

Short communication

## Sensitive Photoelectrochemical Detection of $\text{Cu}^{2+}$ Using CdS Quantum Dots Decorated $\text{TiO}_2$ Nanowires in Combination with a Chemical Reducing Reaction

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Received: 16 August 2016 / Accepted: 19 September 2016 / Published: 10 October 2016

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$\text{TiO}_2$  NWs/CdS hierarchical nanocomposites were prepared for selective photoelectrochemical (PEC) detection of  $\text{Cu}^{2+}$ .  $\text{TiO}_2$  nanowires were first prepared by a simple hydrothermal method. Then, CdS nanocrystals were successfully grown on  $\text{TiO}_2$  NWs through the chemical bath deposition method. The prepared  $\text{TiO}_2$  NWs/CdS nanocomposites were used as the photoanode for PEC sensing of  $\text{Cu}^{2+}$ . The introducing of CdS QDs significantly improved the visible light harvesting efficiency of the photoanode. Moreover, ascorbic acid was used as reducing agent for the rapid conversion of  $\text{Cu}^{2+}$  to  $\text{Cu}^+$ , resulting in the formation of  $\text{Cu}_2\text{S}$  coated on CdS. The formed  $\text{Cu}_2\text{S}$  can act a recombination center which suppresses the charge transfer from the conduction band of CdS to  $\text{TiO}_2$  and results in an attenuated photocurrent. Thus, a PEC sensor could be used for  $\text{Cu}^{2+}$  detection based on the target-induced formation of exciton trapping with the aid of a effective reducing agent. The results showed that the proposed sensor possesses a good selectivity and sensitivity for  $\text{Cu}^{2+}$  detection.

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**Keywords:** Photoelectrochemical,  $\text{TiO}_2$  nanowire, CdS quantum dots, chemical reducing

### 1. INTRODUCTION

Photoelectrochemical (PEC) sensing based on the photoelectric effect of semiconductors is a recently developed analytical approach that represents several attractive merits [1,2]. First, due to the complete separation of detection signal (current) and excitation source (light), the background noise can be effectively reduced. Second, the analytical method possesses the merits of low cost, simple

instruments, and easy miniaturization. As a result, many PEC sensors have been fabricated to determine important species over the past decades [3-6].

Due to their large specific surface area and excellent stability, TiO<sub>2</sub> nonmaterials were often used as photosensitizer supporters and charge collectors in these PEC sensors [7-9]. Especially, one dimensional TiO<sub>2</sub> nanowires showed several advantages for PEC analytical applications, such as providing direction photoelectron injection and transport pathway, as well as spatially accessible structures for surface modification [10-12]. Quantum dots (QDs) have displayed great promising applications because of their high stability against photobleaching, high fluorescence quantum yields and size-controlled properties [13-15]. Notably, CdS QDs have received considerable attention due to the proper band gap and the facile preparation process, thus having been successfully applied for the preparation of PEC sensors.

