

## MoS<sub>2</sub>/carbon nanostructures based hybrid materials

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2D materials and hybrid structures based on them are attracting attention of material scientists over the last years. Theoretical and experimental studies show that catalytic activity, magnetic properties and conductivity of layers MoS<sub>2</sub> are attributed to edge atoms, and basal atoms are not participating in such processes[1, 2]. The edges in MoS<sub>2</sub> are not fully coordinated and, thus, thermodynamically stable, which leads to formation of closed shell structures[3]. To control appearance of edges in MoS<sub>2</sub>, it's necessary to put the particles on the substrate. Graphene substrates are promising, because they allow tuning of their own surface chemical states, conductivity and band structure, widening the range of properties and applications.

MoS<sub>2</sub> could exist in various polymorphic forms, which have different electronic properties and layers structure[4]. Recent studies show, that appearance of 1T polymorph structures could drastically enhance catalytic activity of hybrid structures, and participate in Li-intercalation[5, 6].

In this work, we investigate MoS<sub>2</sub> nanoparticles on few layer graphene formation and it's structure depending on temperature.

All the samples were obtained using high temperature technique, implying MoS<sub>3</sub> deposition on graphene in suspension with further annealing in vacuum at 500-800°C. The materials were studied using transmission electron microscopy, Raman spectroscopy, optical absorption spectroscopy and X-ray photoelectron spectroscopy.

HRTEM images of the product obtained at 500°C is presented on Fig. 1(a, b). It's clearly seen, that dark spots are nanometer-sized clusters of molybdenum sulfide. Cluster structure is different from 2H- or 1T-MoS<sub>2</sub>. There is no clear hexagonal structure, the clusters look like flat laying on graphene, but not spherically shaped. Histogram on fig 1(b) shows size distribution of MoS<sub>x</sub> nanoclusters. The distribution is close to normal with Feret diameter mean value ~ 1 nm.

Synthesis temperature increase results in cluster agglomeration. At 600°C they compose of 2-3 layers with MoS<sub>2</sub> structure and lateral size of ~ 2 nm. At 800°C MoS<sub>2</sub> forms particles with lateral size of size ~20 nm (Fig. 1 (c)) and 5-10 layers thickness. No clusters are observed at this temperature.

Raman measurements show that FWHM (full width at half maximum) of MoS<sub>2</sub> E<sub>2g</sub> and A<sub>1g</sub> lines decrease with synthesis temperature. It clearly indicates MoS<sub>2</sub> mean particles size increase with synthesis temperature increase.

Catalytic activity of the samples in hydrogen production by formic acid decomposition reaction was studied. Prior to measurements, the samples were treated with H<sub>2</sub> at 350°C during 1 hour. Formic acid decomposition starts at 100°C for the samples with the smallest particle size and reaches 100% at 250°C. With sample synthesis temperature increase, the curve shifts by 50°C and conversion rate reaches 1 at 300°C for the samples obtained at 800°C. The result clearly indicates catalytic activity and active site concentration decrease with synthesis temperature decrease.

Formic acid decomposition products mostly compose of CO<sub>2</sub>, hydrogen and methyl formate. When decomposition temperature reaches, 200°C traces of CO are observed, due to non-catalytic decomposition.

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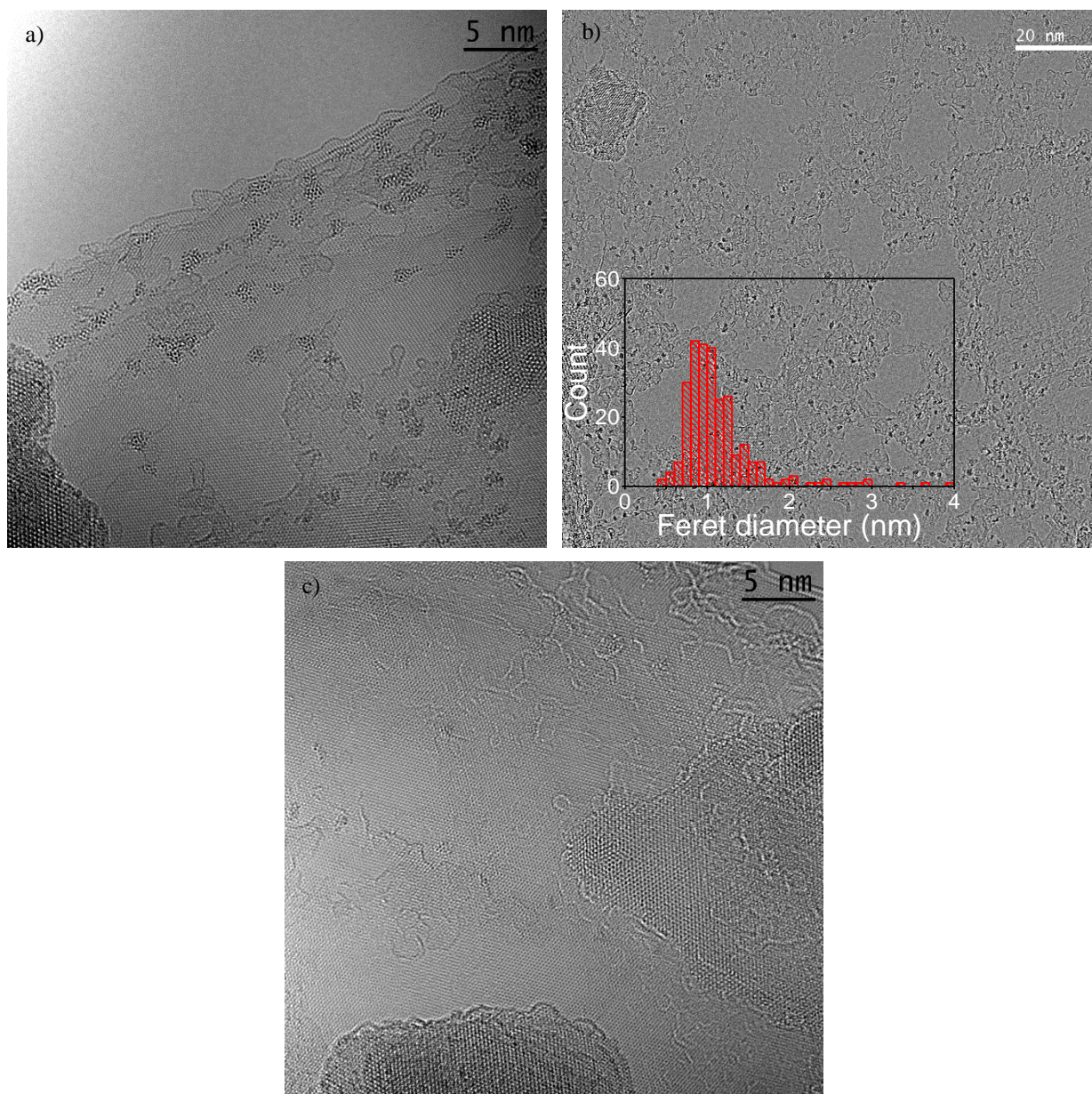


Figure 1. HR TEM images of MoS<sub>2</sub> nanometer-sized particles obtained at different temperatures: 500°C (a, b). HR TEM image of MoS<sub>2</sub> nanoparticles obtained at 800°C (c).