various pH values from 9 to 11, and corresponding Cu₂O/ZnO heterostructures.
The selectivity of Cu$_2$O/ZnO heterostructure based PEC biosensor was confirmed by measuring the photocurrent response not only for common chemical or biological interferences but also for various metal ions with the concentration of 50 mM, showing much smaller or negligible signals compared to that of GSH with the concentration of 200 mM (Figure 8A and B). The excellent selectivity is ascribed to the low applied bias potential which minimized the interference from other reductive species. Furthermore, the relative standard deviation (R.S.D) of the photoreponse to 200 mM GSH was 5.2% for six successive measurements. The R.S.D for detection of 200 mM GSH with six different Cu$_2$O/ZnO based photoanode under the same condition was 6.4%. In addition, the photocurrent density was stable for 2 h in 0.1 M PBS containing 10 µM GSH (Figure S5), and 91% of the initial photocurrent response was maintained after storing for over half month in the repeating test (Figure S6). All the results demonstrated the reproducibility and stability of fabricated heterostructures and their practical potential for PEC biosensing application.

Discussion

The enhanced PEC property and excellent PEC biosensing performance was probably attributed to the following five points: (a) The quasi 1-D nature of ZnO NRs array offered large p-n heterojunction interface area when in combination with Cu$_2$O film; (b) The introduction of Cu$_2$O significantly improved the visible light absorption, so that the solar energy could be utilized more sufficiently; (c) The electronic structure between Cu$_2$O and ZnO was engineered thorough adjusting the carrier concentration in Cu$_2$O and the thickness of Cu$_2$O film. Thereby, the optimal build-in potential was acquired at the Cu$_2$O/ZnO interface, resulting in the efficient charge separation; (d) The step-wise energy band structure facilitated the photoinduced electrons to the electrode while promoted the photoinduced holes to accumulate in the VB of Cu$_2$O and subsequently to be consumed by participating in the oxidation of GSH. This process further prevented the recombination of photogenerated carriers; (e) The individual and vertical alignment of single crystal ZnO NRs provides transport channels for electrons to rapidly reach FTO electrode.

To conclude, the Cu$_2$O/ZnO NRs array all-oxide p-n heterostructure was successfully fabricated, and the electronic structure at the interface between Cu$_2$O and ZnO was engineered through adjusting the carrier concentration of Cu$_2$O. The results demonstrated the electrodeposition of Cu$_2$O at pH 11 acquired the highest carrier concentration, resulting in the largest build-in electric field, which finally led to the highest separation efficiency of photoinduced charge carriers. The optimized heterostructure exhibited enhanced PEC performance and was subsequently adopted for self-powered PEC sensing of GSH. The Cu$_2$O/ZnO based PEC biosensor performed a linear range from 10 µM to 1000 µM and an estimated detection limit of 0.42 µM even at bias potential of 0 V. Moreover, the excellent selectivity, reproducibility and stability suggested that such heterostructure is a competitive candidate for advanced PEC biomolecular detection, maybe for the extended field of PEC water splitting or other solar photovoltaic beacons.

Methods

Reagents. Glutathione (GSH), ascorbic acid (AA), uric acid (UA), lactic acid (LA), glucose, dopamine, bovine serum albumin (BSA), Glycine (Gly), polyetherimide (PEI) were purchased from Sigma-Aldrich. 0.1 M pH 7.4 phosphate buffer saline (PBS) was always employed as the supporting electrolyte. Zinc acetate (Zn(CH$_3$COO)$_2$.2H$_2$O), Zinc nitrate hexahydrate (Zn(NO$_3$)$_2$.6H$_2$O), hexamethylenetetramine (HMTA, (CH$_2$)$_6$N$_4$), Copper sulfate (Cu$_2$SO$_4$) and sodium hydroxide (NaOH) were purchased from Beijing chemical reagent company. Other reagents were of analytical grade and all aqueous solutions were prepared with deionized water.

Figure 6 | (A) EIS Nyquist plots of pristine ZnO NRs array and Cu$_2$O/ZnO heterostructure with or without illumination in 0.1 M PBS at bias potential of 0 V vs.Ag/AgCl. (B) Photoresponse of pristine ZnO NRs array (a) and Cu$_2$O/ZnO heterostructure (b) in 0.1 M PBS, as well as Cu$_2$O/ZnO heterostructure in 0.1 M PBS containing 200 µM GSH (c) under illumination at bias potential of 0 V vs. Ag/AgCl.

