Systematic Investigation of the Piezocatalysis–Adsorption Duality of Polymorphic MoS_2 Nanoflowers

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This study theoretically and experimentally investigates the piezocatalytic and adsorption effects of different phases of polymorphic MoS_2 NFs. To verify whether the polymorphic MoS_2 NFs would exhibit adsorption or piezocatalytic effects, the electrostatic surface charge of these NFs and the RhB solution is varied using sodium hydroxide and nitric acid solutions. The cationic dye is adsorbed on the surfaces of the 1T MoS_2 NFs; however, the few-layer 2H MoS_2 NFs generate a considerable quantity of hydroxyl species for degrading RhB molecules through the mechanical-force-induces piezopotential. This study discovers that the polymorphic MoS_2 NFs exhibit a piezocatalysis–adsorption duality.

Key word：MoS_2; Nanoflowers; Polymorphic; Piezocatalysis–adsorption duality; Wastewater treatment.

1. Introduction

MoS_2 is a promising two-dimensional (2D) material for piezotronicand piezophototronic applications due to its piezoelectric properties[1, 2]. Wu et al. discovered that few-layered MoS_2 nanoflowers (NFs) exhibited ultrahigh degradation activity under ultrasonic vibration in a dark environment[3]. The extraordinary piezo-catalytic characteristic of MoS_2 has been widely recognized and applied in various research fields. However, MoS_2 NFs have high adsorption capacities for various organic dyes because of their negative surface charge, which leads to the adsorption of dyes on the surface of MoS_2 NFs that misunderstand the piezocatalytic effect. The present study employed the hydrothermal process to synthesize polymorphic MoS_2 NFs with a controllable 1T:2H phase ratio. Experiment results indicated that the synthesized 1T and hybrid 1T MoS_2 NFs exhibited excellent adsorption capacity. However, the 2H MoS_2 NFs exhibited a unique piezocatalytic activity; that is, dye molecules were first adsorbed on the surfaces of the MoS_2 NFs and then underwent piezocatalytic decomposition (**Fig. 1a**). Therefore, the 1T:2H phase ratio, number of layers, and piezopotential of MoS_2 NFs play critical roles in determining their piezocatalytic degradation activity.

2. Experimental

Hydrothermal method was used to synthesized three types of polymorphic MoS_2 NFs

Synthesis of 2H MoS_2 NFs

Thiourea and sodium molybdate dihydrate was dissolved in 30.0 mL of deionized (DI) water and then thoroughly mixed through magnetic stirring. Next, 1-butyl-3-methylimidazolium chloride was added to this solution. Subsequently, hydrochloric acid was used to titrate the aforementioned solution. The as-prepared homogeneous solution was transferred into a 100-mL autoclave and heated to 220 °C within 24 h.

Synthesis of 1T/2H MoS_2 NFs

$Na_2MoO_4.2H_2O$ and CH_4N_2S were dissolved in 20 mL of DI water. The pH of the solution was then gradually adjusted by adding 16 mL of propionic acid and 12 mL of DI water. The as-prepared solution was then transferred into a 100-mL autoclave and heated to 180 °C over 4 h.

Synthesis of 1T MoS_2 NFs

Ammonium molybdate tetrahydrate and CH_4N_2S were dissolved in 70 mL of DI water. This solution was transferred into a 100-mL autoclave for heating at 180 °C over 10 h.

After the hydrothermal method, all the MoS_2 powders was washed through centrifugation with DI water and ethanol several times and dried at 70 °C within 6 h in a vacuum oven.