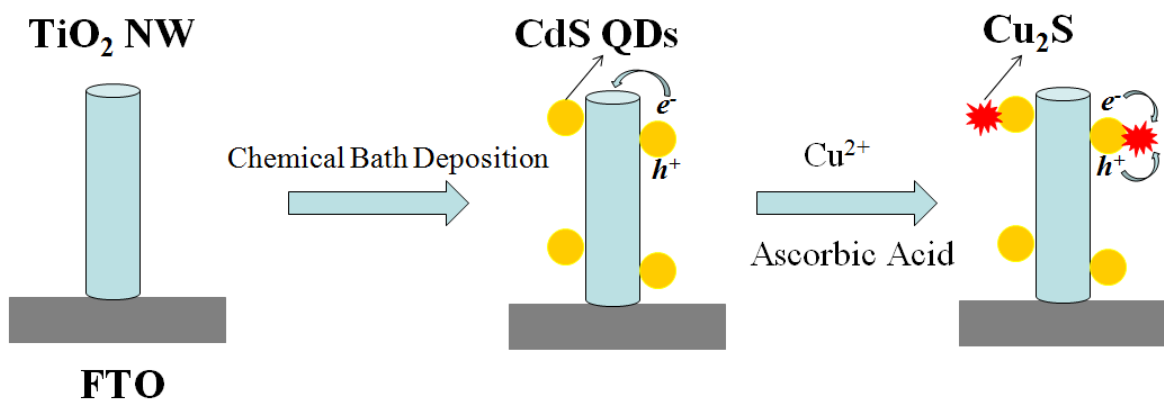
Heavy metal ions have gained great concern, because they can cause serious environmental and health problems. Copper ion is a kind of trace metal ions in the human body. But its abnormal levels are linked to many diseases, such as Menkes disease, Wilson disease, Alzheimer disease, Parkinson disease, et al. [16-18]. Several PEC assays have been developed for the selective sensing of Cu<sup>2+</sup> based on the in situ formed Cu<sub>x</sub>S as a recombination center [19,20]. This reduction process (Cu<sup>2+</sup> to Cu<sub>x</sub>S) mainly occurred at the surface of QDs. The partial conversion suggested that the photochemical reduction was inefficient. Moreover, it is unclear which formation of sulfide (CuS or Cu<sub>2</sub>S) precipitated at the QDs surface. In the recent investigation, ascorbic acid (AA) was introduced to rapidly and quantitatively reduce Cu<sup>2+</sup> into Cu<sub>2</sub>S on the surface of CdS QDs [19]. This thus realized the selective and sensitive photoluminescent detection of Cu<sup>2+</sup>.

Inspired by these thoughts, herein, we present a new strategy for the construction a PEC sensor for the determination of Cu<sup>2+</sup> (Scheme 1). In this work, TiO<sub>2</sub> NWs were first grown on the FTO (F-doped SnO<sub>2</sub>) substrates by a simple hydrothermal method. Then, CdS was coated on TiO<sub>2</sub> NWs by chemical bath deposition (CBD) method. The matched band edges between TiO<sub>2</sub> and CdS facilitated the form of type II heterojunction for electron injection. With the addition of AA, target analyte Cu<sup>2+</sup> was rapidly and effectively reduced into Cu<sup>+</sup> and precipitated as Cu<sub>2</sub>S on CdS QDs. The formed Cu<sub>2</sub>S can act a recombination center for photoelectrons and hole which hinders the electron transfer from the conduction band of CdS QDs to TiO<sub>2</sub> NWs and results in a decreased photocurrent. The proposed PEC sensor has the advantages of high sensitivity and good selectivity.

## 2. EXPERIMENTAL

### 2.1 Chemicals and reagents

FTO glasses (15 Ω/square, transmittance of 80%) were obtained from Hartford Glass Company (Hartford, IN, USA). Other chemicals were analytical grade and received from commercial suppliers without further purification. Before use, the glasses were washed by sonication in acetone, 2-propanol, ethanol, and water subsequently, and then dried using a nitrogen stream. Stock solutions of K<sup>+</sup>, Zn<sup>2+</sup>, Al<sup>3+</sup>, Cu<sup>2+</sup>, Cr<sup>3+</sup>, Pb<sup>2+</sup>, Ni<sup>2+</sup> and Ca<sup>2+</sup> ions were obtained by dissolving a given amount of KCl, Zn(NO<sub>3</sub>)<sub>2</sub>, AlCl<sub>3</sub>, CuSO<sub>4</sub>, Cr(NO<sub>3</sub>)<sub>3</sub>, Pb(NO<sub>3</sub>)<sub>2</sub>, NiCl<sub>2</sub> and CaCl<sub>2</sub> in water, respectively.



**Scheme 1.** Schematic illustrating the preparation of the FTO/TiO<sub>2</sub> NWs/CdS QDs electrode and the mechanism for PEC sensing of Cu<sup>2+</sup>.

