Computer simulations of a metal–sulfide alloy unlock the secrets to designing solar-powered catalysts

26 September 2012

Splitting water molecules (top right) to produce hydrogen will become more efficient with newfound knowledge on the key electronic properties needed to turn special alloys into a long-lived photocatalyst. Credit: iStockphoto.com/da-kuk

Partnerships can pay off when it comes to converting solar into chemical energy. By modeling a cadmium sulfide (CdS)–zinc sulfide (ZnS) alloy with special computational techniques, a Singapore-based research team has identified the key photocatalytic properties that enable this chemical duo to 'split' water molecules into a fuel, hydrogen gas (H_2). The theoretical study was published by Jianwei Zheng from the A*STAR Institute of High Performance Computing and his co-workers.

Chemists had already identified CdS and ZnS semiconductors as promising photocatalysts for water splitting. However, both came with a drawback related to the size of their so-called 'band gap'—the energy difference between occupied and unoccupied electronic states that determine photo-activity. While CdS can readily harvest solar energy because of its small band gap, it needs a metal co-catalyst to produce H_2. On the other hand, ZnS requires high-energy ultraviolet light to initiate water splitting owing to its large band gap.

Recently chemists had overcome these problems by alloying CdS and ZnS together into a 'solid solution': a physical state where Zn ions are distributed homogenously inside the crystal lattice of CdS. Altering the proportion of ZnS in these alloys enables production of photocatalysts with tunable responses to visible light and high H_2 evolution rates in water. Improving the design of a Cd–ZnS solid solution is difficult, because its underlying mechanism is poorly understood.

As a workaround, Zheng and his co-workers used a technique known as 'special quasi-random structures' (SQS) to mimic a completely random alloy with a series of small, periodic models. After carefully working to correlate experimental random hexagonal crystals with their SQS approximations, they calculated the electronic properties of the Cd–ZnS solid solution using hybrid density functional theory—a computational method that gives accurate descriptions of band gaps.

When the researchers gradually increased the Zn content of their model alloy, they saw that the band gap deviated from a linear combination of the two components. This effect, known as band 'bowing', arises from volume deformations within the Cd–ZnS solid solution and is an essential parameter for predicting catalytic solar H_2 production.

Further calculations revealed that the alloy's high catalytic activity stemmed from obvious elevation of the position of unoccupied electronic states, and a subtle change in the position of occupied electronic states, as the amount of Zn increased. But to retain strong light harvesting capabilities and to avoid premature corrosion, the team proposes an equal ratio of ZnS to CdS for optimal photocatalytic water

splitting.

More information: Wu, J.-C., Zheng, J.-W., Zacherl, C. L., Wu, P., Liu, Z.-K. & Xu R. Hybrid functionals study of band bowing, band edges and electronic structures of Cd1–xZnxS solid solution. *Journal of Physical Chemistry C* 115, 19741–19748 (2011). dx.doi.org/10.1021/jp204799q

Provided by Agency for Science, Technology and Research (A*STAR), Singapore