Figure 7 | Photocurrent responses of Cu$_2$O/ZnO heterostructure based photoanode in 0.1 M PBS in the presence of 0, 10, 40, 80, 100, 200, 500, 1000 µM GSH (from bottom to top) at 0 V (vs. Ag/AgCl) under illumination. Inset: linear calibration curve.
The samples were characterized by Field emission scanning electron microscopy (FESEM, Zeiss, SUPRA-55, German), X-ray diffractometer (XRD, Rigaku, DMAX-RB, Japan), and X-ray photo-electron spectroscopy (XPS, Axis UltraDLD, SHIMADZU, Japan). The PEC related experiments were carried out using an electrochemical workstation (Solartron SI 1260) under AM 1.5G illumination provided by a solar simulator (Oriel, 91159A, 100 mW/cm²).

Preparation of Cu2O/ZnO NRs array based photoanode. The ordered ZnO NRs array was prepared by the hydrothermal growth method on fluorine doped tin oxide (FTO) substrates. The ZnO seed layer was acquired by spin coating a colloidal array was prepared by the hydrothermal growth method on fluorine doped tin oxide (FTO) substrates. The ZnO seed layer was acquired by spin coating a colloidal array was prepared by the hydrothermal growth method on fluorine doped tin oxide (FTO) substrates. The ZnO seed layer was acquired by spin coating a colloidal array was prepared by the hydrothermal growth method on fluorine doped tin oxide (FTO) substrates.

The ordered ZnO NRs array was prepared by the hydrothermal growth method on fluorine doped tin oxide (FTO) substrates. The ZnO seed layer was acquired by spin coating a colloidal array was prepared by the hydrothermal growth method on fluorine doped tin oxide (FTO) substrates. The ZnO seed layer was acquired by spin coating a colloidal array was prepared by the hydrothermal growth method on fluorine doped tin oxide (FTO) substrates.

Enhanced photoresponse of Cu2O/ZnO heterostructure with piezoelectric properties. A new approach to enhance the piezoelectric properties of Cu2O/ZnO heterostructure was proposed. The results indicated that the piezoelectric properties of Cu2O/ZnO heterostructure were improved by controlling the heterojunction orientation and surface microstructure. The enhanced piezoelectric properties of Cu2O/ZnO heterostructure were attributed to the synergistic effect of the heterojunction and surface morphology.

Figure 8 | Photocurrent responses of Cu2O/ZnO heterostructure based PEC biosensors in the presence of GSH (200 μM) and (A) dopamine, LA, UA, BSA, glucose, AA, Gly with the concentration of 50 μM, as well as (B) various metal ions such as Cu2+, Mg2+, Ca2+, Na+, Fe3+, Zn2+, K+ and Ba2+ with the concentration of 50 μM at bias potential of 0 V (vs. Ag/AgCl).

