Reversible bi-stable electronic states of CoPc molecules on two-dimensional VSe_2

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Introduction

The functionalization of two-dimensional (2D) transition-metal dichalcogenides (TMDs) with molecules could not only boost their intrinsic properties but also lead to interesting interface applications. For the first time, we succeeded in synthesizing the monolayer VSe_2 with single crystal quality on highly oriented pyrolytic graphite (HOPG) by molecular beam epitaxy (MBE). Cobalt phthalocyanine (CoPc) molecules deposited onto VSe_2/HOPG show bi-stable electronic states with a ~0.5 eV difference of energy bandgaps. The switch from one state to the other can be realized by applying bias pulses and the switching direction is controlled by the voltage polarity. Our preliminary study indicates that the different electronic states are not caused by adsorption or VSe_2 defects, but some other mechanism, which is still under study. The strong interfacial coupling offers a viable route to manipulate the charge and spin states of molecules through underlying 2D materials, giving rise to important applications in molecular electronics and spintronics.

Results and Discussion

1. The monolayer VSe_2 grown on HOPG MBE

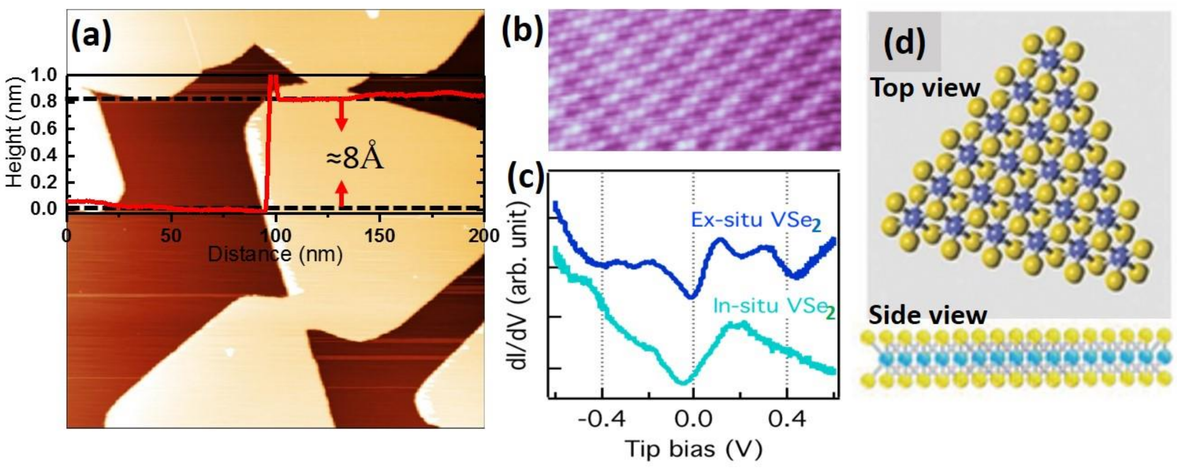

Figure 1: (a) STM image of monolayer VSe_2 with a thickness of ~8Å (200×200nm^2, V_{tip}=-0.5V, I_{se}t=39nA). (b) Atomic resolution STM image of VSe_2 (5×10 nm^2; V_{tip} = 200 mV, I_{set} = 200 pA). (c) Spatially averaged STS spectrum indicates a non-zero LDOS and thus metallic character of 2D VSe_2 grown on in-situ cleaved HOPG (V_{tip} = –0.3 V, I_{set} = 60 pA). For comparison, an averaged tunneling spectrum (V_{tip} = 0.1 V, I_{set} = 173 pA) taken for that on ex-situ cleaved substrate is also illustrated, revealing a small but clear gap-like feature at the Fermi level.(d) Top-view and side-view structural models of triangular single crystals (Reference 1).

STM images show good quality of the monolayer, which exhibits well-defined triangle crystal shapes with a thickness of 8Å. STS result (Figure 1c) confirms the metallic character of the grown 2D films.

2. Bi-stable electronic states of CoPc molecules on two-dimensional VSe_2

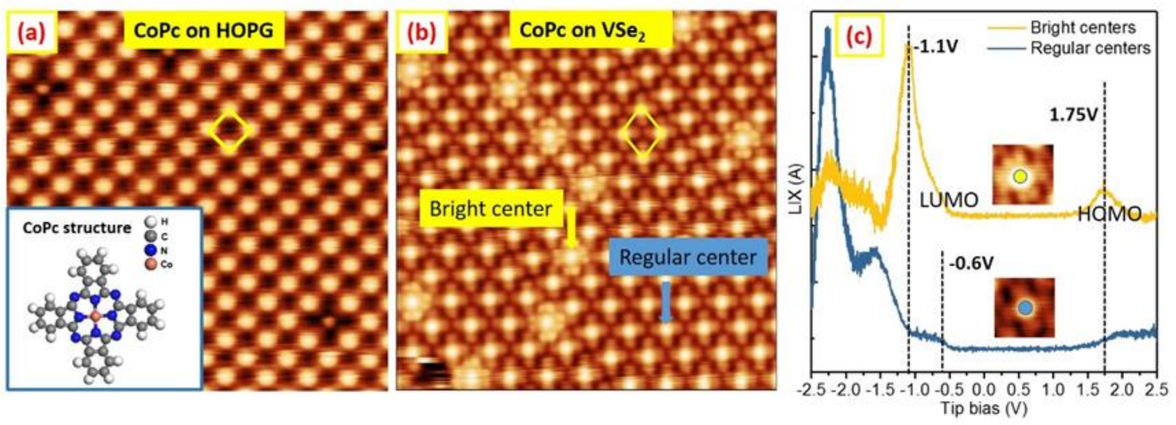

Figure 2: (a) STM image of CoPc on HOPG (20×20nm^2, V_{tip}=-1.1V, I_{set}=18pA). CoPc shows only one electronic state except some vacancies. (b) STM image of CoPc on VSe_2 (20×20nm^2, V_{tip}=-1.4V, I_{set}=22pA). CoPc shows two electronic states: bright and regular. (c) STS spectra taken from central Co atoms of bright and regular molecules show that the bright molecules has a bandgap of ~2.85 eV which is ~0.5 eV larger than that of the regular molecules.

