Protection of WO_3 electrodes against dissolution and photocorrosion through TiO_2 ALD coating

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INTRODUCTION

In addition to iron oxide in the form of hematite, tungsten trioxide is another widely used n-type semiconductor metal oxide for photoelectrochemical applications. Due to its higher bandgap (~2.7 eV)[1], the theoretical maximum energy conversion efficiency is lower (~12 %) but still significantly higher than that of TiO_2 (~4%). Hematite exhibits low stability in acidic media ($pH \leq 2$), where it undergoes dissolution, while WO_3 shows poor stability in alkaline media ($pH > 7$). Recently, TiO_2 or SnO_2 overlayers have been utilized to enhance the stability of hematite photoanodes in acidic environments. In addition to dissolution, pH-dependent alterations of the surface and photoelectrochemical corrosion occurred. The Faradaic efficiency of this process was reduced from 0.026 % to 0.014 % when a 2 nm TiO_2 layer was applied[2,3]. The present work studies the influence of protective ALD TiO_2 films of various thicknesses on the properties of WO_3 photoanodes.

EXPERIMENTAL/THEORETICAL STUDY

WO_3 layers were prepared by spray pyrolysis of a peroxotungstic acid solution on FTO/glass substrates, post-annealing at 550 °C was used to improve the crystallinity. WO_3 electrodes were then covered with thin layers of TiO_2 of thickness 2, 8, 20 and 50 nm to extend their operational range in photoelectrochemical cells from acidic to higher pH media.

RESULTS AND DISCUSSION

TiO_2-covered WO_3 electrodes exhibited much smaller decrease in photocurrents compared to TiO_2-covered α-Fe_2O_3 electrodes. The reason for this is attributed to the more favorable relative position of the valence band energies of the WO_3 and TiO_2 semiconductors, which allows easier transfer of photogenerated holes from the absorber material to the capping layer. The presence of TiO_2 capping layers extended the chemical and photoelectrochemical stability range of WO_3 in contact with electrolytes up to pH 8, where the "lifetime" of photocurrents increased from 3 to 25 hours for 20 nm thick TiO_2 capping layers. The efficiency of photocorrosion in pH 8 solutions decreased by a factor of 20 when the WO_3 electrodes were covered with TiO_2.

CONCLUSION

Significant advantages in terms of performance and stability, especially when enhanced by protective overlayers such as TiO_2 or SnO_2, makes WO_3 a promising material for advancing renewable energy technologies such as water splitting and solar energy harvesting.

REFERENCES

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