Visible-light Activation of TiO_2 Photoanode by Loading CoO_x

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Photocatalytic water splitting has attracted attention in recent years due to rising interest in artificial photosynthesis. Among various semiconductors, TiO_2 is a promising candidate as a water-splitting photocatalyst due to its superior photoreactivity, long-term stability and low cost. However, TiO_2 is only active under ultraviolet light, and thus solar to hydrogen (STH) efficiency reaches only 3.3% even if quantum efficiency (Q.E.) is 100%. Therefore, it is necessary to activate TiO_2 towards visible-light water splitting to improve STH efficiency. Recently, we reported that TiO_2 modified with $Co(OH)_2$ is capable of oxidizing water into O_2 under visible-light irradiation at wavelengths of up to 850 nm.[1] It showed a potential to use cobalt-based compounds to activate TiO_2 towards visible-light water splitting.

In this work, CoO_x was loaded on a TiO_2/FTO electrode to activate TiO_2 towards visible-light water splitting. TiO_2 film was fabricated by soaking a cleaned FTO substrate in a 0.15 M $TiCl_4$ aqueous solution at 343 K for 120 min, then rinsed with distilled water and finally annealed at 723 K for 30 min in air. CoO_x was loaded on the as-prepared TiO_2/FTO electrode by soaking TiO_2/FTO electrode in a 0.1 M $Co(NO_3)_2$ aqueous solution for 30 min followed by heating in air at 423 K for 60 min.

From X-ray diffraction (XRD) analyses of TiO_2/FTO, CoO_x/FTO and CoO_x/TiO_2/FTO electrodes, no diffraction peaks assigned to TiO_2 or cobalt oxide were observed, which indicated that fabricated films consisted of amorphous phase. Scanning electron microscopy (SEM) observation showed that CoO_x particles having a diameter of 5-10 μm were loaded on TiO_2/FTO substrate. UV-visible spectroscopy confirmed visible-light absorption of CoO_x/TiO_2/FTO electrode (Fig. 1), which were not observed in TiO_2/FTO and CoO_x/FTO electrodes. This suggests that there is a relatively strong electronic interaction between CoO_x and TiO_2, which contributes to the visible-light absorption of the CoO_x/TiO_2/FTO electrode. The energy gap of CoO_x/TiO_2/FTO was estimated to be approximately 1.85 eV from the onset wavelength (670 nm) of the absorption.

Photoelectrochemical measurement under visible light (λ > 500 nm) was performed for TiO_2/FTO, CoO_x/FTO and CoO_x/TiO_2/FTO electrodes. Anodic photocurrent, assignable to water oxidation, was observed only for CoO_x/TiO_2/FTO electrode (Fig. 2). This suggests that the prepared CoO_x/TiO_2 electrode functions as a visible-light active photoanode for water splitting.

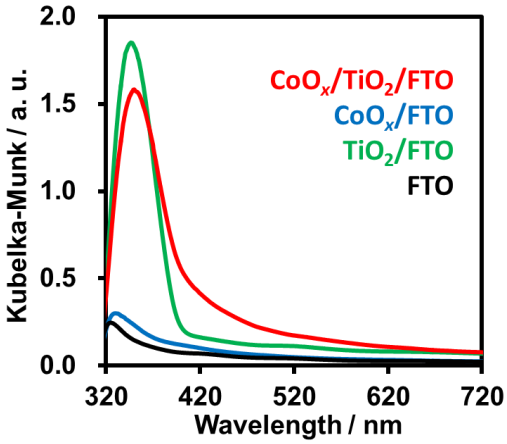

Fig. 1 UV-visible spectroscopy of FTO, TiO_2/FTO, CoO_x/FTO and CoO_x/TiO_2/FTO.

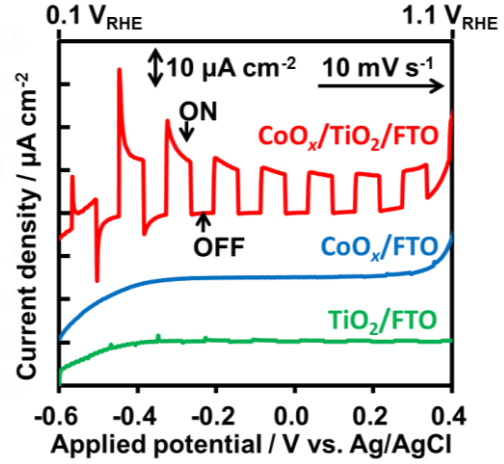

Fig. 2 PEC measurements of TiO_2/FTO, CoO_x/FTO and CoO_x/TiO_2/FTO. [0.1 M Na_2SO_4 (aq), pH = 9, 300 W Xe lamp (20 A, λ > 500 nm), 10 mV s^{-1}]

REFERENCES

[1] K. Maeda, K. Ishimaki, Y. Tokunaga, D. Lu, M. Eguchi, Angew. Chem. Int. Ed., 55 (2016) 8309.