Enhancing of catalytic activity of MoS_2 single layers through spontaneous oxidation under ambient conditions

J. Peto[1] T. Ollar[2] P. Vancso[1,3] Z. Popov[4,5] G. Magda[1] G. Dobrik[1] C. Hwang[6] P. Sorokin[5] L. Tapaszto[1]

[1]Hungarian Academy of Sciences, Centre for Energy Research, Institute of Technical Physics and Materials Science, 2DNanoelectronics Lendület Research Group, Budapest, Hungary
[2]Hungarian Academy of Sciences, Centre for Energy Research, Institute for Energy Security and Environmental Safety, Surface Chemistry and Catalysis Department, Budapest, Hungary
[3]Department of Physics, University of Namur, Namur, Belgium
[4]Emanuel Institute of Biochemical Physics RAS, Moscow, Russia
[5]National University of Science and Technology MISiS, Moscow, Russia
[6]Korea Research Institute for Standards and Science, Daejeon, South Kore

The chemical inertness of the defect-free basal plane confers environmental stability to MoS_2 single layers, but it also limits their chemical versatility and catalytic activity. The stability of pristine MoS_2 basal plane against oxidation under ambient conditions is a widely accepted assumption however, we found [1] that oxygen gradually incorporates into the basal plane of 2D MoS_2 crystals through a substitutional oxidation reaction, by replacing individual sulfur atoms, while fully preserving the original crystal lattice during ambient exposure. The scanning tunneling microscopy measurements and DFT calculations reveal a slow oxygen-substitution reaction, during which individual sulfur atoms are replaced one by one by oxygen, giving rise to solid-solution-type 2D $MoS_{2-x}O_x$ crystals. Oxygen substitution sites present all over the basal plane act as single-atom reaction centers, substantially increasing the catalytic activity of the entire MoS_2 basal plane for the electrochemical H_2 evolution reaction. The observed oxidation process enables the chemical modification of single atomic sites of 2D crystals opening new routes towards their efficient defect engineering. This work was supported by the Russian Scientific Foundation (project no. 18-73-10135).

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