## 2.2 Formation of the TiO<sub>2</sub> nanowire arrays

The TiO<sub>2</sub> NWs were directly grown on a FTO glass according to the reported methods [21,22]. Typically, 9 mL of HCl solution (37 wt %) was added to 9 mL of H<sub>2</sub>O. This step was followed by the addition of 0.5 mL of tetrabutyl titanate. After stirring for 5 min, the mixed solution was poured into the Teflon reactor. Then, the cleaned FTO substrates were placed in the reactor. After heating at 150 °C for 8 h, the autoclave was cooled to room temperature. Then, the FTO substrates were taken out and rinsed thoroughly with ethanol/water. The substrates were then sintered at 500 °C for 0.5 h. This led to the formation of TiO<sub>2</sub> NWs on the FTO surface. The resulted glass chip was denoted as the FTO/TiO<sub>2</sub> NWs electrode.

## 2.3 Fabrication of TiO<sub>2</sub> NWs/CdS QDs electrodes

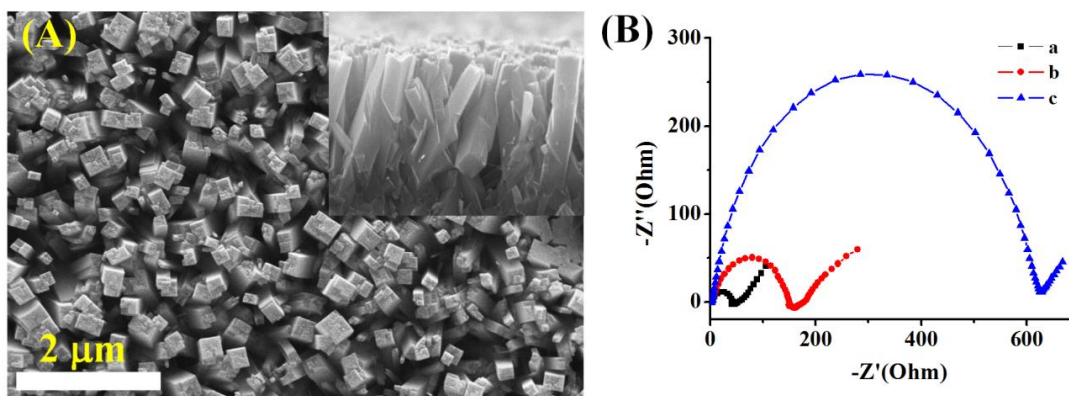
CdS QDs were coated onto the surface of TiO<sub>2</sub> NWs by the CBD method [22]. Typically, the FTO/TiO<sub>2</sub> NWs electrodes were immersed in the 0.05 M Cd(NO<sub>3</sub>)<sub>2</sub> solution for 2~3 min. After washed with water, the electrodes were immersed in the solution of 0.05 M Na<sub>2</sub>S for 2~3 min and then rinsed with water again. Such incubation cycle was repeated for 10 times. The resulted QDs-coated FTO/TiO<sub>2</sub> NWs electrode was referred to FTO/TiO<sub>2</sub> NWs/CdS QDs electrode.

## 2.4 Photoelectrochemical measurements and Cu<sup>2+</sup> sensing

The PEC measurement was carried out in a home-built cell. The irradiation source was provided by a Cary Eclipse fluorescence spectrophotometer with the excitation slit width at 20 nm. Photocurrent was collected using a CHI 440 electrochemical workstation. The prepared FTO/TiO<sub>2</sub> NWs/CdS QDs electrode, Pt wire, and Ag/AgCl were used as working electrode, counter electrode, and reference electrode, respectively. Before measurement, the working electrode was first incubated with a solution containing AA (0.1 M) and the target analyte Cu<sup>2+</sup> for 10 min. The PEC measurements were performed in a phosphate buffer solution (0.1 M, pH 7.4) containing 0.1 M TEOA.

### 3. RESULTS AND DISCUSSION

#### 3.1 Characterization of TiO<sub>2</sub> NWs and the TiO<sub>2</sub> NWs/CdS QDs electrode



**Figure 1.** (A) SEM images of TiO<sub>2</sub> NWs grown on FTO substrate. (B) EIS of various electrodes: (a) the bare FTO electrode, (b) FTO/TiO<sub>2</sub> NWs, (c) FTO/TiO<sub>2</sub> NWs/CdS QDs.

