Scientists enhance light emission in 2D semiconductors by a factor of 100

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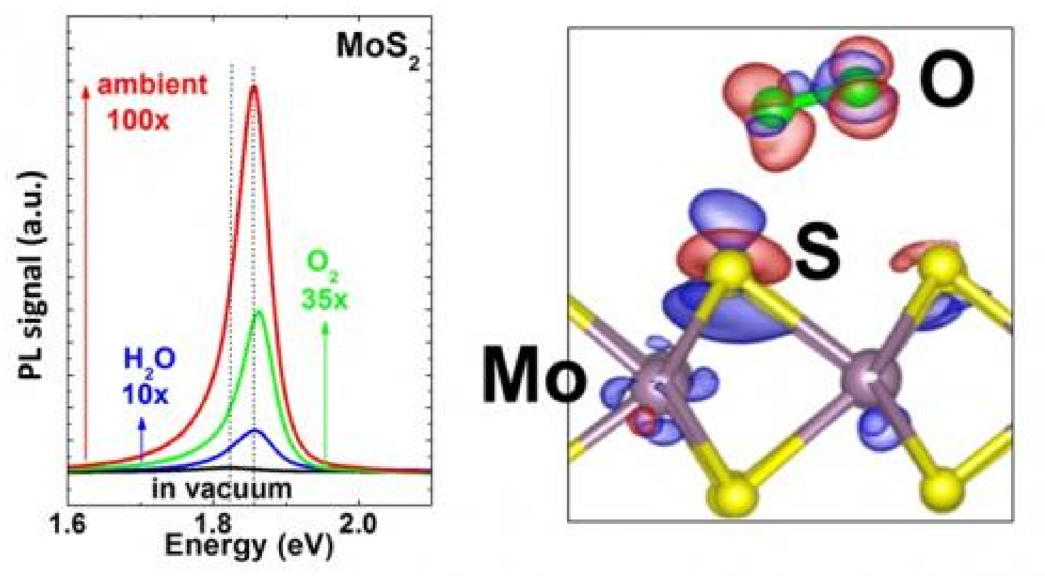

(Left) Graph showing the change in photoluminescence of MoS2 upon exposure to H2O alone, O2 alone, and ambient air at pressures of 7, 200, and 760 Torr, respectively. (Right) Figure showing the charge density difference between pristine MoS2 and O2-adsorbed MoS2. Credit: Sefaattin Tongay, et al. ©2013 American Chemical Society

(Phys.org) —The mention of a two-dimensional material with excellent electrical and optical properties may first bring to mind graphene. However, this description also fits another class of materials called transition metal dichalcogenides (TMDs). Although TMDs in bulk form have been studied for decades—before graphene was even discovered—only recently they have been isolated to monolayers. With recent advances in nanomaterial characterization, scientists have recognized the potential of monolayer TMDs in applications such as LEDs, optical energy conversion, and other 2D optoelectronics technologies.

Monolayer TMDs are direct band gap semiconductors and, for that reason, are expected to be good light emitters. But so far, monolayer TMDs have emitted light only at low intensities and low efficiencies. And because the underlying physics of monolayer TMD light emission has remained elusive, scientists have found it difficult to make improvements.

Now a new study performed by researchers in the Materials Science and Engineering Departments at the University of California, Berkeley, and MIT, as well as from the Institute of Semiconductors at the Chinese Academy of Sciences in Beijing, China, has demonstrated an enhancement in the light emission intensity of TMDs by a factor of 100. The study is published in a recent issue of *Nano Letters*.

"The significance of this work is the demonstration and understanding of the light modulation by molecular and electrical gating," coauthor Sefaattin Tongay, a post-doctoral researcher at Berkeley, told *Phys.org*. "We have presented a detailed understanding of the observed modulation and achieved remarkable light emission intensities. These results have a far-reaching impact in the field, as monolayer TMDs have large surface-to-volume ratio and therefore are very sensitive to ambient conditions. Our results are proving a detailed understanding of changes in the optical properties caused by the interaction between gas molecules and monolayer TMDs. Here, we are taking advantage of this property and modulating the light emission reversibly up to 100 times by simple gas and electrical gating methods."

