Near-unity photoluminescence quantum yield in MoS₂

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Two-dimensional (2D) transition metal dichalcogenides have emerged as a promising material system for optoelectronic applications, but their primary figure of merit, the room-temperature photoluminescence quantum yield (QY), is extremely low. The prototypical 2D material molybdenum disulfide (MoS₂) is reported to have a maximum QY of 0.6%, which indicates a considerable defect density. Here we report on an air-stable, solution-based chemical treatment by an organic superacid that removes defect-mediated nonradiative recombination, thus resulting in a final QY of more than 95%, with a longest-observed lifetime of 10.8 ± 0.6 nanoseconds. Our ability to obtain optoelectronic monolayers with near-perfect properties opens the door for the development of highly efficient light-emitting diodes, lasers, and solar cells based on 2D materials.

REFERENCES AND NOTES

Monolayer transition metal dichalcogenides (TMDCs) have properties that make them highly suitable for optoelectronics (1, 2), including the ability to form van der Waals heterostructures without the need for lattice matching (3, 4), circular dichroism arising from the direct band gap occurring at the K and K’ points of the Brillouin zone (5), and widely tunable band structure through the application of external forces such as electric field and strain (6). Unlike III-V semiconductors, the optical properties of TMDCs are dominated by excitons with strong binding energies (on the order of 300 meV) (7–9) and large radii (~1.6 nm) (10). However, TMDCs have exhibited poor luminescence quantum yield (QY)—that is, the number of photons the material radiates is much lower than the number of generated electron-hole pairs. QY values ranging from 0.01 to 6% have been reported, indicating a high density of defect states and mediocre electronic quality (21–23). The origin of the low quantum yield observed in these materials is attributed to defect-mediated nonradiative recombination and bielectric recombination at higher excitation powers (21, 23).

Two-dimensional (2D) monolayers are amenable to surface passivation by chemical treatments. We studied a wide range of chemical treatments and describe here an air-stable, solution-based process using an organic superacid that removes the contribution of defect-mediated nonradiative recombination acting on electronically active defect sites by uniformly passivating them, repairing them, or both. With the use of this process, the photoluminescence (PL) in MoS₂ monolayers


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increased by more than two orders of magnitude, resulting in a QY > 95% and a characteristic lifetime of 10.8 ± 0.6 ns at low excitation densities.

In this study, we treated MoS2 monolayers with a nonoxidizing organic superacid: bis(trifluoromethane) sulfonimide (TFSI). Superacids are strong protonating agents and have a Hammett acidity function (H0) that is lower than that of pure sulfuric acid. (Details of the sample preparation and treatment procedure are discussed in the supplementary materials and methods (14).)

The PL spectra of a MoS2 monolayer measured before and after TFSI treatment (Fig. 1A) show a 190-fold increase in the PL peak intensity, with no change in the overall spectral shape. The magnitude of the enhancement depended strongly on the quality of the original as-exfoliated monolayer (14). (The term “as-exfoliated” indicates that the MoS2 flakes were not processed after exfoliation.) PL images of a monolayer (Fig. 1, B and C, and fig. S4) (14), taken before and after treatment at the same illumination conditions, show that the enhancement from the superacid treatment is spatially uniform.

Calibrated steady-state PL measurements (14) showed that the spectral shape of the emission remained unchanged over a pump intensity dynamic range spanning six orders of magnitude (10^4 to 10^7 W cm^-2) (fig. S2) (14). From the pump-power dependence of the calibrated luminescence intensity (Fig. 2A), we extracted the QY (Fig. 2B). As-exfoliated samples exhibited low QY, with a peak efficiency of 1% measured at 10^7 W cm^-2. The absolute efficiency (12, 13) and observed power law (13) are consistent with previous reports for exfoliated MoS2. After TFSI treatment, the QY reached a plateau at a low pump intensity (<10^2 W cm^-2), with a maximum value greater than 95%. The near-unity QY suggests that, within this range of incident power, there was negligible nonradiative recombination occurring in the sample. Although pure radiative recombination is commonly observed for fluorescent molecules that inherently have no dangling bonds, only a few semiconductors, such as GaAs double heterostructures (15) and surface-passivated quantum dots (16), show this behavior at room temperature.

