Convection-Flow-Assisted Preparation of a Strong Electron Dopant, Benzyl Viologen, for Surface-Charge Transfer Doping of Molybdenum Disulfide

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Transition metal dichalcogenides (TMDCs) have received attention as atomically thin post-silicon semiconducting materials. Tuning the carrier concentrations of the TMDCs is important, but their thin structure requires a non-destructive modulation method. Recently, a surface-charge transfer doping method was developed based on contacting molecules on TMDCs, and the method succeeded in achieving a large modulation of the electronic structures. The successful dopant is a neutral benzyl viologen (BV⁺); however, the problem remains of how to effectively prepare the BV⁺ molecules. A reduction process with NaBH₄ in water has been proposed as a preparation method, but the NaBH₄ simultaneously reacts vigorously with the water. Here, a simple method is developed, in which the reaction vial is placed on a hotplate and a fragment of air-stable metal is used instead of NaBH₄ to prepare the BV⁺ dopant molecules. The prepared BV⁺ molecules show a strong doping ability in terms of achieving a degenerate situation of a TMDC, MoS₂. A key finding in this preparation method is that a convection flow in the vial effectively transports the produced BV⁺ to a collection solvent. This method is simple and safe and facilitates the tuning of the optoelectronic properties of nanomaterials by the easily-handled dopant molecules.

Transition metal dichalcogenides (TMDCs) are attractive for use in developing atomically thin optoelectronic devices due to TMDCs’ flat crystalline surface at a sub-nanometer thickness,[1–3] their possessing band gaps,[4,5] and their chemical,[4,5] mechanical,[6] and electrical durability.[7] Various optoelectronic applications, such as metal-oxide-semiconductor field-effect transistors (MOSFETs),[8] tunnel FETs,[9] optical sensors,[10] photovoltaics,[11] and light-emitting diodes,[12] have been demonstrated. Further advancement of these high-performance semiconducting devices requires modulating the carrier concentrations of the TMDC body.[13,14] However, the thin structural nature of the TMDCs makes it difficult to control carrier concentrations via established methods, such as ion implantation, as they may destroy the crystalline lattice.

Surface charge-transfer doping methods were recently developed to modulate the carrier concentration of TMDCs.[15–20] The method uses molecules,[13–17] polymers,[18] inorganic compounds[19] or alkali metals[20] that contact the TMDC surface and transfer electrons from either material to the other. Of the dopants studied, one of the strongest and air-stable dopant is the benzyl viologen (BV⁺). The BV molecule is known as a redox-active molecule, which exhibits two electron-transfer isomers (BV⁺-¹, monovalent (BV⁺), and neutral BV⁺ (BV⁺) (Figure 1a). The important point is that the

[Image 1](https://doi.org/10.1002/open.201900169)

Figure 1. (a) Illustrative image of the synthesis/purification system of the strong electron dopant, BV⁺ molecule. The BV⁺ molecule is generated and transported to the upper toluene layer, which shows a strong electron doping ability for MoS₂. (b) Plausible reduction scheme of BV with metal plates. (c) The macroscopic pictures of the solution at 0 h and 24 h of the reaction on a hotplate at 60 °C with an indium plate. The solutions are bubbled with N₂ gas. (d) Visualization of the convection flow generated from the indium plate at 60 °C. The reaction solution is not bubbled with N₂ gas beforehand.

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neutral isomer of the BV\(^0\) molecule shows a strong electron-donor ability.\(^{21-23}\) Previously, BV\(^0\) molecules were found to be able to dope electrons to a typical TMDC, MoS\(_2\), and convert the MoS\(_2\) from a semi-conductive to a metallic state.\(^{19}\) Contrary to the usefulness of the reducing ability, a redundant process to use the BV\(^0\) molecule is synthetic procedure. In a reported process, BV\(^0\) molecules are synthesized from a chloride form of BV (BV\(^+\) isomer; benzyl viologen dichloride) by reduction with sodium borohydride (NaBH\(_4\)) in an aqueous solution.\(^{21}\) The generated BV molecule is a neutral isomer (BV\(^0\)) and extracted in a binary toluene layer on the aqueous solution. The NaBH\(_4\) reacts vigorously with the water and from this vigorous reaction generates a large amount of hydrogen gas while simultaneously reducing BV\(^+\) to BV\(^0\) isomer. The powder form of NaBH\(_4\) is also redundant in terms of the handling process due to its hygroscopic nature, and it requires sufficient safety guideline due to its relatively high reducing ability.

