

Mesoporous quaternary semiconductor oxides for improved photocatalytic hydrogen production

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Detailed and reliable studies on the optimum pore morphology of mesoporous photocatalysts for photocatalytic water splitting are surprisingly not available. Mesoporous materials often exhibit pore walls of only several nanometers, which can be favorable for photocatalysis due to very short diffusion pathways for charge carriers. However, the increased surface area might neglect improved activities due to enhanced surface recombination.

We chose the complex semiconductor photocatalyst CsTaWO₆ as model system for studying the optimum mesoporous morphology of semiconductors for hydrogen production. CsTaWO₆ is known to generate hydrogen from alcoholic solutions without any co-catalyst,^[1] is known to be amenable for homogeneous anion doping from the gas phase,^[1,2,3] and exhibits only one crystal structure (cubic defect-pyrochlore structure) without any temperature-induced phase transitions known. The latter is crucial to avoid any influence on photocatalytic activity by the formation of multicomponent heterojunctions.^[4]

We have prepared highly crystalline mesoporous CsTaWO₆ via evaporation-induced self-assembly (EISA) process using the commercial block-copolymer P-123,^[5] and *via* hard-templating in mesoporous silica KIT-6.^[6]

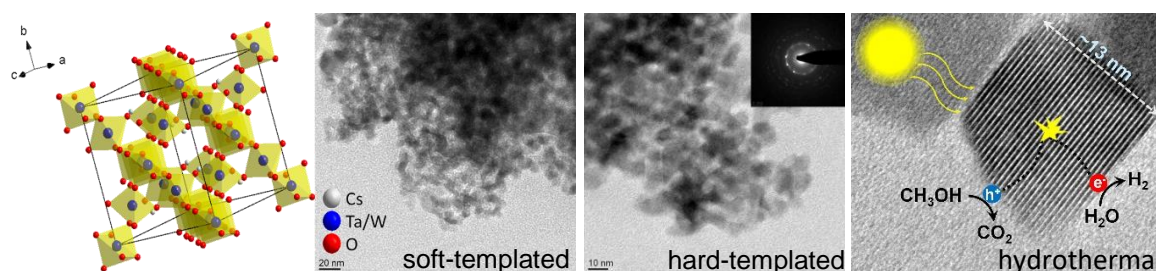


Figure 1. from left to right: Defect-pyrochlore crystal structure of CsTaWO₆; TEM image of soft-templated mesoporous CsTaWO₆; TEM image of hard-templated mesoporous CsTaWO₆; TEM image of a single-crystal CsTaWO₆ nanoparticle.

Different additives during soft-templating were used to vary only the pore morphologies, resulting in BET surface areas measured by N₂ physisorption up to 78 m² g⁻¹ and pore sizes ranging from 5 to 10 nm, depending on the additives. Although pore ordering is not fully established, we find photocatalytic hydrogen evolution activities being independent on

surface area, but rather depending on pore size distribution, indicating that transport of electrolyte and gaseous products in the pores are rate determining factors in photocatalytic hydrogen production.

Hard-templated phase pure samples of mesoporous CsTaWO₆ with surface area up to 115 m² g⁻¹ confirm the hydrogen evolution dependence on pore size rather than surface area.

Moreover, we have identified an optimum crystallite size for CsTaWO₆ to maximize hydrogen production, by investigating size-defined single-crystalline nanoparticles of CsTaWO₆ (Fig. 1 right) prepared *via* hydrothermal synthesis.^[7] 13 nm were identified to be the ideal crystallite size, as an optimum ratio of surface recombination and charge carrier diffusion pathway.

Currently, we are developing highly ordered phase pure mesoporous CsTaWO₆ via soft-templating for further investigations.

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