1. Liang, M. et al. Photoelectrochemical Sensor for the Rapid Detection of in Situ DNA Damage Induced by Enzyme-Catalyzed Fenton Reaction. Environ. Sci. Technol. 42, 635–639 (2008).
2. Zhang, X. et al. A New Photoelectrochemical Aptasensor for the Detection of Thrombin Based on Functionalized Graphene and CdSe Nanocomposites Multilayers. Chem. Commun. 47, 4929–4931 (2011).
3. Zhao, X. et al. Fabrication of Glutathione Photoelectrochemical Biosensor Using Graphene–CdS Nanocomposites. Analyst 137, 3697–3703 (2012).
4. Liu, F. et al. Application of ZnO/graphene and S6 Aptamers for Sensitive Photoelectrochemical Detection of SK-BR-3 Breast Cancer Cells Based on a Disposable Indium Tin Oxide Device. Biosens. Bioelectron. 51, 413–420 (2014).
5. Zhan, W. et al. Semiconductor@Metal–Organic Framework Core–Shell Heterostructures: A Case of ZnO@ZIF-8 Nanorods with Selective Photocatalytic Activities. J. Am. Chem. Soc. 135, 1926–1933 (2013).
6. Yang, J. et al. Photoelectrochemical Detection of Glutathione by IrOx–Hemin–TiO2 Nanowire Arrays. Nano Lett. 13, 5350–5354 (2013).
7. Zhao, W. et al. Bismuth Oxyiodide Nanoflakes/Titania Nanotubes Arrayed on Heterojunction and Its Application for Photocatalytic Bioenergy. Sci. Rep. 4, 4426–4431 (2014).
8. Lin, P. et al. Enhanced photovoltaic of Cu2O/ZnO heterojunction with piezo-modulated interface engineering. Nano Res. 7, 860–884 (2014).
9. Deo, M. et al. Cu2O/ZnO Hetero-Nanobrush: Hierarchical Field Emission and Photocatalytic Properties. J. Mater. Chem. 22, 17055–17062 (2012).
10. Musselman, K. P. et al. A Novel Buffering Technique for Aqueous Processing of Zinc Oxide Nanostructures and Interfaces, and Corresponding Improvement of Electrodeposited ZnO–Cu2O Photovoltaics. Adv. Funct. Mater. 21, 573–582 (2011).
11. Cui, J. & Gibson, U. J. A Simple Two-Step Electrodeposition of Cu2O/ZnO Nanopillar Solar Cells. J. Phys. Chem. C 114, 6408–6412 (2010).
12. Wang, R.-C. & Lin, H.-Y. Simple Fabrication and Improved Photovoltaic Performance of Cu2O–ZnO Core–Shell Heterojunction Nanorod Arrays. Sens. Actuators, B 149, 94–97 (2010).
13. Zoolfakar, A. S. et al. Enhancing the Current Density of Electrodeposited ZnO–Cu2O Solar Cells by Engineering Their Heterointerfaces. J. Mater. Chem. 22, 21767–21775 (2012).
14. Jiang, T. et al. Carrier Concentration-Dependent Electron Transfer in Cu2O/ZnO Nanorod Arrays and Their Photocatalytic Performance. Nanoscale 5, 2938–2944 (2013).
15. Ren, S. et al. Electrodeposition of Hierarchical ZnO/Cu2O Nanorod Films for Highly Efficient Visible-Light-Driven Photocatalytic Applications. J. Appl. Phys. 115, 064301 (2014).
16. Marin, A. T. et al. Novel Atmospheric Growth Technique to Improve Both Light Absorption and Charge Collection in ZnO/Cu2O Thin Film Solar Cells. Adv. Funct. Mater. 23, 3413–3419 (2013).
17. Kramm, B. et al. The Band Alignment of Cu2O/ZnO and Cu2O/GaN Heterostructures. Appl. Phys. Lett. 100, 094102 (2012).
18. Musselman, K. P. et al. Incompatible Length Scales in Nanostructured Cu2O Solar Cells. Adv. Funct. Mater. 22, 2202–2208 (2012).
19. Deo, M. et al. Strong Photo-Response in A Flip-Chip Nanowire p-Cu2O/n-ZnO Heterojunction. Nanoscale 3, 4706–4712 (2011).
20. Sheng, W. et al. Quantum Dot-Sensitized Hierarchical Micro/Nanowire Architecture for Photoelectrochemical Water Splitting. ACS Nano 8, 7163–7169 (2014).
21. Kargar, A. et al. 3D Branched Nanowire Photoelectrochemical Electrodes for Efficient Solar Water Splitting. ACS Nano 7, 9407–9415 (2013).
22. Zhang, Y. et al. Scanning Probe Study on the Piezoelectric Effect in ZnO Nanomaterials and Nanodevices. Adv. Mater. 24, 4647–4655 (2012).
23. Kargar, A. et al. 3D Branched Nanowire Photoelectrochemical Electrodes for Efficient Solar Water Splitting. ACS Nano 7, 9407–9415 (2013).
24. Hou, Y. et al. Photoelectrocatalytic Activity of a Cu2O-Loaded Self-Organized Highly Oriented TiO2 Nanotube Array Electrode for 4-chlorophenol Degradation. Environ. Sci. Technol. 43, 858–863 (2008).
25. Wang, M. et al. p–n Heterojunction Photoelectrodes Composed of Cu2O-Loaded TiO2 Nanotube Arrays with Enhanced Photoelectrochemical and Photoelectrocatalytic Activities. Environ. Sci. Chem. 6, 1211–1220 (2013).
26. Cao, D. et al. High-Efficiency Ferroelectric-Film Solar Cells with An p-Type Cu2O Cathode Buffer Layer. Nano Lett. 12, 2803–2809 (2012).
27. Wang, W. et al. pH-Dependence of Conduction Type in Cuprous Oxide Synthesized from Solution. J. Appl. Phys. 107, 123717 (2010).
28. Yuhas, B. D. & Yang, P. Nanowire-Based All-Oxide Solar Cells. Adv. Mater. 25, 4647–4655 (2012).
29. Wagner, C. D. et al. Handbook of X-ray Photoelectron Spectroscopy: A Reference Book of Standard Spectra for Identification and Interpretation of XPS Data. [Mullenberg, G. E. (ed.)] [82–83] (Perkin-Elmer Corporation, Eden Prairie, 1995).
30. Xiao, L. et al. p-Type and n-Type Cu2O Semiconductor Thin Films: Controllable Preparation by Simple Solvothermal Method and Photoelectrochemical Properties. Electrochim. Acta 56, 2735–2739 (2011).
31. Wei, H. et al. Photovoltaic Efficiency Enhancement of Cu2O Solar Cells Achieved by Controlling Homojunction Orientation and Surface Microstructure. J. Phys. Chem. C 116, 10510–10515 (2012).
33. Chen, G. et al. Photoelectrocatalytic Oxidation of Glutathione Based on Porous TiO$_2$–Pt Nanowhiskers. *Langmuir* **28**, 12393–12399 (2012).
34. Yang, K. et al. Gold Nanoparticle Modified Silicon Nanowires as Biosensors. *Nanotechnology* **17**, S276 (2006).
35. Antwi, C. et al. Use of Microchip Electrophoresis and A Palladium/Mercury Amalgam Electrode for the Separation and Detection of Thiols. *Anal. Method.* **3**, 1072–1078 (2011).
36. Ndamanisha, J. C. et al. Application of Electrochemical Properties of Ordered Mesoporous Carbon to the Determination of Glutathione and Cysteine. *Anal. Biochem.* **386**, 79–84 (2009).
37. Tu, W. et al. Low-Potential Photoelectrochemical Biosensing Using Porphyrin-Functionalized TiO$_2$ Nanoparticles. *Anal. Chem.* **82**, 8711–8716 (2010).
38. Law, M. et al. Nanowire Dye-Sensitized Solar Cells. *Nat. Mater.* **4**, 455–459 (2005).
39. Kang, Z. et al. Enhanced Photoelectrochemical Property of Zno Nanorods Array Synthesized on Reduced Graphene Oxide for Self-Powered Biosensing Application. *Biosens. & Bioelectron.* **64**, 499–504 (2015).
40. Zhang, Z. et al. Functional Nanogenerators as Vibration Sensors Enhanced by Piezotronic Effects. *Nano Res.* **7**, 190–198 (2014).

