

## The improved photoelectrochemical stability of a $\text{CuBi}_2\text{O}_4$ photocathode provided by graphene quantum dots cocatalysts

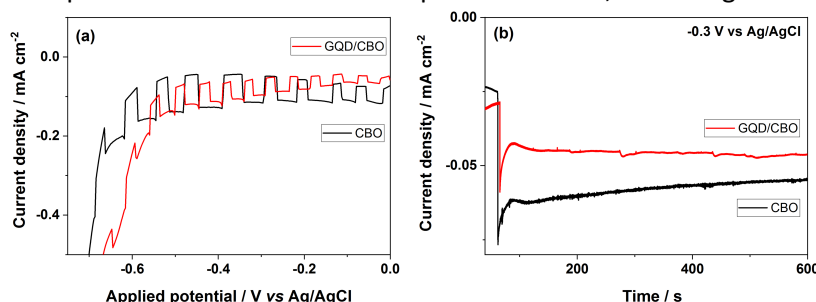
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Among several semiconductors that have recently surfaced as photocatalysts for the sunlight-driven water splitting, copper bismuth oxide ( $\text{CuBi}_2\text{O}_4$ ) has been considered one of the most promising. It is a cheap and non-toxic material that possesses improved structural and photochemical features compared to some of the most employed photocatalysts.<sup>1</sup> These features include smaller band gap, longer charge carriers diffusion and adequate valence band energy for the water reduction semi-reaction. Nonetheless, some drastic limitations still hinder the performance of  $\text{CuBi}_2\text{O}_4$ , such as high electron transfer resistance at the solid/liquid interface and structural instability under irradiation. To circumvent those limitations, we loaded the surface of the  $\text{CuBi}_2\text{O}_4$  thin films with graphene quantum dots (GQD) as cocatalysts to promote rapid electron transfer pathway and to inhibit photocorrosion.<sup>2</sup> In this work, visible-light absorbing phase-pure  $\text{CuBi}_2\text{O}_4$  ultrathin films, with band gap of 2.0 eV, was obtained through an electrodeposition method. Graphene quantum dots were synthesized through a hydrothermal route using pyrene as the precursor and loaded onto the surface of  $\text{CuBi}_2\text{O}_4$  through a spin coating method. Photoelectrochemical tests in a  $\text{Na}_2\text{SO}_4$  electrolyte (pH 6.5) of the pristine  $\text{CuBi}_2\text{O}_4$  ultrathin films resulted in a photocurrent density of  $-0.116 \text{ mA cm}^{-2}$  at  $-0.3 \text{ V}_{\text{Ag/AgCl}}$ . After the surface modification with GQD, the photocurrent density changed to  $-0.102 \text{ mA cm}^{-2}$  at  $-0.3 \text{ V}_{\text{Ag/AgCl}}$  (Fig. 1a). However, water reduction overpotential reduced and the photocurrent stability showed an improvement, as it retained 79 % of the initial photocurrent density over the course of 600 s under simulated sun light irradiation (AM 1.5G,  $100 \text{ mW cm}^{-2}$ ). The bare photoelectrode retained only 61 % of the initial photocurrent density (Fig. 1b). Future work involves the optimization of the GQD loading and post-thermal treatment under inert atmosphere to further improve the charge transfer rates, which still hinder the performance of our modified photoelectrode, according to our results.



**Figure 1.** Photoelectrochemical (a) and chronoamperometry (b) measurements of  $\text{CuBi}_2\text{O}_4$  and GQD-modified  $\text{CuBi}_2\text{O}_4$  electrodes in  $\text{Na}_2\text{SO}_4$  electrolyte under a simulated sunlight irradiation.

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### References

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