3. Results and discussion

The prepared polymorphic MoS_2 NFs exhibited a rich 2H phase, hybrid 1T and 2H (1T/2H) phase, and rich 1T phase had identical spherical flower-like morphologies with an average size of less than 1 μm (**Figs. 1b–d**). X-ray diffraction (XRD) revealed that the as-prepared 2H MoS_2 NFs had a hexagonal morphology (JCPDS card No. 37-1492; **Fig. 1e**)[3]. The XRD patterns of the 1T/2H and 1T MoS_2 NFs exhibited prominent and broad (100) peaks, suggesting that these NFs had a defect-rich structure with nanometer-sized domains along the basal planes. The Raman spectra of the 1T/2H and 1T phases included 1T peaks at 146, 236, and 336 cm^{-1} (**Fig. 1f**). Moreover, intense peaks were observed for the 2H MoS_2 NFs and could be ascribed to the typical $E_{2g}{}^1$ and A_{1g} vibration modes with no 1T signals. The difference (Δ) between the aforementioned vibration modes was also evaluated, and the results (**Fig. 1g**) indicated that the vibration modes in the 2H MoS_2 NFs exhibited a considerably broader and lower intensity than those in the bulk MoS_2 and that the distance between these modes was shorter (Δ = ~ 23.5 cm^{-1}) as compared with bulk MoS_2 (Δ = ~26.2 cm^{-1}). As the distance between the peaks assigned to the $E_{2g}{}^1$ and A_{1g} vibration modes decreased, the number of few-layer structures in the MoS_2 NFs increased. High-resolution transmission electron microscopy (HRTEM) images of the 2H, 1T/2H, and 1T phases are depicted in **Figs. 1h–m**. **Fig. 1h** and its inset image depict the lattice intensity profile at the edge sites of the MoS_2 NFs. The interplanar spacing of the 2H phase was estimated to be 0.62–0.64 nm, corresponding to the (002) plane of 2H MoS_2[3]. Moreover, the interatomic distance of MoS_2 was 0.32 nm (**Fig. 1i** and its inset image), which is consistent with the honeycomb lattice characteristic of the 2H phase. In addition, **Fig. 1j** illustrates the coexistence of the 1T and 2H phases. The 1T/2H phase boundary is displayed in **Fig. 1k** and its inset image. As shown in **Fig. 1l** and its inset image, the interplanar spacing of the 1T phase was approximately 0.65–0.67 nm, indicating the existence of 1T MoS_2. **Fig. 1m** and its inset image depict a trigonal 1T MoS_2 lattice with an interatomic distance of 0.27 nm

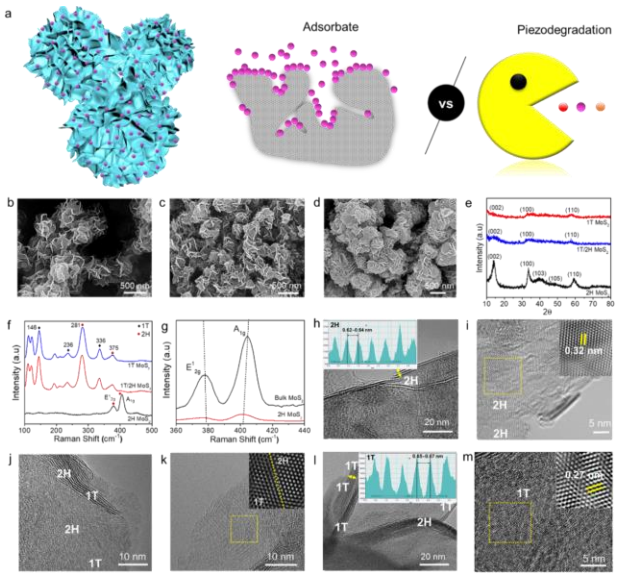

Fig. 1. (a) Schematic diagram clarifies the decolorization of MoS_2 for dye molecules by the piezocatalytic or adsorption effect. SEM images of (b) 2H MoS_2 NFs, (c) 1T/2H MoS_2 NFs, and (d) 1T MoS_2 NFs. (e) XRD patterns and (f) Raman spectra of 2H MoS_2 NFs, 1T/2H MoS_2 NFs, and 1T MoS_2 NFs; (g) The Raman spectra comparison of 2H MoS_2 NFs and bulk MoS_2. (h) HRTEM image with the corresponding intensity profile of 2H phase (i) The corresponding lattices image of 2H MoS_2 NFs. (j) HRTEM images showing 1T/2H phases and inset (k) showing the phase boundary of the 1T/2H phase. (l) HRTEM image with the corresponding intensity profile of 1T phase. (m) HRTEM of 1T phase and inset image, displaying lattice image of 1T MoS_2.

