Visible-Light-Prompt Photoelectrochemical Sensor of Copper(II) Ions based on CdS Nanorods Modified with Au Nanoparticles and Graphene Quantum Dots

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Abstract: Excessive consumption of Cu$^{2+}$ ions can cause damage to liver and kidney. Thus, significant efforts have been devoted to detecting Cu$^{2+}$ ions in the environment and biological systems. An interconnected triplet structure of CdS/Au/GQDs was designed as the photo-to-electron conversion medium for real-time and selective visible-light-prompt photoelectrochemical (PEC) sensor of Cu$^{2+}$ ions in real-water samples. The synergistic interaction of CdS/Au/GQDs enabled smooth transportation of charge carrier to the charge collector, providing a channel to inhibit the charge recombination reaction. Moreover, the presence of Cu$^{2+}$ ion on the photoelectrode activated the quenching of the charge transfer efficiency, thus promoting sensitive PEC determination of Cu$^{2+}$ ions level. The real-time monitoring of Cu$^{2+}$ ions in mineral water, tap water and reverse osmosis water were performed with satisfactory results, confirming the capability of the as-fabricated photoelectrode as a practical detector for trace element of Cu$^{2+}$ ions.

Keywords: Photoelectrochemical, Cadmium Sulphide, Gold, Graphene Quantum Dots, Copper Sensing.

INTRODUCTION
A new type of multi-functional hybrid nanostructure of CdS nanorods (NRs)/Au nanoparticles (NPs) modified graphene quantum dots (GQDs) has successfully been designed. Herein, CdS act as the photocatalytic active centre which in contact with charge collector. Meanwhile, Au was used as an assistant catalyst which endowed the resonant photon scattering, and thus mediated the charge transfer to the photocatalytic active centre. More importantly, both GQDs and CdS play the key role as photosensitizer where the photoexcited charge carriers take place. The practicable mechanism of the CdS/Au/GQDs in amplifying the PEC performances were proposed after carefully characterized and analysed. Owing to the fast and facile charge separation which resulted from the favourable band alignment of the energy levels between the GQDs and the semiconductor-metal of CdS/Au, the promising concept of hybrid architecture represent superior environmental monitoring devices based on PEC detection of Cu$^{2+}$.

MATERIALS AND METHODS
CdS NRs/Au NPs/GQDs were prepared using the reflux approach. Here, 100 ml of 10% w/v of freshly prepared CdS NRs powder was mixed with the Au NPs-GQDs solution. The mixture was left for 4 h to grow the Au NPs-GQDs over the CdS NRs. Afterward, the solution was placed in a three-necked flask and directly heated at 100 °C in a reflux system in a nitrogen gas atmosphere for 1 h. This step was conducted in order to grow the Au NPs-GQDs on the CdS NRs structure. A final dark yellow colloidal solution was obtained. After cooling down, the resultant mixture was centrifuged and washed with ethanol and deionized water three times. Lastly, the precipitates were dried at room temperature for 24 h to yield dark yellowish powders of CdS NRs/Au NPs/GQDs. For comparison, CdS NRs/Au NPs and CdS NRs/GQDs were also prepared through a similar method.
RESULTS AND DISCUSSION

DPV analysis was conducted because it permits a better analytical signal by eliminating the non-faradaic current compared to LSV. The simultaneous determination of all ions mixture of Cu$^{2+}$, Ba$^{2+}$, Co$^{2+}$, Li$^+$, Ni$^{2+}$, Mn$^{2+}$, K$^+$, Zn$^{2+}$, Na$^{2+}$, Mg$^{2+}$, Ag$^+$ and Fe$^{2+}$ was feasible, with up to ten times smaller concentration of Cu$^{2+}$ than other ions (Fig. 1). The DPV peak current at around 0.2 V in various concentration of ions solution was observed. This well-defined peak was correspond to the Cu$^{2+}$ peak [1]. Fortunately, all other metal ions revealed no peak in DPV measurement even when wide potential was applied, ascribing that the modified photoelectrode was selective for Cu$^{2+}$ with very little interference from Fe$^{2+}$.

Fig. 1: DVP peaks of simultaneous detection of Cu$^{2+}$, Ba$^{2+}$, Co$^{2+}$, Li$^+$, Ni$^{2+}$, Mn$^{2+}$, K$^+$, Zn$^{2+}$, Na$^{2+}$, Mg$^{2+}$, Ag$^+$ and Fe$^{2+}$ at different concentrations.

CONCLUSIONS

In summary, the fabrication and exploration on CdS/Au/GQDs nanocomposite has provide a new paradigm for the construction of unconventional visible-light activated photoelectrode, and further establish a facile and advance strategy for designing a photoelectrode with high selectivity, sensitivity, low cost and reliable for PEC dynamic sensing of Cu$^{2+}$ towards real sample.

REFERENCES