Unlike graphene, which is an organic material made solely of carbon atoms, the TMDs that the scientists studied here are inorganic materials where each molecule is made of one transition metal and two chalcogenides. Their chemical formula is MX_2, with common examples being MoS_2, $MoSe_2$, WS_2 and WSe_2.

In their experiments, the researchers first prepared monolayer MoS_2 flakes that were just 0.7 nm, or three atoms, thick. Then, to make the flakes more sensitive to gas molecules, the researchers annealed the flakes by placing them in a vacuum chamber at high temperature. After annealing, the monolayer flakes were exposed to different types of gases at controlled gas pressures.

Upon exposure to H_2O, O_2, or H_2O and O_2 together, the MoS2 flakes' light emission intensity increased by 10, 35, and 100 times, respectively. The researchers did not observe the same enhancement in an inert gas (N_2 and Ar) environment, which suggests that the effect seems to be directly related to the interaction between the O_2 and H_2O and the monolayer TMD.

The researchers also found that the effect is fully reversible when the gas is pumped out of the chamber, at which point the intensity immediately reverts back to its original value. As the scientists noted, reversible light emission intensity is an important criteria for various optics applications. The reversibility also suggests that the O_2 and H_2O molecules are physisorbed rather than chemisorbed on the MoS2 surface. As physically absorbed molecules, the molecular structure remains unchanged, unlike for chemically absorbed molecules.

Even more interestingly, the researchers found that while $MoSe_2$ exhibits similar gas sensitivity to MoS_2, WSe_2 shows the opposite behavior; that is, its light emission intensity decreases upon exposure to O_2 and/or H_2O.

These observations, along with simulations, enabled the researchers to propose a physical mechanism for explaining the effect. They think that, when the gas molecules are physisorbed onto the MoS_2 (or $MoSe_2$) surface, some of the free electrons from the surface are transferred to the gas molecules, depleting the MoS_2 (or $MoSe_2$) of its free electrons. Normally, the excitons in the surface would become bound to electrons and become negatively charged "trions." But without the excess free electrons, the excitons remain neutral and stable, promoting more intense light emission.

"This [modulation] is possible for the system we studied because of its two-dimensional nature, which not only gives the maximum surface-to-volume ratio (therefore maximum surface sites to interact with gas molecules), but also confines electrons to the degree that greatly enhances the interactions among electrons, holes and light," explained coauthor Junqiao Wu, a professor at the University of California, Berkeley.

This mechanism also explains why WSe2 shows the opposite behavior as MoS_2 and $MoSe_2$. The MoS_2 and $MoSe_2$ surfaces have free electrons in the first place because they are both n-type doped semiconductors. WSe_2, on the other hand, is a p-typed doped semiconductor and has free holes rather than electrons. So for WSe_2, the O_2 and/or H_2O gas molecules cause the holes to accumulate, rather than be depleted, on the WSe_2 surface. As a result, the WSe_2 contains even more trions than before it was exposed to the gas molecules, which decreases its light emission intensity.

The researchers also demonstrated similar light emission modulation in electrically gated devices in a controlled gas environment. However, the modulation in this case was negligible when the device was operating in vacuum conditions. The finding suggests that electrical gating can also modulate light emission by controlling the gas physisorption on monolayer TMDs.

The ability to reversibly control the light emission intensity of semiconducting TMDs by controlling gas pressure and electrical gating could have far-reaching effects for the fields of condensed matter physics, optics, materials science and engineering, and electronics. The researchers predict that, with the new understanding of how the interaction between gas and monolayer TMDs affects the TMDs' optical properties, further enhancements in the light emission intensity can be achieved. For instance, experimenting with different gas molecules, modifying the monolayer surface with chemical agents that increase sensitivity to gas molecules, and intentionally creating point defects in the monolayer to promote physisorption could further enhance the light emission intensity, making monolayer TMDs even more suitable for optoelectronics applications.

In the future, the researchers plan to work on developing new materials with unusual characteristics by engineering their physical properties, as they did here.

"We will study the effects of any imperfections in general in such two-dimensional semiconductors, including atomic defects, substrate effects, as well as interactions with molecule adsorbates," Wu said.

More information: Sefaattin Tongay, et al. "Broad-Range Modulation of Light Emission in Two-Dimensional Semiconductors by Molecular Physisorption Gating." *Nano Letters*. DOI: 10.1021/nl4011172