Exfoliated WS_2 Nanosheets as Photoanodes in Photoelectrochemical Cells

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The group 6 of layered transition metal dichalcogenides (TMDs) in their bulk form have long been investigated as suitable materials for applications in photoelectrochemical cells (PECs). Their small band gap enables the absorption of the solar spectrum leading to higher solar conversion efficiency when compared to large band-gap metal oxide semiconductors such as TiO_2, WO_3 and α-Fe_2O_3 widely utilized in PECs for water oxidation. Early works on PECs based on bulk single crystals and polycrystalline films of MoS_2 and WS_2 have shown chemical stability against photocorrosion and solar energy conversion efficiencies for MoS_2 and WSe_2 up to 6% and 17% respectively.[1, 2] However, scalable synthesis of high quality TMDs crystals presented challenges that have hindered further employment in PECs.
A renewed interest in these materials appeared recently owing to their layered nature and the possibility to easily exfoliate them in monolayer sheets because of the weak *van der Waals* forces between the layers. Single layered TMDs of group 6 have now emerged as new semiconducting 2D materials with unique electrical, optical, chemical and mechanical properties complementary to graphene. Their electronic band structure presents a cross over from indirect-to-direct band-gap when the thickness is reduced to single layer.[3] The resulting direct band gap is in the visible range, which can give access to a wide range of optoelectronic applications. WS_2 presents a band gap of 2eV, rendering it suitable for phtoassisted water splitting. Further, theoretical studies and early works have shown that the orbital energy levels of WS_2 is favorable for charge transfer for water oxidation.[4]
We employed n-doped monolayered WS_2 platelets as photoanodes in a complete PEC (Figure 1), and WS_2 monolayer films exhibit photocurrent at excitation wavelengths below the direct band gap edge. The material was exfoliated using Lithium intercalation into WS_2 powders followed by exfoliation in water, leading to the formation of a stable aqueous suspension of monolayered WS_2 platelets.[5] Uniform and continuous films of monolayer WS_2 of different thicknesses ranging from 3 to 10nm were fabricated and photoelectrochemically characterised by linear sweep, cyclic voltammetry and chronoamperometry under UV irradiation. WS_2 electrodes exhibited positive photocurrent density values up to 1mA/cm^2 at relative low applied potential versus the Ag/AgCl R.E.. Stability was studied over days enabling possible utilization of such material in practical devices. Chronoamperometry characterizations suggest that improvements in the stacking of WS_2 nanosheets could enhance the transport of photoexcited carriers. These results demonstrate the capability of monolayer WS_2–based electrodes to be employed in PECs for the production of solar fuels.[6]

References

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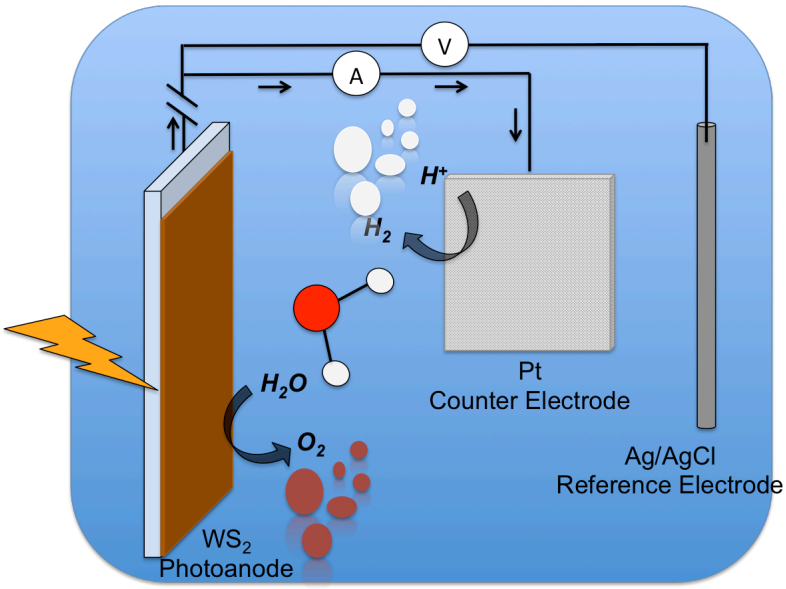

Figure 1: Pictorial representation of a PEC based on a nanosheets-WS_2 electrode employed as photoanode. After charge carriers separation, the photogenerated holes in WS_2 can act as oxidising species leading to molecular O_2 evolution from water oxidation, whereas the protons are reduced at a Pt mesh counter electrode.