Sodium hydroxide (NaOH) and nitric acid (HNO_3) solutions were alternately added to solution samples containing the 1T, 1T/2H, and 2H MoS_2 NFs to modulate the electrostatic charge of MoS_2 and determine whether the decolorization of RhB solution by these NFs was caused by adsorption or piezocatalytic effects. As shown in **Fig. 2a**, nearly 100% of the RhB dye molecules could be desorbed from the surfaces of the 1T MoS_2 NFs when NaOH was added. After adding HNO_3, the decolorization ratio of the RhB solution containing 1T MoS_2 was approximately 97%. However, the RhB dye molecules were still approximately 80% desorbed from the surfaces of the 1T MoS_2 NFs after repeatedly adding NaOH, demonstrating that the 1T phase exhibited only adsorption effects under ultrasonic vibration. The corresponding photographs are shown in **Fig. 2b**. Similarly, **Fig. 2c** indicates that approximately 46% of the RhB dye was desorbed after the first addition of NaOH. When HNO_3 was added, the surface potential of the 1T/2H MoS_2 NFs became negative again, leading to the adsorption of RhB dye molecules. However, the dye desorption ratio was maintained at approximately 46% after the second addition of NaOH, signifying that the piezocatalytic process could decompose 54% of the dye molecules. The corresponding photograph is shown in **Fig. 2d**. By contrast, the dye solution could be entirely decomposed by the 2H phase under ultrasonic vibration (**Fig. 2e**). The dye solution consistently remained transparent when NaOH and HNO_3 were added, demonstrating the strong piezocatalytic decomposition ability of the 2H phase. Because of the completed decomposition of the dye, no dye molecules could be desorbed from the surfaces of the 2H MoS_2 NFs when alternately adding alkali and acid solutions, as shown in **Fig. 2f**. These results indicate that the 2H phase ratio and few-layer structures with piezoelectricity play critical roles in determining the piezo-degradation activity of MoS_2 NFs. Cyclic tests were conducted on all samples to evaluate their repeatability regarding the removal of dye molecules and to determine the corresponding adsorption and piezo-degradation effects. The dye decolorization ratio of the 1T MoS_2 NFs exhibited 100% at the first cyclic test (**Fig. 2g**). However, after the second and third cyclic tests, the decolorization rate of the 1T MoS_2 NFs decreased considerably, demonstrating that the 1T MoS_2 NFs exhibited considerable adsorption effects. The dye decolorization rate of the 1T/2H MoS_2 NFs exhibited a marginal decay after the second cyclic test and a more obvious decay after the third cyclic test (**Fig. 2h**). By contrast, the 2H MoS_2 NFs completely degraded the RhB dye after the third cyclic test (**Fig. 2i**); hence, among them, 2H MoS_2 NFs exhibited a remarkable piezocatalytic effect. The overall piezo-degradation and physical adsorption mechanism of 2H and 1T MoS_2 NFs discussed above were shown in **Fig. 2j** and **Fig. 2k**, respectively.

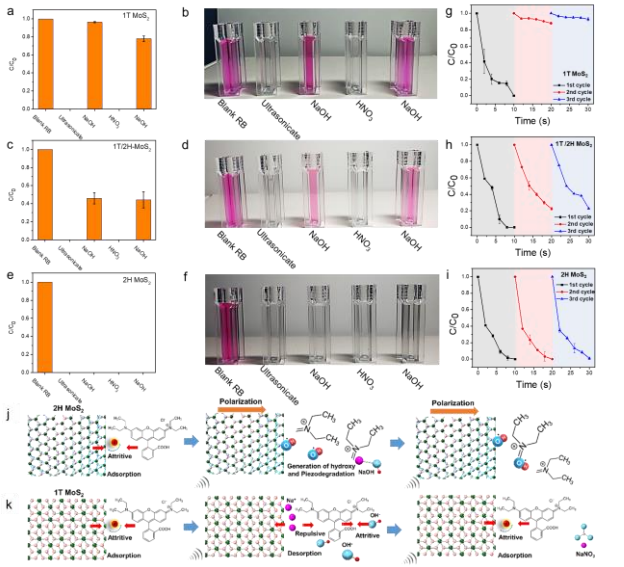

Fig. 2. After 10 s ultrasonication in the dark, the charge surface modulation uses NaOH, HNO_3, and NaOH to evaluate adsorption and piezo-degradation activity. (a)-(b) 1T MoS_2 NFs, (c)-(d) 1T/2H MoS_2 NFs, and (e)-(f) 2H MoS_2 NFs. The three consecutive cycling test of (g) 1T MoS_2 NFs, (h) 1T/2H MoS_2 NFs, and (i) 2H MoS_2 NFs.

4. Conclusion

This study discovered the piezocatalysis–adsorption duality in polymorphic MoS_2 NFs. Owing to their negatively charged surfaces, the 1T MoS_2 NFs synthesized in this study exhibited a strong adsorption affinity toward RhB. By contrast, few-layer 2H MoS_2 NFs exhibited strong piezocatalytic effects under ultrasonic vibration, which led to the complete RhB decomposition. When HNO_3 and NaOH were alternately added to the RhB solution, the adsorption-desorption behaviors of the 1T, 1T/2H, and 2H MoS_2 NFs exhibited approximately 100%, 46%, and 0%, respectively. This study confirmed that the polymorphic MoS_2 NFs exhibit a unique piezocatalysis–adsorption duality. The 1T-dominated MoS_2 exhibits electrostatic adsorption, while 2H MoS_2 NFs show a unique piezocatalytic effect. This finding provides a valuable reference for studying and understanding the mechanisms underlying the role of 2D TMDs piezocatalysts in electrochemical degradation reactions.

References

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