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A new approach to prepare solution-processable 2-D semiconductors

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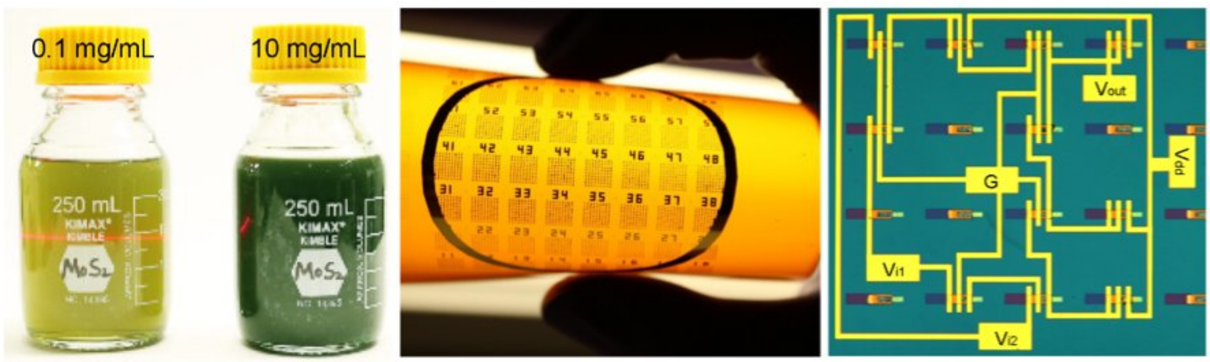

Solution-processable large-area electronics from MoS2 2D nanosheets ink. Credit: Duan Lab @UCLA Department of Chemistry & Biochemistry

Researchers at the University of California, Los Angeles (UCLA), the University of Texas at Austin, and Hunan University (China) have recently devised a new method of preparing highly uniform, solution-processable, phase-pure semiconducting nanosheets. Their approach, outlined in a paper published in *Nature*, involves the electrochemical intercalation of quaternary ammonium molecules into 2-D crystals, followed by a mild sonication and exfoliation process.

Two-dimensional (2-D) materials consist of atomically thin crystal layers bound by the van der Waals force. Recently, the popularity of these materials has been on the rise, primarily due to their many potential applications in electronics, optoelectronics and catalysis.

This is especially true for solution-processable 2-D semiconductor nanosheets, such as MoS_2, which show particular potential for the development of large-area thin-film electronics. Compared to conventional zero- and one-dimensional nanostructures, which are typically restricted by surface dangling bonds and associated trapping states at grain boundaries, 2-D nanosheets have dangling-bond-free surfaces, resulting in a clean interface within a thin film and thus excellent charge transport.

Despite their potential benefits, preparing high-quality solution-processable 2-D semiconductor nanosheets comes with a number of challenges. For instance, MoS_2 nanosheets and thin films created using lithium intercalation and exfoliation are negatively affected by the presence of the metallic 1T phase, and thus show poor electrical performance.

"In the conventional lithium (Li) intercalation process, the insertion of each Li^+ ion entails the injection of one electron into the host crystals," Prof. Xiangfeng Duan, one of the researchers who carried out the study, told TechXplore. "The intercalation of a large number of Li^+ leads to massive electron injection into the MoS_2 crystal (1 e per formula unit in $LiMoS_2$) that induces the undesired semiconducting 2H to metallic 1T phase transition."

Past studies suggest that this unfavourable phase transition only occurs when the electron injection exceeds a certain threshold, that of 0.29 e per MoS_2 formula unit. Based on these findings, Duan and his colleagues devised a new approach to prepare semiconductor 2-D nanosheets, in which the electron injections are chemically manipulated to be below this observed threshold.

"We came up with the idea to reduce the electron injection into the hosting 2-D crystals and prevent the undesired phase transition by replacing the small Li^+ ($d \approx 2$ Å) with larger cations, such as quaternary ammonium ($d \approx 20$ Å for THAB)" Prof. Duan explained. "The bulky size of the quaternary ammonium molecules naturally limits the number of molecules that can fit into the hosting crystal and thus the number of electrons injected, which prevents the undesired phase transition to the metallic 1T phase."

In their study, the researchers successfully prepared highly uniform, solution-processable, phase-pure semiconducting nanosheets, with the electrochemical intercalation of quaternary ammonium molecules into 2-D crystals, followed by a mild sonication and exfoliation process in solvent. They placed a thin piece of cleaved MoS_2 crystal and a graphite rod in an electrochemical cell, acting as cathode and anode, respectively. A quaternary ammonium bromide (i.e. THAB, TBAB, etc.) solution in acetonitrile was used as the electrolyte. Successively, the researchers' bath sonicated the intercalated material in a PVP/DMF solution in order to attain a dispersion of semiconducting MoS_2 nanosheets.

"The unique advantage of this process is the successful preservation of the favored semiconducting 2H phase of MoS_2, which was previously found to be challenging using conventional Li intercalation and exfoliation processes," Prof. Duan said. "The intercalation with large quaternary alkyl ammonium molecules (i.e., THAB) offers a mild approach to greatly expand the MoS_2 lattice for the facile exfoliation without injecting excessive electrons into the MoS_2 layers, which prevents the undesired phase transition to 1T-MoS_2 (compared to Li intercalation and exfoliation)."

This new liquid-phase exfoliation process proposed by Prof. Duan and his colleagues can be generally applied to a wide range of 2-D crystals (including MoS_2, WSe_2, In_2Se_3, black phosphorus and so on) with wellpreserved electronic and optoelectronic properties. This could help to overcome some of the challenges with producing high-quality, solution-processable 2-D semiconductor nanosheets.

"The most interesting finding of our study is the development of a scalable and low-cost solution-based approach to fabricating high-performance, flexible thin-film transistors (TFTs) and electronic circuits based on 2-D semiconductor ink," Prof. Duan said. "The atomically thin and intrinsically flexible 2-D nanosheets represent attractive building blocks for flexible/wearable electronics, similar to pieces of paper that can be easily bent, folded and flattened."

The TFTs that the researchers produced using their MoS_2 2-D nanosheet ink showed greatly improved device performance over existing solution-processed MoS_2 TFTs, with at least one order of magnitude increase in carrier mobility and three to four orders of magnitude increase in switching ratio. Their new approach is easily scalable with a high yield, enabling complex logic gates and computational circuits that were so far unattainable using other 2-D inks.

"The solution-phase fabrication process of flexible TFTs and circuits is intrinsically scalable and cost-effective and can be readily made into the large scale ($> m^2$) when combined with printing approach and industrial roll-to-roll productions," Prof. Duan explained. "TFTs are the fundamental building blocks for many large-area electronic applications, including the well-known TFT-LCD, a liquid-crystal display that uses TFT technology to improve image qualities such as addressability and contrast."

In future, the new approach devised by Prof. Duan and his colleagues could help to create even higher quality 2-D semiconducting nanosheets, with many exciting applications. For instance, the use of MoS_2 2-D nanosheets ink could dramatically reduce the fabrication costs of flexible displays on the next-generation TVs, monitors, phones, e-readers, and radio frequency identification (RFIDs) or other wearable electronics.

"We now plan to extend our approach to other similar layered crystals with even better electronic properties, and also to further improve the device integration processes and thus device performance," Prof. Duan said. "At the same time, we are exploring new printing approaches with these newly formulated inks for the scalable and cheaper production of TFTs."

More information: Zhaoyang Lin et al. Solution-processable 2D semiconductors for high-performance large-area electronics, *Nature* (2018). DOI: 10.1038/s41586-018-0574-4