NEWS AND VIEWS

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# Defect engineering in two-dimensional materials

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Since the discovery of graphene in 2004, two-dimensional (2D) materials have attracted worldwide interest. They are proved to be the most promising materials for next generation electronic and optoelectronic devices, including transistor, photodetector, sensor, modulator and light-emitting diode. Defects, e.g. vacancies, adatoms, edges, grain boundaries, and substitutional impurities, are inevitable in 2D materials[1]. They will influence the performance of the materials in many aspects such as mechanical, electrical, optical and optoelectronic properties. For example, the presence of sulfur vacancies (SVs) leads to electron donor states within the electronic bandgap. This increases electron concentration and results in n-type characteristic in as-prepared $MoS_2$. They could also give rise to hopping transport behavior in low carrier density and act as scattering centers to reduce the carrier mobility in $MoS_2$. Thus, defect engineering, namely, eliminating the unfavorable defects and introducing beneficial defects is very meaningful, and would be a promising strategy to realize high performance electronic and optoelectronic devices based on 2D materials.

Recently, Lien *et al.* demonstrated that the photoluminescence (PL) quantum yield (QY) of $MoS_2$ and $WS_2$ monolayers reaches near-unity through electrostatic doping under low pump fluence, without any chemical passivation[2]. It is suggested that defects have no detrimental effect on the PL QY of monolayer TMDCs and all neutral excitons radiatively recombine even in the presence of native defects. This work provides a new pathway for realize high performance optoelectronics based on 2D materials. However, several issues are still unclear at this stage. It will be interesting to find out why the neutral exciton does not interact with defects, while the trion does. Secondly, the PL QY dramatically drops with the increase of photocarrier generation rate. A deeper understanding to the non-radiative recombination pathways under high generation rate is desired, e.g. biexciton annihilation, defect-mediated decay, and other Auger-like processes. Thirdly, the near-unity QY has not been realized in selenide-based TMDCs, which could be due to the difference in electronic band structure, or the presence of different types of defects. An 30 times enhancement of PL QY was achieved in selenide-based TMDCs ($MoSe_2$) by exposure to hydrohalic acid vapors, such as HCl, HBr, and HI[3]. The reduction of Se vacancies was observed after acid treatment, but the role of defects in carrier recombination still needs further study. This suggests that defects in 2D materials and their influence on optical and optoelectronic properties are rather complicated. In our previous work, a strong PL enhancement (thousands of times) under relative high pump fluence was observed in cracked/defective regions after high temperature annealing of monolayer $MoS_2$[4]. The enhancement was attributed to the oxygen chemical bonding at the defect sites. Apart from the trion to exciton conversion, non-radiative recombination of excitons at defect sites was suppressed. Since the PL enhancement occurs at the defect sites, controlling the defect concentration and introducing oxygen adsorption become a promising method for manipulating the optical properties of $MoS_2$. Mild oxygen plasma was also employed to introduce defects into $MoS_2$ and active oxygen ions can be easily bonded at the defect sites. The PL enhancement could be as high as 100 times, even under high pump fluence.

Referring to electronic and optoelectronic devices, many efforts have been given to study the influence of defects. Yu *et al.* achieved a high mobility of 80 $cm^2V^{-1}s^{-1}$ in a $MoS_2$ field effect transistor (FET) by healing of SVs via thiol chemistry[5]. The healing was realized via the chemical reaction between SVs and trimethoxysilane (MPS). The density of SVs decreased by 4 folds after the reaction and the reduction of scattering from SVs leaded to increased mobility. Self-healing of SVs using poly(4-styrenesulfonate) (PSS) treatment was also demonstrated[6]. The hydrogenation of PSS guides the sulfur adatom clusters on the as-grown $MoS_2$ to heal the vacancies. The electron concentration of healed $MoS_2$ decreased by 643 times, and a lateral homojunction with a perfect rectifying behavior was fabricated. We also improved the performance of $ReS_2$ photodetectors through molecule decoration[7]. The schematic diagram of carrier recombination and trapping kinetics and transient response of as-prepared and Protoporphyrin ($H_2PP$) decorated $ReS_2$ is shown in Fig. 1. The ultraslow response speed of as-prepared $ReS_2$ photoconductor is attributed to deep traps induced by the large amount of SVs. $H_2PP$ molecules were utilized to passive the SVs. After the removal of most SVs, carrier recombination and shallow traps start to dominate the decay time of the photoconductor. As a result, the response speed was improved by 3–4 orders of magnitude. Meanwhile, the specific detectivity of the photodetector was greatly enhanced (as high as ~$1.89 \times 10^{13}$ Jones) due to reduction of dark current through charge transfer between $ReS_2$ and molecules. The introduction of defects into 2D materials can also improve their properties. Plasma irradiation introduces Se vacancies into $WSe_2$, leading to n-type doping and lower the metal contact resistance[8]. An improvement of 20 times ON current and nearly ideal subthreshold swing value of 66 mV/dec was hence achieved. The oxidation of Mo in the surface of $MoS_2$ after oxygen plasma treatment tunes the Schottky barrier height from

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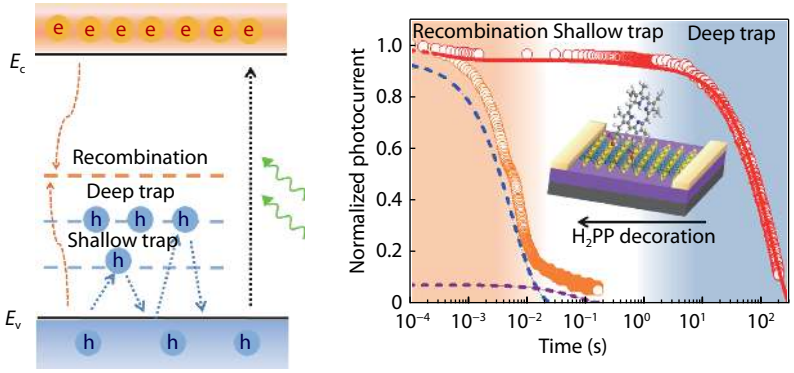


Fig. 1. (Color online) Schematic diagram of carrier recombination and trapping kinetics (left) and transient response of as-prepared and $H_2PP$ decorated $ReS_2$ photoconductor (right)[7].

a narrow distribution (from 0.2 to 0.3 eV) to a broader distribution (from 0.2 to 0.8 eV), which allows both electron and hole injection[9].

In summary, defects play an important role in modulating the properties of 2D materials. Implementing 2D materials in future electronic and optoelectronic devices through defect engineering is still confronted with many challenges that demand further study. The characterization of defects in atomic level and the correlation between the types of defects and the optical, electrical and optoelectronic properties are highly desired. The investigation of ultrafast carrier dynamic in 2D materials in the presence of defects would be very helpful for the deep understanding of roles of defects. The final goal is to precisely manipulate the defects, including density and types, in order to design and fabricate 2D materials with precisely controlled properties for electronic and optoelectronic applications.

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