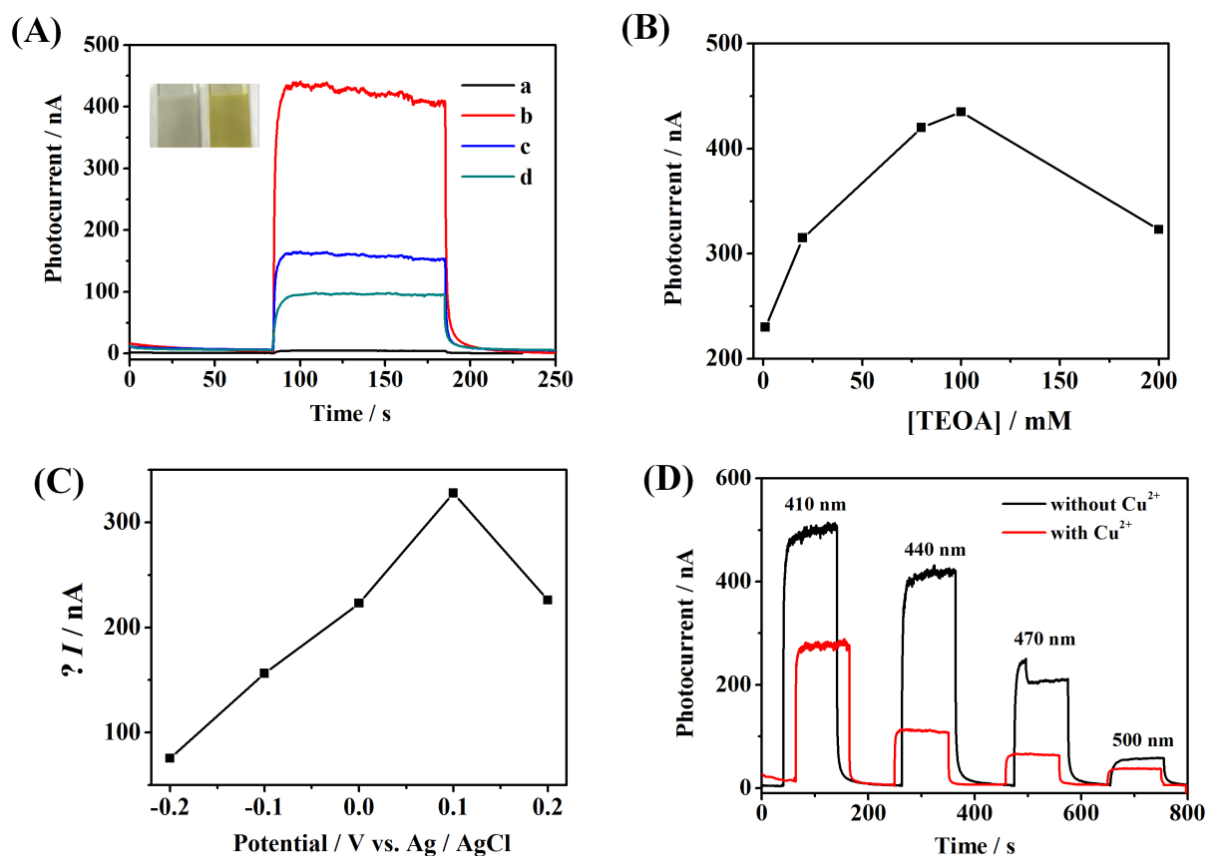
The highly ordered TiO<sub>2</sub> nanowires on a FTO substrate were formed based on a simple hydrothermal method. The morphology of the TiO<sub>2</sub> NWs was characterized by SEM technique. Figure 1A shows the top facet and cross-sectional image (see the inset) of the resulted TiO<sub>2</sub> NWs film. The TiO<sub>2</sub> array is comprised of vertically aligned and tetragonal shaped nanowires. The nanowire has a feature size of a typical length of ~3 μm and an average diameter of ~200 nm. In this hydrothermal synthesis, HCl was employed to maintain an acidic condition, which impeded the hydrolysis of Ti(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>. Additionally, the Cl<sup>-</sup> ion facilitated anisotropic growth of one-dimensional TiO<sub>2</sub> nanocrystal. This is understandable because Cl<sup>-</sup> ion can be readily absorbed onto the rutile (110) plane to retard its growth [21].

