

Defect Engineering of Au@MoS₂ Nanostructures for Conventional and Plasmon-Enhanced Hydrogen Evolution Reaction

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2D materials such as MoS₂ has received a lot of attention for key electrochemical processes such as the hydrogen evolution reaction (HER). A lot of efforts have been dedicated to increase the HER activity of MoS₂ basal plane by phase and defects engineering. Core@shell systems such as Au@MoS₂ nanostructures (Fig. 1a) present an enhancement of their HER properties with respect to MoS₂ due to charge transfer effects [1]. In this work, we show that the structural and HER properties of Au@MoS₂ structures can be further enhanced by performing a thermal treatment under reducing conditions. In addition of the extensive catalytic tests performed in acidic conditions, the samples were investigated by combining ex-situ and in-situ aberration-corrected STEM under controlled atmosphere as well as Raman and XPS spectroscopies. We show that the thermal treatments lead to a decrease of the number of external MoS₂ layers as function of the temperature (Fig. 1b). In particular, 56% of the Au@MoS₂ structures annealed at 800°C under H₂ atmosphere present an incomplete MoS₂ layer. This sample shows the highest HER performances with an overpotential of 203 mV vs RHE at 10 mA/cm² (Fig. 1c) and a Tafel slope of 55 mV/dec which is similar to the value reported for edges sites in MoS₂ [2]. Measurements of the electrochemical double-layer capacitance also shows that it presents the highest number of active sites which is consistent with the greater number of incomplete shell layers observed by TEM. We also explored the plasmonic-assisted HER performances of these nanostructures under LED illumination (Fig. 2) and observed an enhancement by about 10% of the current density, depending on the wavelength used. All these results on the tailoring of the microstructural and HER properties of Au@MoS₂ nanostructures will be discussed in details [3].

References

[1] R. Baz-Ziv et al., ACS Appl. Ener. Matter. 2, 8, 6043-6050 (2019),

[2] T.F. Jaramillo et al., Science 317 100 (2007),

[3] J.J. Quintana Gonzalez et al., submitted.

Figures

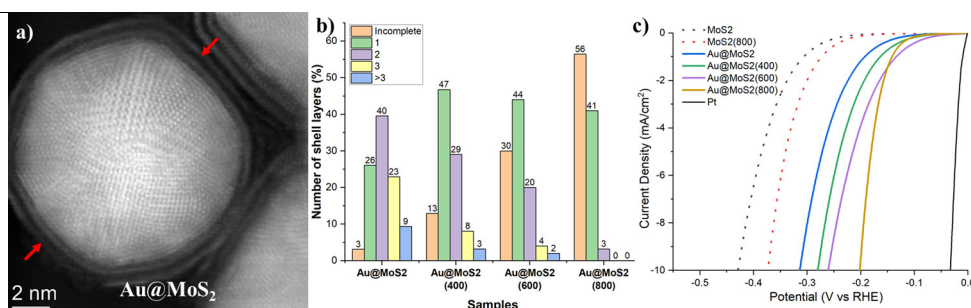


Figure 1: Aberration-corrected STEM image of the initial Au@MoS₂ sample, b) Evolution of the number of shell layers c) LSV curves obtained in 0.5 M H₂SO₄ at 10 mV·s⁻¹.

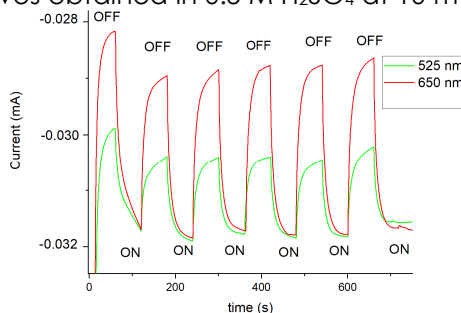


Figure 2: Evolution of the current under illumination at a fixed potential of -0.4 V.