In recent years, photocatalysis has attracted a great deal of attention as a popular research topic regarding the application of solar energy. In the field of photocatalysis, photoelectrochemical (PEC) water splitting is considered as a potential approach for new energy generation due to its capability of producing hydrogen. The most important factor affecting the hydrogen production efficiency by PEC water‐ splitting is the preparation of highly active photoelectrodes. To date, a series of n-type semiconductors have been widely reported as photoanodes, such as BiVO4, ZnO, FeI2O3, etc., while the options for photocathode materials are relatively limited.

CuBi2O4, a natural mineral, has the advantages of being economical, easy to access and chemically stable. Meanwhile, as a p-type semiconductor with strong response to visible light (band gap: 1.70eV), CuBi2O4 has a promising prospect to be widely applied for the preparation of photocathode. Currently, studies on CuBi2O4 as photocathode has been focusing on the synthesis and theoretical calculation, with limited research concerning promoting interfacial carrier separation. In the current study, CuBi2O4 was successfully prepared through electrochemical deposition. Following the modification with amorphous titanium dioxide (TiO2) and platinum (Pt) as the cocatalyst, the modified CuBi2O4 materials were tested as photocathode for PEC hydrogen production. It was found that the formation of CuBi2O4/TiO2 heterojunction improved the activity of the photocathode. The modified Pt/TiO2/CuBi2O4 photocathode showed a photocurrent of 0.35 mA/cm2 at the bias voltage of 0.6 V, which was twice of the photocurrent result tested for Pt/CuBi2O4. According to XRD, the prepared CuBi2O4 showed pure phase with high crystallinity, while the surface TiO2 was amorphous. The CuBi2O4 photocathode layer was composed of particles of 100-150nm as suggested by SEM. Good visible light absorption properties of the prepared CuBi2O4 were confirmed by UV-vis. The modification with TiO2 did not evidently alter the light absorption properties of CuBi2O4, nor did it cause any composition damage to CuBi2O4 as shown by XPS. However, as revealed by the photoelectrochemical measurements, the thickness and crystallinity of the TiO2 layer would affect the activity of CuBi2O4 photocathode.