The fabrication process of the FTO/TiO<sub>2</sub> NWs/CdS QDs electrode was also confirmed by electrochemical impedance spectroscopy (EIS) technique, an effective tool for characterizing the interface properties of electrode [23]. The electrontransfer resistance ( $R_{et}$ ), which equals the semicircle portion, reflects the restricted diffusion of the redox probe through the multilayer system and relates directly to film permeability. Figure 1B shows the impedance spectra of the FTO substrates before and after different modification. The  $R_{et}$  obtained on the FTO substrate was small (curve a,  $R_{et} = 42 \Omega$ ). After the grown of TiO<sub>2</sub> NWs on the FTO surface, the  $R_{et}$  got much bigger ( $R_{et} = 175 \Omega$ ). This demonstrated that the insulating TiO<sub>2</sub> NWs layers hindered the access of the [Fe(CN<sub>6</sub>)]<sup>3-/4-</sup> probe to the electrode surface. The  $R_{et}$  value further increased to 620 Ω after the deposition of CdS QDs. The increase in  $R_{et}$  can be ascribed to the fact that the negatively charged CdS QDs repel the negatively charged redox probes.

#### 3.2 Photoelectrochemical measurements

When the FTO/TiO<sub>2</sub> NWs electrode was consequently treated with Cd(NO<sub>3</sub>)<sub>2</sub> and Na<sub>2</sub>S solution, the electrode color changed from white to yellow (see the inset in Figure 2A,) indicating that the CdS QDs was successfully decorated onto TiO<sub>2</sub> NWs. The PEC responses of different electrodes

under various conditions were recorded. The FTO/TiO<sub>2</sub> NWs electrode exhibited negligible photocurrent response under 440 nm irradiation, which could be attributed to the large band gap of TiO<sub>2</sub> (3.2 eV, corresponding to ~390 nm). After coating CdS, the photocurrent intensity of the FTO/TiO<sub>2</sub> NWs/CdS QDs electrode was significantly increased (Figure 2A, curve b). This suggested that the sensitization effect of CdS QDs was very effective. After incubation with Cu<sup>2+</sup> (in the absence of AA), the FTO/TiO<sub>2</sub> NWs/CdS QDs electrode showed a decreased photocurrent response (Figure 2A curve c), because of the formation of electron-hole recombination center Cu<sub>2</sub>S. While incubation the FTO/TiO<sub>2</sub> NWs/CdS QDs electrode with Cu<sup>2+</sup> in the presence of AA, a more drastically decrease in photocurrent response was observed (Figure 2A curve d), which indicated that the presence of AA can promote the formation of exciton trapping center.



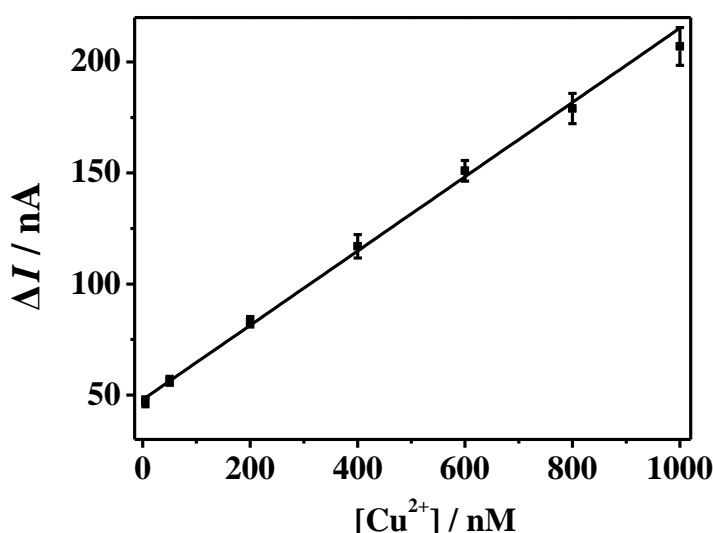
**Figure 2.** (A) Photocurrent responses of (a) the FTO/TiO<sub>2</sub> NWs electrode, (b) FTO/ TiO<sub>2</sub> NWs/CdS QDs electrode, (c) FTO/ TiO<sub>2</sub> NWs/CdS QDs electrode incubating with Cu<sup>2+</sup> (100 μM), (d) FTO/ TiO<sub>2</sub> NWs/CdS QDs incubating with Cu<sup>2+</sup> (100 μM) and AA (1 mM), inset shows the photographic images of FTO/ TiO<sub>2</sub> NWs (left) and FTO/ TiO<sub>2</sub> NWs/CdS QDs (right). Effects of (B) the concentration of TEOA, (C) the applied bias voltage, and (D) wavelength of exciting light on the photocurrent response of the PEC sensor.