3. The annealing temperature-dependent bight/regular ratio

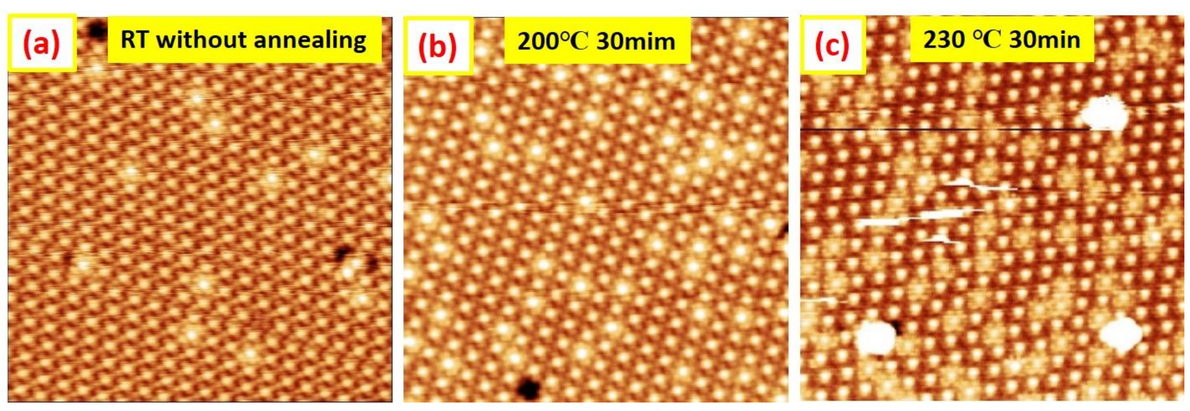

Figure 3: Annealing temperature-dependence of the bright/regular ratio: (a) room temperature without annealing, (b) 200℃ for 30min and (c) 230℃ for 30min. (V_{tip}=-1.97V, I_{set}=17nA, 30×30nm^2)

The ratio of bright to regular molecules on VSe_2 can be tuned widely from <5% to ~40% by simply changing the annealing temperature.

4. Tip-bias controlled switch between bright and regular states

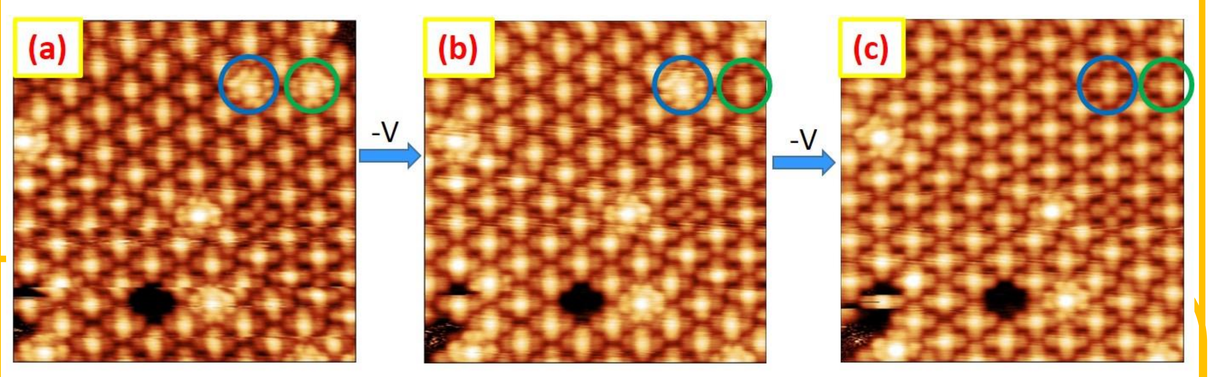

Figure 4: Tip-bias controlled switch between bright and regular states. (a)-(c) Negative tip bias pulse (-2.5V) switches the bright molecules (indicated by blue and green circles) to regular ones (V_{tip}=-1.96V, I_{set}=60pA, 15×15nm^2). (d)-(e) Positive tip bias pulse (2.5V) switches the regular molecules (indicated by yellow circle) to bright ones (V_{tip}=-1.1V, I_{set}=110pA and 50pA respectively, 20×20nm^2).

Conclusion

CoPc molecules absorbed on 2D-VSe_2 show two distinct electronic states: bright and regular, in sharp contrast to those absorbed on HOPG. STS reveals that those bright molecules have a band gap of ~2.85eV which is larger than that of the regular molecules by 0.5 eV. The ratio of bright to regular molecules on VSe_2 can be tuned widely from <5% to ~40% by simply changing the annealing temperature. Furthermore, reversible switching between these two molecular states can be achieved by applying a voltage pulse through the STM tip, and the switching direction is controlled by the voltage polarity . This seems to suggest certain correlation between the two molecular states and the charge-states of individual molecules. However, the exact electronic structures of molecules that correspond to the two different molecular states are still unclear. Consequently, the exact mechanism that leads to the bi-stable molecular states of CoPc initially grown on VSe_2 without external stimuli needs further study.

Reference: 1, Zhang, Z. *et al.* Van der Waals Epitaxial Growth of 2D Metallic Vanadium Diselenide Single Crystals and their Extra-High Electrical Conductivity. *Adv. Mater.* **1702359,** 1702359 (2017).