Enhanced Photo-response of FeS_2 Films:

The Role of Marcasite-Pyrite Phase Junctions

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Introduction

The interest in iron pyrite (cubic FeS_2) as a photovoltaic (PV) material has picked up recently because of its earth-abundance, nontoxicity and suitable band gap for efficient visible light absorption (~0.95 eV).[1] On the other hand, the low open-circuit voltage (VOC) of 200 mV limits its solar energy conversion efficiency (PV cell or Photo-electrochemical cell) to ~3 %. The presence of orthorhombic marcasite FeS_2 is generally believed to be detrimental to photochemical performance because of its much smaller band gap. Nevertheless, several theoretical calculations published in recent years predict that marcasite should have a band gap of 0.8-1.0 eV, which is quite similar to that of pyrite.

Results

Here, we report for the first time the beneficial role of marcasite in iron sulfide based photo-electrochemical applications.[2] A novel strategy is adopted for fabricating mixed phase marcasite-pyrite (p/m-FeS_2) films. The dramatic improvement of the photo-response of p/m-FeS_2 can be ascribed to the presence of pyrite-marcasite phase junctions. Consistently, we demonstrate, through state-of-the-art materials simulation based on DFT, that a staggered band alignment with offsets of 0.43 eV and 0.71 eV exists between the valence and conduction bands of marcasite and pyrite, respectively. This staggered type II heterojunction alignment with both bands of marcasite higher in energy than pyrite point to efficient charge separation in the mixed systems, as the primary origin of the observed high photoactivity (photo-current) of the mixed marcasite-pyrite thin films over the individual pyrite counterpart.

[1] Cabán-Acevedo et al. (2014) *J. Am. Chem. Soc.*136, 17163-17179.

[2] Wu et al. (2016) *Adv. Mater.* 28, 9602-9607.