At high pump power, we observed a sharp drop-off in the QY, possibly caused by nonradiative biexcitonic recombination. We consider several models to explain the carrier density–dependent recombination mechanisms in MoS2 before and after TFSI treatment. Here, n and p are the 2D electron and hole concentrations, respectively. At high-level injection, the dopant concentration is much less than the number of optically generated carriers, allowing n = p. The traditional interpretation without excitons (17) invokes a total recombination, R, as R = An + Bn^2 + Cn^3, where A is the Shockley-Read-Hall (SRH) recombination rate, B is the radiative recombination rate, and C is the Auger recombination rate. The QY is given as the radiative recombination rate over the total recombination. Auger processes dominate at high carrier concentrations, whereas SRH recombination dominates at lower carrier concentrations. In the SRH regime (i.e., low pump power), QY increases with pump intensity. This behavior, however, was not observed in previous MoS2 studies (12, 13) or in this work.

The standard model poorly describes our QY data (fig. S10) (14), which are strongly influenced by bound excitons (9). As a result, the radiative rate is proportional to the total exciton population, 〈N〉 (18). At high exciton densities, nonradiative biexcitonic recombination can dominate, leading to a recombination rate proportional to 〈N〉^2 (18). Previous reports also suggest that the luminescence in as-exfoliated samples is limited by nonradiative defect-mediated processes (19, 20), resulting in low QY. Although the precise nature of the defect-mediated nonradiative recombination is unclear, a simple analytical model can be developed to describe our experimental results. The total excitation rate, R, in MoS2 is balanced by recombination where

\[ R = B_{nr}n^2 + B_p n^2 \] (1)

where B_{nr} is the nonradiative defect-mediated recombination rate and B_p is the formation rate of excitons. The generated excitons can then either...
For the case of the TFSI-treated sample, $B_{nr} n^2 = \tau^{-1}_i (N) + C_{rx} (N)^2$ (19), where $\tau_i$ is the radiative lifetime and $C_{rx}$ is the biexcitonic recombination rate. The QY is then given as

$$QY = \frac{\tau^{-1}_i (N)}{\tau^{-1}_i (N) + B_{nr} n^2 + C_{rx} (N)^2} \tag{2}$$

For the case of the TFSI-treated sample, $B_{nr}$ is negligible because the QY at low pump powers is >95%, allowing us to extract a biexcitonic recombination coefficient $C_{rx} = 2.8 \text{ cm}^2 \text{s}^{-1}$. For the as-exfoliated sample, the defect-mediated nonradiative recombination can be fit to $B_{nr} = 1.5 \times 10^6 \text{ cm}^2 \text{s}^{-1}$, using the same $C_{rx}$ value. The fitting results are plotted as the dashed curves in Fig. 2B.

To investigate the carrier recombination dynamics, we performed time-resolved measurements on both as-exfoliated and chemically treated samples. The luminescence decay was nonexponential, but not in the standard form known for bimolecular ($Dn^2$) recombination (17). As-exfoliated monolayers of MoS$_2$ had extremely short lifetimes on the order of 100 ps (Fig. 3A and fig. S8) (14), consistent with previous reports (21). After treatment, we saw a substantial increase in the lifetime, which is shown at several pump fluences in Fig. 3A. Fitting was performed with a single exponential decay that described only the initial characteristic lifetime for a given pump intensity. After the pump pulse, the exciton population decayed, which resulted in nonexponential decay through reduced nonradiative excitonic recombination. At the lowest measurable pump fluences, we observed a luminescence lifetime of 10.8 ± 0.6 ns in the treated sample, compared with ~0.3 ns in the untreated case at a pump fluence of $5 \times 10^{-4} \mu \text{J cm}^{-2}$ (Fig. 3C). The contrast between panels A and B of Fig. 3 is consistent with the QY trend.

Urbach tails, which depict the sharpness of the band edges (22), were derived from the steady-state PL spectra via the van Roosbroeck–Shockley equation and are plotted in fig. S8. After treatment with TFSI, a noticeable decrease in the Urbach energy ($E_u$) from 17.4 to 13.3 meV was observed, indicating a reduction in the overall disorder from potential fluctuations and improved band-edge sharpness (22). A spatial map showing Urbach energy (fig. S8) (14) further indicates that the treatment was highly uniform. To evaluate stability, the QY in air for chemically treated MoS$_2$ was measured daily at a constant pump power over the course of 1 week, during which the sample was stored without any passivation in ambient lab conditions (20°C to 22°C, 40 to 60% relative humidity), as shown in fig. S9 (14). The QY remained above 80% during this period, indicating that the treatment resulted in samples that were relatively stable.

