A general one-step approach for in situ decoration of MoS$_2$ nanosheets with inorganic nanoparticles

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Experimental Section

Synthesis of noble metal nanoparticles decorated MoS$_2$ nanosheets (MoS$_2$-Pt and MoS$_2$-Au). Typically, MoS$_2$-COOH (20 mg) was dispersed in DEG (30 mL) and the mixture was treated with an ultrasonic bath (40 kHz) for 15 min. Then, K$_2$PtCl$_4$ (20.8 mg, 0.05 mmol) or HAuCl$_4$$\cdot$3H$_2$O (19.7 mg, 0.05 mmol) was added and stirred for 30 min. The above mixture was heated to 200 °C for 20 min under the protection of argon flow and constant stirring. 7.5 mg of NaBH$_4$ in 10 mL of DEG was injected rapidly into the above hot mixture. The resulting mixture was further heated at 200 °C for 1 h. The final product of MoS$_2$-Au or MoS$_2$-Pt was separated by centrifugation and washed with water.

For comparison, MoS$_2$-Pt was also synthesized by using sodium citrate instead of NaBH$_4$ as reducing agent. In addition, graphene was also employed as substrate to
fabricate graphene-Pt nanohybrid with the same synthetic procedure as MoS$_2$-Pt.

**Synthesis of Fe$_3$O$_4$ nanoparticles decorated MoS$_2$ nanosheets (MoS$_2$-Fe$_3$O$_4$).** Typically, NaOH (100 mg) was added into DEG (10 mL), heated at 120 °C for 1 h in a argon atmosphere, and cooled down to 70 °C to produce a NaOH/DEG stock solution. MoS$_2$-COOH (20 mg) was dispersed in DEG (30 mL) and the mixture was treated with an ultrasonic bath (40 kHz) for 15 min. Then, FeCl$_3$ (80 mg, 0.49 mmol) was added and stirred for 30 min. The above mixture was heated to 200 °C for 20 min under the protection of argon flow and constant stirring. 3.5 mL of 70 °C NaOH/DEG stock solution was injected rapidly into the above hot mixture. The resulting mixture was further heated at 200 °C for 1 h. The final product of MoS$_2$-Fe$_3$O$_4$ was separated by centrifugation and washed with water.

**Synthesis of semiconductor nanoparticles decorated MoS$_2$ nanosheets (MoS$_2$-CdS and MoS$_2$-PbS).** Typically, MoS$_2$-COOH (20 mg) was dispersed in DEG (30 mL) and the mixture was treated with an ultrasonic bath (40 kHz) for 15 min. Then, CdCl$_2$ (18.4 mg, 0.1 mmol) or Pb(CH$_3$COO)$_2$·3H$_2$O (40 mg, 0.1 mmol) was added and stirred for 30 min. The above mixture was heated to 200 °C for 20 min under the protection of argon flow and constant stirring. 25 mg of Na$_2$S·9H$_2$O in 10 mL of DEG solution was injected rapidly into the above hot mixture. The resulting mixture was further heated at 200 °C for 1 h. The final product of MoS$_2$-CdS and MoS$_2$-PbS was separated by centrifugation and washed with water.
Fig. S1. (a) Representative AFM image of MoS$_2$-COOH nanosheets. (b) Height profile of corresponding planes along the lines in (a).
Fig. S2. (a) FTIR spectra of MPA, MoS$_2$-COOH and unmodified MoS$_2$ nanosheets. XPS survey spectrum (b) and C1s spectrum (c) of MoS$_2$-COOH. (d) TGA curves of MoS$_2$-COOH and unmodified MoS$_2$ nanosheets.

