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Direct Covalent Functionalization of Single Layer 2H-MoS_2 Electrografting of Diazonium Salt: Influence of S vacancy and S-C bond on Photoluminescence of 2H-MoS_2

Two-dimension materials such as graphene, hexagonal boron nitride (h-BN) and transition metal dichalcogenides (TMD) have lots of advantages for various applications due to their two-dimensional (2D) geometric structure. Among them, 2D-TMD materials, has attracted great attention as an alternative to graphene, since it has semiconducting properties while graphene has metallic properties. Thus, it cannot also be used in electronic applications, but also in optical and optoelectronic applications. Although single layer MoS_2 has a bandgap of ~1.8 eV, the modulation of its bandgap is further required to absorb or emit the wider range of light. Surface modification is one of approaches, but the one-step functionalization on 2H-TMDs has been known to be difficult, while various reactions on 1T- TMDs have been demonstrated. The origin of the limitation is attributed to the difficulty of electron transfer from 2H-TMD to reacting molecules due to due to its semiconducting property and neutral charge state, which is a prerequisite process for the surface functionalization. Herein, we present the novel approach facilitating the direct surface functionalization of 4-bromobenzene diazonium tetraborate (4BBDT) on 2H-MoS_2, one of TMD materials, by electrochemical process. The successful functionalization was confirmed by Atomic force microscopy, Raman spectroscopy and spatially resolved X-ray photoelectron spectroscopy (XPS) combined with scanning photoelectron microscopy (SPEM). The widened band-gap of modified 2H-MoS_2 was also confirmed by photoluminescence spectroscopy. In addition, the modified optical bandgap was confirmed on the aryl-functionalized MoS_2 sheet by photoluminescence (PL) measurement. The systematic experimental studies combined with theoretical calculation have revealed the influence of S vacancy and S-C bond, created by the electrochemical modification, on the change in PL of the modified MoS_2. We believe that our demonstration does not only provide fundamental insights for developing the surface functionalization reaction on 2D materials, but also can advance the practical applications of TMD-based optoelectric devices.

References

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Figures

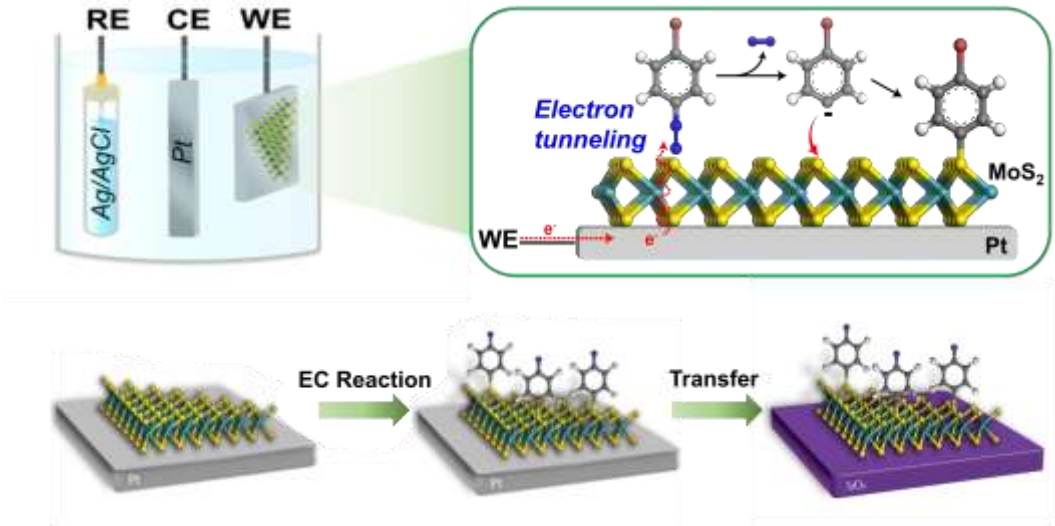

Figure 1: Schematic illustrations showing the experimental set up for electrografting of 4-BBDT on MoS_2/Pt, and the expected reaction