An easy-handling, safe, and effective method for producing and using BV\(^0\) molecules without NaBH\(_4\) should be attractive for developing TMDCs for use in optoelectronic devices. Here, we demonstrate a simple strategy for synthesizing BV\(^0\) molecules from a BV\(^+\) aqueous solution by reduction with indium or manganese metal fragments (Figure 1a, and 1b). The system consists of bilayer solutions of bottom aqueous BV\(^+\) solution and upper toluene; after dropping the metal into the solution, the reaction is gradually progressed on a hotplate at 60 °C. The BV\(^0\) can be extracted and separated from the source BV\(^+\) by extracting the upper toluene layer (Figure 1a, and 1c). The toluene solution shows the strong doping ability of MoS\(_2\) MOSFET as previously reported. In addition to the simplicity of the method used for generating BV\(^0\), extraction mechanism is also important for the effective preparation of the BV\(^0\) molecules. On the hotplate at 60 °C, a non-equilibrium convection flow was governed by the temperature distribution between the bottom and the top of the vial (Figure 1d). The synthesized neutral BV\(^0\) molecules (hydrophobic in character) were transported effectively from the bottom aqueous solution to the upper toluene by the convection flow. In the extraction and transportation process, other isomers of BV\(^+\) and BV\(^-\) in water were separated. This work facilitates using a strong electron dopant to modulate nanoelectronic materials such as water were separated. This work facilitates using a strong reducing BV\(^0\) generates a large amount of hydrogen gas while simultaneously developing TMDCs for use in optoelectronic devices. Here, we

Contrary to the expectation, the reaction with indium generated pale yellow in toluene with a ~430 nm peak and a low Abs of ~0.18 on the UV/Vis spectrum (Figures 2d, S2, S3), which is similar to the reaction result without indium (Figures 2b and S1). The Al fragment showed an initial reaction forming BV\(^+\) (violet stream); however, the reaction stopped after a while (Figure S2). This behavior would have been due to the passivation of the aluminum surface with oxide. In fact, the fresh surface of the Al shows the reactivity to form a BV\(^+\) violet stream, and the larger the fresh surface area of the tiny Al fragments shows apparent reaction to form the BV\(^+\) violet stream. On the other hand, the aged (as-obtained and non-treated) Al surface, which would be covered with oxide, shows no reactivity (Figure S2). According to the observations, the reduction potential of the metals would have been a key factor in generating the reduced form of BV isomers, and the metals of indium and manganese further progressed the reaction to form the two-electron reduced BV\(^0\) molecules.

The extracted BV\(^0\) molecules in the toluene solution (from indium-based synthesis) was treated for a bulk-MoS\(_2\) MOSFETs (Figure 3a). The MoS\(_2\) was mechanically exfoliated on a 260 nm thermally grown SiO\(_2\) on p-type Si wafer, and the device was fabricated with a standard lithographic technique. The original

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device showed usual n-type behavior with an ON/OFF ratio in the drain current ($I_D$) of $\sim 4$ in a range of applying gate voltage ($V_G$) between $-30$ V and $30$ V (Figure 3a). The output characteristic curves also show the gate dependency of the MOSFET (Figure S4). The treated MOSFET with the synthesized BV$_0$ (toluene solution from indium-based synthesis) showed completely different electrostatic behaviors; a higher drain current with a small gate dependency was observed, indicating that the synthesized molecules dope electrons strongly to the MoS$_2$ MOSFET which is close to a metallic state. To further confirm the electron transfer doping, a monolayer MoS$_2$ was treated with the synthesized molecules. With the treatment, the Raman signal of the A’ mode (out-of-plane vibration) shifted to a lower energy, while the Raman signal of the E’ mode (in-plane vibration) was maintained, which is consistent with previous reports of electron doping with BV$_0$ molecules (Figure 3b). The yellow-colored solution of the upper toluene layer shows a signal around 420–430 nm that is red-shifted from the solution with N$_2$ bubbling (Figures 4b and S3). To identify whether it is a BV$_0$ molecule, the toluene solution in Figure 4a was applied to a MoS$_2$ MOSFET (Figure 4c). Even after the treatment process (immersion in the toluene solution) for 24 hours, the MOSFET showed an ON/OFF ratio of $\sim 3$; rather, the $I_D$ at $V_G = 30$ V