The successful introduction of carboxylic groups was elucidated by FTIR and XPS. For comparison, we also synthesized MoS$_2$ nanosheets using the same procedure as MoS$_2$-COOH except the addition of mercaptopropionic acid (MPA) ligand and this sample was designated as unmodified MoS$_2$. As can be seen in Fig. S2a, the MPA sample shows a strong absorption band at 2574 cm$^{-1}$ corresponding to the –SH stretching. After conjugation with MoS$_2$, this band disappeared in the resulted MoS$_2$-COOH sample, possibly caused by the interaction between –SH with MoS$_2$. The exfoliation process leads to deformation of MoS$_2$’s crystal structure and
formation of numerous internal edges and defects. On the other hand, previous works suggested that the sites of internal edges and defects possess high affinities toward –SH group.\textsuperscript{1,2} In addition, the MoS\textsubscript{2}-COOH sample shows obvious absorption bands at 2980, 2870 and 1457 cm\textsuperscript{-1} due to the C-H stretching, 1101 cm\textsuperscript{-1} corresponding to C-O stretching, and 1044 cm\textsuperscript{-1} associated with C-S stretching, demonstrated the successful conjugation of MPA ligand.

According to the full survey spectrum (Fig. S2b), the elements of Mo, S, C and O are found for the MoS\textsubscript{2}-COOH sample. The mass percent of C and O were calculated according to the XPS results and found that the MoS\textsubscript{2}-COOH sample shows much higher content of C (2.6 wt% and 0.9 wt% for MoS\textsubscript{2}-COOH and unmodified MoS\textsubscript{2}, respectively) and O (1.9-2.5 wt% and 0.2 wt% for MoS\textsubscript{2}-COOH and unmodified MoS\textsubscript{2}, respectively) than that of unmodified MoS\textsubscript{2} nanosheets, further confirmed the successful attachment of carboxylic groups. In addition, the high-resolution C\textsubscript{1}s spectrum indicates the presence of O=C-O and C-C bonds for the MoS\textsubscript{2}-COOH sample (Fig. S2c). The content of carboxylic groups on the surface of MoS\textsubscript{2}-COOH was determined by TGA as shown in Figure S2d. The unmodified MoS\textsubscript{2} sample shows very low weight loss (about 1.3 wt%) between 150-700 °C, presumably due to the presence of residual organic component resulted from \textit{n}-BuLi. In contrast, the MoS\textsubscript{2}-COOH sample shows much higher weight loss between 150-700 °C (7.1 wt%), further confirming that the carboxylic groups have been successfully introduced onto the surface of MoS\textsubscript{2} nanosheets.

Reference


Fig. S3. Representative TEM images of MoS$_2$-Pt (a), MoS$_2$-Au (b), MoS$_2$-Fe$_3$O$_4$ (c), MoS$_2$-CdS (d) and MoS$_2$-PbS (e). (f) Magnetization curve (at 300 K) of MoS$_2$-Fe$_3$O$_4$. 
Fig. S4. Photographs of MoS$_2$-Fe$_3$O$_4$/PVA nanocomposite film.
Fig. S5. Representative TEM images of MoS$_2$-Pt (a,b) and MoS$_2$-CdS (c,d) by using unmodified MoS$_2$ as a support.
Fig. S6

(a) (b)

Fig. S6. TEM images of graphene-Pt.
Fig. S7. TEM images of MoS$_2$-Pt by using sodium citrate as reducing agent.
**Fig. S8.** Representative TEM images of MoS$_2$-Fe$_3$O$_4$ with $R_{wt}$ (FeCl$_3$/MoS$_2$-COOH) value of 1/1 (a) and 4/1 (b). (c) EDS spectrum of MoS$_2$-Fe$_3$O$_4$ shown in (a). (d) Magnetization curves (at 300 K) of MoS$_2$-Fe$_3$O$_4$ with $R_{wt}$ (FeCl$_3$/MoS$_2$-COOH) value of 1/1 and 4/1.
Fig. S9. Representative TEM images of MoS$_2$-Fe$_3$O$_4$/Pt sample.
Fig. S10. (a) Concentration change in 4-nitrophenol compounds ($C_t/C_0$) in the presence of MoS$_2$-Fe$_3$O$_4$/Pt nanocatalysts. (b) Plot of $\ln (C_t/C_0)$ against time for the reduction of 4-nitrophenol with MoS$_2$-Fe$_3$O$_4$/Pt nanocatalysts.