We then turned our attention to the effect of TFSI treatment on other properties of MoS$_2$. The monolayer surface was imaged by atomic force microscopy (AFM) before and after treatment (Fig. 4A). No visible change to the surface morphology was observed. We also investigated the effect of the treatment on the electrical properties of a back-gated MoS$_2$ transistor. The transfer characteristics of this majority carrier device before and after treatment showed a shift in the threshold voltage toward zero, indicating that the native n-type doping in the MoS$_2$ was removed while the same drive current was maintained (Fig. 4B). An improvement in the subthreshold slope indicated that the treatment reduces interface trap states. The Raman spectra of an as-exfoliated and treated monolayer (Fig. 4C) showed that there was no change in the relative intensity or peak position. Thus, the structure of MoS$_2$ was not altered during treatment, and the lattice was not subjected to any induced strain (23). Because absolute absorption was used in the calibration of QY, we performed careful absorption measurements using two different methods (14), both before and after treatment (Fig. 4D). At the pump wavelength (514.5 nm), no measurable change of the absolute absorption from the treatment was observed. The strong resonances at 1.88 and 2.04 eV (corresponding to the A and B excitons, respectively) are consistent with previous reports (21). We then performed surface-sensitive x-ray photoelectron spectroscopy (XPS) on bulk MoS$_2$ from the same crystal used for micromechanical exfoliation. The Mo 3d and S 2p core levels (Fig. 4E) showed no observable change in oxidation state and bonding after treatment (24). Thus, an array of different techniques for materials characterization shows that the structure of the MoS$_2$ remains intact after TFSI treatment, with only the minority carrier properties (i.e., QY and lifetime) enhanced.

The effect of treatment by a wide variety of molecules is shown in table S1 and discussed in the supplementary text. Various polar, nonpolar, and fluorinated molecules, including strong acids and the solvents used for TFSI treatment (dichlorobenzene and dichloroethane), were explored. Treatment with the phenylated derivative of superacid TFSI was also performed (fig. S11) (14). These treatments all led to no or minimal (less than one order of magnitude) enhancement in PL QY.

The exact mechanism by which the TFSI passivates surface defects is not fully understood. Exfoliated MoS$_2$ surfaces contain regions with a large number of defect sites in the form of sulfur vacancies, adatoms on the surface, and numerous impurities (25–27). In fig. S12A (14), the calculated midgap energy is shown for several defect types, including a sulfur vacancy, adsorbed —OH, and adsorbed water. Deep-level traps—which contribute to defect-mediated nonradiative recombination, resulting in a low QY (27)—are observed for all of these cases. The strong protonating nature of the superacid can remove absorbed water, hydroxyl groups, oxygen, and other contaminants on the surface. Although these reactions will not remove the contribution of defects to nonradiative recombination, they will open the active defect sites to passivation by a second mechanism. One possibility is the protonation of the three dangling bonds at each sulfur vacancy site. However, density
2D semiconductors (light-emitting diodes, lasers, and solar cells). These enable the development of new high-performance electronic properties. The existence of monolayers is a critical route to eliminate their effect on optoelectronic performance of 2D systems and presents a practical approach to improving the near-unity luminescence yield. This result sheds light on the importance of defects in limiting the performance of 2D materials.

Fig. 4. Material and device characterization. (A) AFM images taken before and after TFSI treatment. (B) Transfer characteristics of a monolayer MoS2 transistor, both before and after treatment. VDS, drain-source voltage; S, source; D, drain; G, gate. (C) Raman spectrum of as-exfoliated and TFSI-treated MoS2 samples. (D) Absorption spectrum of the as-exfoliated and treated MoS2 samples. A and B indicate the exciton resonances. (E) XPS spectrum of the S 2p and Mo 3d core levels before and after treatment. The insets show that there is no appearance of SO2 or change in the MoO2 peak intensity after treatment.

REFERENCES AND NOTES
14. Materials and methods are available as supplementary materials on Science Online.

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SUPPLEMENTARY MATERIALS
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Materials and Methods
Supplementary Text
Figs. S1 to S13
Tables S1 and S2
References (31–48)
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