Figure 2. (a) Illustrative image of the experimental procedure on a hotplate. (b) UV/Vis spectra for the extracted toluene layer 24 h after the reaction. Each curve shows the synthesized solution with an indium plate at $60^\circ$C, without an indium plate at $60^\circ$C, and with an indium plate at $20^\circ$C. (c, d) UV-Vis spectrum of the 24 h-reacted toluene solution. The reaction is processed with (c) manganese and (d) aluminum. The inset is the picture of the solution obtained after the 24 h reaction. The reaction solutions are bubbled with N$_2$ gas beforehand. (e) Reduction potentials of Al, Mn, In and BV molecules in respect to the standard hydrogen electrode (SHE).
decreases slightly with increasing the treatment time. Therefore, the molecules generated via the process without N₂ bubbling were different from the electron dopant BV⁰; most likely the product was an oxygen-reacted species.

The reaction system without N₂ bubbling is useful as a visualization model for the reaction, because the lifetime of the violet BV⁻ generated from the metal surface in the aqueous solution is limited. Additionally, the solution is transparent; as such, the streamline in the vial can be visualized (as shown in Figures 1d and 4a). Furthermore, the generated neutral molecules (most likely oxygen-reacted species), which were extracted in the upper toluene layer (meaning they are hydrophobic neutral molecules), would be useful as a model for analyzing the generated hydrophobic BV⁰ molecules in the aqueous solution.

Since the BV⁰ is a neutral molecule, solvation in water is limited. It requires a transportation mechanism of the generated BV⁰ molecules from the metal surface at the bottom aqueous solution to the upper toluene layer. We considered the macroscopic behavior of the reaction solution by comparing two heating systems of 1) a hotplate that generated a large temperature gradient (Figure 5a) and 2) heating the reaction vial uniformly in an oven with a small temperature gradient (Figure 5b). The temperatures of the surface on the hotplate and in the oven were 60°C. The heating on the hotplate showed a convection flow (Figure 1d) and generated BV⁰ in the upper toluene layer (Figures 1c and 2b). On the other hand, heating the vial uniformly in an oven, a diffusion of BV⁻ above the indium surface was observed (Figure 5c, and the illustrative image is Figure 5b). Twenty-four hours after the reaction, the bottom aqueous layer showed a dark purple solution, indicating a large amount of BV⁻ generation similar to that of heating on a hotplate, while the upper toluene layer showed a pale-yellow solution (Figure 5d). Figure 5e showed a UV/Vis spectrum for the toluene layer generated by the uniform heating in the oven, and the Abs was just 0.04 at 399 nm. The spectrum in toluene layer of the synthesis in the oven showed BV⁰ generation, but the Abs was 1/19 of the process on the hotplate. Since Abs is proportional to the concentration of the product, the generation rate of BV⁰ was 1/19 via heating in the oven compared to heating on the hotplate.

The difference between the heating conditions was the temperature distribution at the bottom and top of the vial (Figure 5a and b). Convection flow (known as Rayleigh-Bénard convection) can be generated by a certain temperature difference (ΔT) between the top and bottom of the vial, generating a denser liquid in the top that flows down to the bottom.[27–29] This phenomenon is evaluated with Rayleigh number (Ra) as

\[ Ra = \frac{g\beta\Delta T L^3}{v\alpha} \]  

where g, β, v, α, and L are the acceleration of gravity, the thermal expansion coefficient, the kinematic viscosity, the thermal diffusivity, and the system length, respectively. The critical Ra is known to be 1,708[29] above that point, the instability and the convection flow is generated. Figure S5 shows the estimated Ra vs. ΔT curve in water, and that the convection flow would be generated even with a small temperature distribution (ΔT over ~0.03°C from equation (1)). All
parameters except $\Delta T$ would have the same values in the two heating scenarios of the hotplate and the oven. In the hotplate scenario, the bottom temperature is higher than the top temperature, as illustrated in Figure 5a. Although the temperature distribution should be exhibited even in the heating in the oven, especially at the moment of placing the vial in the oven, the $\Delta T$ would be tiny after reaching a steady state, the convection flow would not be generated and the BV* molecules generated at the metal surface would have no way to transport to the upper toluene layer which was centimeter separated from the bottom. As a result, the system in the oven did not show an efficient generation of BV* dopant molecules.

