

Metallic 2D crystals for bifunctional, pH-universal electrocatalysts for water splitting reactions

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ABSTRACT:

The design of efficient electrocatalysts for water splitting reactions is crucial to unlock the “Hydrogen economy”, *i.e.*, the vision of using molecular hydrogen (H₂) as carbon-free fuels produced by renewable energy sources.[1] Unfortunately, the costs and the scarcity of their most effective catalysts, *e.g.*, Pt-group elements for hydrogen evolution reactions (HER) at the cathode, and RuO₂/IrO₂ for oxygen evolution reactions (OER) at the anode, hinder massive commercial electrolyzers. Therefore, it is mandatory to search for alternative non-precious catalysts, or at least to reduce the content of precious metals, with the goal to maintain state-of-the-art electrochemical performances.[2] Recently, two-dimensional (2D) transition metal dichalcogenides (TMDs) have been investigated as catalytic models to perform the HER.[3] In particular, the catalytic activity of the most established TMDs (*i.e.*, group-6 TMDs, such as MoS₂ and WS₂) originates from unsaturated edges of semiconducting (2H) phase and metallic (1T) phase.[4] However, both the basal plane inertness in their natural phase and the susceptibility of the electronic structure of their catalytic sites to electrolytic media, result in insufficient specific catalytic performances (*e.g.*, catalytic activities normalized to catalyst mass). Contrary to group-6 TMDs, metallic group-5 TMDs (*e.g.*, TaS₂, NbS₂ and VSe₂) have been predicted to display both edges and basal planes as the catalytic sites in their natural phases. In our work, we produce 2D group-5 TMD through scalable liquid-phase exfoliation of the bulk crystals, to be used as efficient bifunctional catalyst for HER and OER, either in acidic or alkaline media.[5,6,7] To fully exploit the potential of such electrocatalysts, we nanoengineer their structural properties by means of: 1) thermal treatments in reactive atmosphere, 2) chemical treatments with lithium salts and 3) liquid-phase microwave treatments. The reactivity of group-5 TMDs is also used to drive their topochemical transformation in non-layered (but 2D) metallic oxides (*e.g.*, room temperature-stable rutile VO₂), which also act as effective electrocatalysts. The hybridization of group-5 TMDs is used as universal strategy to tune the Gibbs free energy of the adsorbed atomic hydrogen onto the surface of heterogeneous electrodes to the optimal thermo-neutral value. Beyond to reach catalytic activities approaching to the state-of-the-art for both HER and OER, we shed light on the phase, morphological and chemical changes of the materials during their electrochemical operations. Our results provide fundamental understandings for the development of efficient and viable electrocatalysts based on metallic 2D TMDs.

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