Adsorption and Intercalation of Hydrogen on/into WS_2 Nanoparticles for Energy Storage: Modelling and Experiment

Alex Laikhtman,[1] Alla Zak,[1] Jose Ignacio Martinez,[2] Julio A. Alonso[3]

[1]*Physics Department, Holon Institute of Technology (HIT), Holon, Israel,* [2]*Materials Science Factory, Institute of Material Science of Madrid (ICMM-CSIC), Madrid, Spain,* [3]*Department of Theoretical, Atomic and Optical Physics, University of Valladolid, Valladolid, Spain*

The chemical configuration and interaction mechanism of hydrogen adsorbed on nanoparticles of WS_2 are investigated. Our recent approaches of using hydrogen activated by microwave or radiofrequency plasma dramatically increased the efficiency of its adsorption making WS_2 a good candidate for soli state hydrogen storage media [1, 2]. The obtained results are demonstrated in Fig. 1.

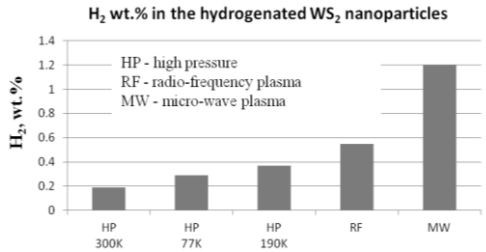

Fig. 1. Hydrogen concentration in WS_2 nanoparticles following different types of hydrogenation.

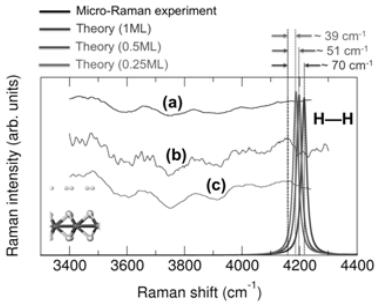

Fig. 2. Measured micro-Raman spectra of WS_2: (a) non-hydrogenated, (b) plasma hydrogenated, (c) annealed to 450 °C. The bold lines are the calculated Raman peaks of physisorbed H_2 molecules for various H_2 coverages.

To get insight on the chemical configuration, we combined the experimental analysis methods with theoretical modeling based on the density functional theory (DFT). Micro-Raman spectroscopy was used as a primary tool to elucidate chemical bonding of hydrogen and to distinguish between chemi- and physisorption. Hydrogen adsorbed in molecular form (H_2) was clearly identified in all the plasma-hydrogenated WS_2 nanoparticles samples, both experimentally and using DFT modelling, as shown in Fig. 2. DFT provides an efficient and practical workbench to investigate the interaction of molecular and atomic hydrogen with WS_2 nanoparticles [3]. It shows that molecular H_2 physisorbs on the surface of those materials on top of W atoms, as shown in Fig. 3, while atomic H may chemisorb on top of S atoms. Diffusion of H_2 on the surface of WS_2 encounters small activation barriers and agrees with the observed dependence of H_2 concentration with temperature.

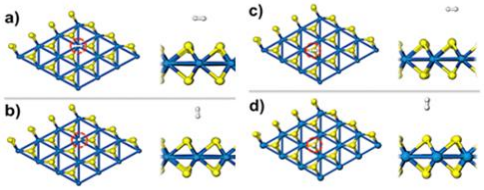

Fig. 3. Top and side views of H_2 molecule adsorbed: a) on top of a W atom of a single WS_2 layer with the molecular axis parallel to the layer; b) on top of a W atom with the axis perpendicular to the layer; c) on top of a S atom with the axis parallel to the layer; d) on top of a S atom with the axis perpendicular to the layer.

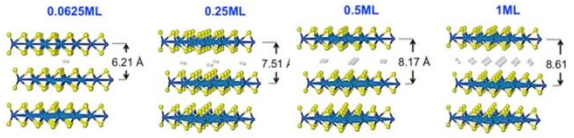

Fig. 4. Optimal structures for intercalation of H_2 in WS_2 trilayer for different H_2 content.

Intercalation of H_2 between adjacent WS_2 layers revealed an endothermic behavior due to interlayer expansion shown in Fig. 4. A remarkable result, however, is that the presence of a full H_2 monolayer adsorbed on top of the first WS_2 layer of a WS_2 multilayer system strongly facilitates the intercalation of H_2 between WS_2 layers underneath. This opens up an additional gate to intercalation processes.

References

[1] A. Laikhtman et al., Int. J Hydrogen Energy 39 (2014) 9837-9841.

[2] A. Laikhtman et al., J. Phys. Chem. C 121 (2017) 11747-11756.

[3] J. I. Martínez, A. Laikhtman, H. R. Moon, A. Zak, J. A. Alonso, Phys. Chem. Chem. Phys. 20 (2018) 12061-12074.

E-mail: alexl@hit.ac.il