To visualize the transportation on a microscopic scale, the aqueous solution on the hotplate was further analyzed. For this purpose, the analyzed sample used was the solution untreated by N$_2$ bubbling. Under a microscope, tiny droplets with a diameter of $\sim$10 $\mu$m were observed, which was phase-separated from the aqueous solution (Figure 5f). The UV/Vis spectrum of the aqueous solution showed a signal around 400 nm, indicating that the generated droplet had been transported and produced the yellow toluene layer (Figures 4a, b and 5g). In the N$_2$ bubbling case, although it was difficult to visualize due to the dense BV* violet color (Figure 1c), the neutral BV* molecules would form a similar droplet by phase separation from water and be transported to the upper toluene layer by the convection flow. From the results above, the dopant molecule, BV*, generated on the indium and manganese surfaces would be effectively transported by the non-equilibrium convection flow from the bottom solution to the upper hydrophobic toluene layer (Figure 5h); simultaneously in the transportation, the BV* molecules could be separated from BV$^+$ and BV$^{2+}$ isomers.

In summary, generation of the neutral BV* molecules with indium and manganese fragments as a metal-reduction system was demonstrated. The method was achieved by simply dropping the air-stable metal fragments into the vial. The generated BV* molecules effectively doped bulk MoS$_2$, MOSFETs and monolayer MoS$_2$, confirmed by MOSFET behavior, PL and Raman spectroscopy. In addition, the important finding is that the temperature gradient facilitates the transportation of the produced BV* molecules from the aqueous solution to the upper toluene layer by the generated convection flow, and simultaneous purification from the aqueous isomers of BV$^+$ and BV$^{2+}$ was incorporated. This synthetic method would be useful for the nanoelectronic fields of TMDCs, graphene and carbon nanotubes to achieve strong doping via the simple and easy
Experimental Section

Sample Preparation Process

Benzyl viologen dichloride (BV$_2^+$ isomer, Sigma-Aldrich) was dissolved in Milli-Q water to prepare 7 mg/ml of solution. The toluene (Sigma-Aldrich) layer (2 ml) was placed on the BV$_2^+$ aqueous solution of 2 ml and heated on a hotplate or in the oven. Both the toluene and the BV$_2^+$ aqueous solutions were N$_2$ bubbled for 30 min each beforehand, and further bubbling was performed on the bilayer solution for 5 min. The heating was done under a dark condition. For heating in the oven, the vial was wrapped in aluminum foil. The surface temperature of the hotplate and the temperature in the oven were controlled and monitored in advance. Indium metal (Sigma-Aldrich) was pre-treated with 1% HCl and rinsed with Milli-Q water sufficiently before use. Manganese (The Nilaco Corporation) and Al (The Nilaco Corporation) were used as obtained. The metals were cut for the aluminum. The indium for the indium (Silicon Valley MOSFET) was prepared. Electrical characteristics were measured using a semiconductor parameter analyzer (Keysight, B1500a). Photoluminescence and Raman spectra were obtained using a spectrometer equipped with an EMCCD camera (HORIBA Scientific). The diameter of the incident beam was about 2 μm, and the laser power was ~27 W cm$^{-2}$ for Raman spectroscopy and 2.7 W cm$^{-2}$ for PL spectroscopy.

Physical Measurements

Optical microscope observation was carried out with an Olympus BX51. UV/Vis spectra were obtained with a JASCO Co. V-650 spectrometer. The solutions were diluted with a neat solvent beforehand to be a quarter concentration of as prepared. Electrical characteristics were measured using a semiconductor parameter analyzer (Keysight, B1500a). Photoluminescence and Raman spectra were obtained using a LabRAM HR800 equipped with an EMCCD camera (HORIBA Scientific). The diameter of the incident beam was about 2 μm, and the laser power was ~27 W cm$^{-2}$ for Raman spectroscopy and 2.7 W cm$^{-2}$ for PL spectroscopy.

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Conflict of Interest

The authors declare no conflict of interest.

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