The photoelectrochemical performance of the PEC sensor largely depended TEOA concentration, wavelength of the irradiation source, bias voltage (Figure 2). The concentration of TEOA was one of the key factors that affected the photocurrent as it can act as the electron donor to

harvest the photogenerated hole. The photocurrent response was observed by changing the content of TEOA in the electrolyte solution. The photocurrent increased with increasing concentration of TEOA up to 100 mM and then decreased with further addition of TEOA (Figure 2B). Thus, the concentration was set at 100 mM TEOA for the next experiments. The bias voltage applied to the electrode is another important parameter for the photocurrent response. We found that the photocurrent response significantly increased as the applied potential ranging from -0.2 to 0.1 V and trended to decrease beyond 0.1 V (Figure 2C). The wavelength of irradiation source was an important factor influencing the PEC response. The maximum photocurrent variation was obtained when a incident light wavelength of 440 nm was used (Figure 2D). Therefore, the irradiation wavelength was set at 440 nm.

### 3.3 Photoelectrochemical sensing of $\text{Cu}^{2+}$

Under the above optimized conditions, the variation of photocurrent was applied for the quantitatively detection of  $\text{Cu}^{2+}$ . Figure 3 shows the dependence of photocurrent variation on the  $\text{Cu}^{2+}$  concentration. The value of the photocurrent variation was proportional to the  $\text{Cu}^{2+}$  concentration in the range of 5 nM ~ 1  $\mu\text{M}$ ,  $R = 0.997$ . The calibration curve can be expressed as  $\Delta I/\text{nA} = 0.1673 \times [\text{Cu}^{2+}]/\text{nM} + 47.93$ . The limit of detection (LOD) was calculated 1.3 nM ( $S/N = 3$ ). This value is much lower than the maximum contaminant level (~ 20  $\mu\text{M}$ ) for copper in drinking water set by the U.S. Environmental Protection Agency [24]. Thus, the proposed PEC sensor is sensitive enough to monitor  $\text{Cu}^{2+}$  for environmental assessment. The performances of proposed method for  $\text{Cu}^{2+}$  sensing were also compared with other recently reported PEC or EC assays (Table 1). It can be concluded that our method exhibited superior or comparable analytical merits compared to others.

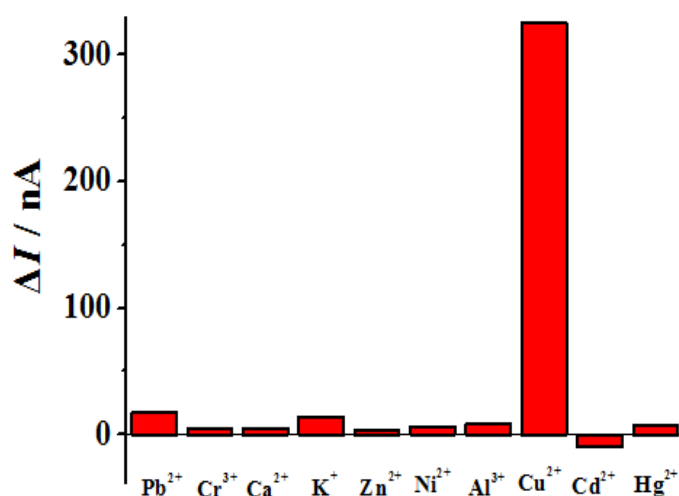


**Figure 3.** Calibration curve of the PEC sensor for  $\text{Cu}^{2+}$ . Error bars were derived from the standard deviation of three measurements.