**Acknowledgments**
This work was supported by the National Major Research Program of China (2013CB932600), the Major Project of International Cooperation and Exchanges (2012DFA50990), the Program of Introducing Talents of Discipline to Universities, the National Natural Science Foundation of China (51132001, 51172022, 51372023, 31371203), the Research Fund of Co-construction Program from Beijing Municipal Commission of Education, the Fundamental Research Funds for the Central Universities, the Program for Changjiang Scholars and Innovative Research Team in University.

**Author contributions**
Y.Z. and Z.K. designed the experiments and wrote the manuscript text. Y.L., Xi.Z. and H.Y. carried out the material synthesis and characterization. Z.K., Y.W. and X.Y. analyzed the data. Z.B., Z.Z., P.L., and Xu. Z. provided the support for theoretical explanation. All authors discussed the results and commented on the manuscript.

**Additional information**
Supplementary information accompanies this paper at http://www.nature.com/scientificreports

**Competing financial interests:** The authors declare no competing financial interests.

**How to cite this article:** Kang, Z. et al. Electronic Structure Engineering of Cu$_2$O Film/ZnO Nanorods Array All-Oxide p-n Heterostructure for Enhanced Photoelectrochemical Property and Self-powered Biosensing Application. *Sci. Rep.* **5**, 7882; DOI:10.1038/srep07882 (2015).

This work is licensed under a Creative Commons Attribution 4.0 International License. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in the credit line; if the material is not included under the Creative Commons license, users will need to obtain permission from the license holder in order to reproduce the material. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/