**Table 1.** Comparison of the analytical performances for determination of  $\text{Cu}^{2+}$  ion based on photoelectrochemical (PEC) or electrochemical (EC) methods

Methods	Working Electrode	Linear range	LOD	Incubation	Reference
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				time	
PEC	ITO/CdS	0.02~20 $\mu\text{M}$	10 nM	–	[25]
PEC	ITO/ZnO/CdS	0.02~40 $\mu\text{M}$	10 nM	–	[26]
PEC	FTO/CdTe	0.06~100 $\mu\text{M}$	5.9 nM	–	[20]
PEC	GCE /Cd <sub>x</sub> Zn <sub>1-x</sub> S@rGO	0.02~20 $\mu\text{M}$	6.7 nM	–	[27]
EC	GCE/SiAt-SPCPE	0.075~2.5 $\mu\text{M}$	31 nM	10 min	[28]
EC	AE/AuNPs-RBH	0.1 pM~1 nM	12.5 fM	60 min	[29]
EC	GCE/GR@AuNPs	5~100 nM	0.028 nM	3 min	[30]
PEC	FTO/TiO <sub>2</sub> /CdS	0.005~1 $\mu\text{M}$	1.3 nM	10 min	This Work



**Figure 4.** Photocurrent response of the PEC sensor upon incubating with Pb<sup>2+</sup>, Cr<sup>3+</sup>, Ca<sup>2+</sup>, K<sup>+</sup>, Zn<sup>2+</sup>, Ni<sup>2+</sup>, Al<sup>3+</sup>, Cu<sup>2+</sup>, Cd<sup>2+</sup> and Hg<sup>2+</sup>. The concentration of each ion was 100  $\mu\text{M}$ .

To evaluate the selectivity for Cu<sup>2+</sup> detection, the influence of various metal ions on the photocurrent response of FTO/TiO<sub>2</sub> NWs/CdS QDs electrode was examined. As shown in Figure 4, all these interfering metal ions only produced negligible photocurrent response. This indicated that the proposed PEC assay shows an excellent selectivity. Therefore, based on the sensitive and selective decrease effect of Cu<sup>2+</sup> on the photocurrent of FTO/TiO<sub>2</sub> NWs/CdS QDs electrode, a sensitive PEC Cu<sup>2+</sup> sensor could be developed. To further evaluate the analytical reliability and application potential of the proposed method, the content of copper element in a human hair was determined. The hair sample was prepared according to the reported procedure [31]. The content of copper in human hair was found to be 12.8  $\mu\text{g}\cdot\text{g}^{-1}$ , which was close to the value of 13.6  $\mu\text{g}\cdot\text{g}^{-1}$  obtained by atomic absorption

spectroscopy (AAS). The result confirmed that the proposed method is applicable for the detection of copper in real sample.

#### 4. CONCLUSION

In conclusion, a PEC assay was proposed for the determination of  $\text{Cu}^{2+}$  based on  $\text{TiO}_2$  NWs/CdS hierarchical nanocomposites. Ascorbic acid was used as reducing agent for the efficient conversion of  $\text{Cu}^{2+}$  to  $\text{Cu}^+$ . The in situ formed  $\text{Cu}_2\text{S}$  at the CdS surface inhibited the photoelectron transfer from CdS to the conduction band of  $\text{TiO}_2$  and led to the decrease of photocurrent. The proposed  $\text{Cu}^{2+}$  PEC sensor showed a low detection limit (1.3 nM) and a wider linear range (5 nM ~ 1  $\mu\text{M}$ ). This method also has the advantages of easy fabrication, rapid response, and good selectivity.

#### ACKNOWLEDGEMENTS

Partial support of this work by the National Natural Science Foundation of China (21305004), the Joint Fund for Fostering Talents of National Natural Science Foundation of China and Henan Province (U1304205) and the Science & Technology Foundation of Henan Province (17A150001) is gratefully acknowledged.

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