Supporting Information

Sequential Growth of Hierarchical N-Doped Carbon-MoS_2 Nanocomposites with Variable Nanostructures

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Experimental Section

All these nanomaterials follow the same chemicals addition sequence, as follows: CTAB, F127 and cysteine were dissolved in the solution of water and ethanol. After 30 minutes stirring at 30 °C, sodium molybdate dihydrate (Na_2MoO_4 $2H_2O$) was added, and subsequently 3-aminophenol and formaldehyde solution were added in every 10 minutes. The only difference is the addition amount of Na_2MoO_4 $2H_2O$ and cysteine.

Synthesis of NC-MoS_2 yolk-shell nanocomposites.

0.13 g of CTAB, 0.10 g F127 and 0.60 g cysteine were dissolved in the solution containing 20 mL of water and 8 mL of ethanol. After 30 minutes stirring at 30 °C, 0.30 g of sodium molybdate dihydrate (Na_2MoO_4 $2H_2O$) was added, and subsequently 0.20 g of 3-aminophenol and 0.28 mL of formaldehyde solution were added in every 10 minutes. The suspension was kept at 30 °C for 24 h. Then the resulting mixture was transferred into a Teflon-lined autoclave and kept at 220 °C under a static condition for 24 h. The solid product was recovered by centrifugation and washed with water and ethanol for three times each and then vacuum-dried at 80 °C for 6 h. To obtain NC-MoS_2 samples, the sample is pyrolysed under nitrogen flow in the tube furnace using a heating rate of 1°C min^{-1} up to 350 °C, dwelling for 2 h, and resuming heating rate at 1 °C min^{-1} up to 800 °C and then dwelling for 6 h.

Synthesis of NC-MoS_2 core-shell nanocomposites (Figure 1C).

0.13 g of CTAB, 0.10 g F127 and 0.60 g cysteine were dissolved in the solution containing 20 mL of water and 8 mL of ethanol. After 30 minutes stirring at 30 °C, 0.10 g of sodium molybdate dihydrate (Na_2MoO_4 $2H_2O$) was added, and subsequently 0.20

g of 3-aminophenol and 0.28 mL of formaldehyde solution were added in every 10 minutes. The suspension was kept at 30 °C for 24 h. Then the resulting mixture was transferred into a Teflon-lined autoclave and kept at 220 °C under a static condition for 24 h. The solid product was recovered by centrifugation and washed with water and ethanol for three times each and then vacuum-dried at 80 °C for 6 h. To obtain NC-MoS_2 samples, the sample is pyrolysed under nitrogen flow in the tube furnace using a heating rate of 1°C min^{-1} up to 350 °C, dwelling for 2 h, and resuming heating rate at 1 °C min^{-1} up to 800 °C and then dwelling for 6 h.

For NC-MoS_2 core-shell nanocomposites (Figure S1), the synthesis process is similar, the only difference is the $Na_2MoO_4\,2H_2O$ amount, 0.05 g instead of 0.10 g.

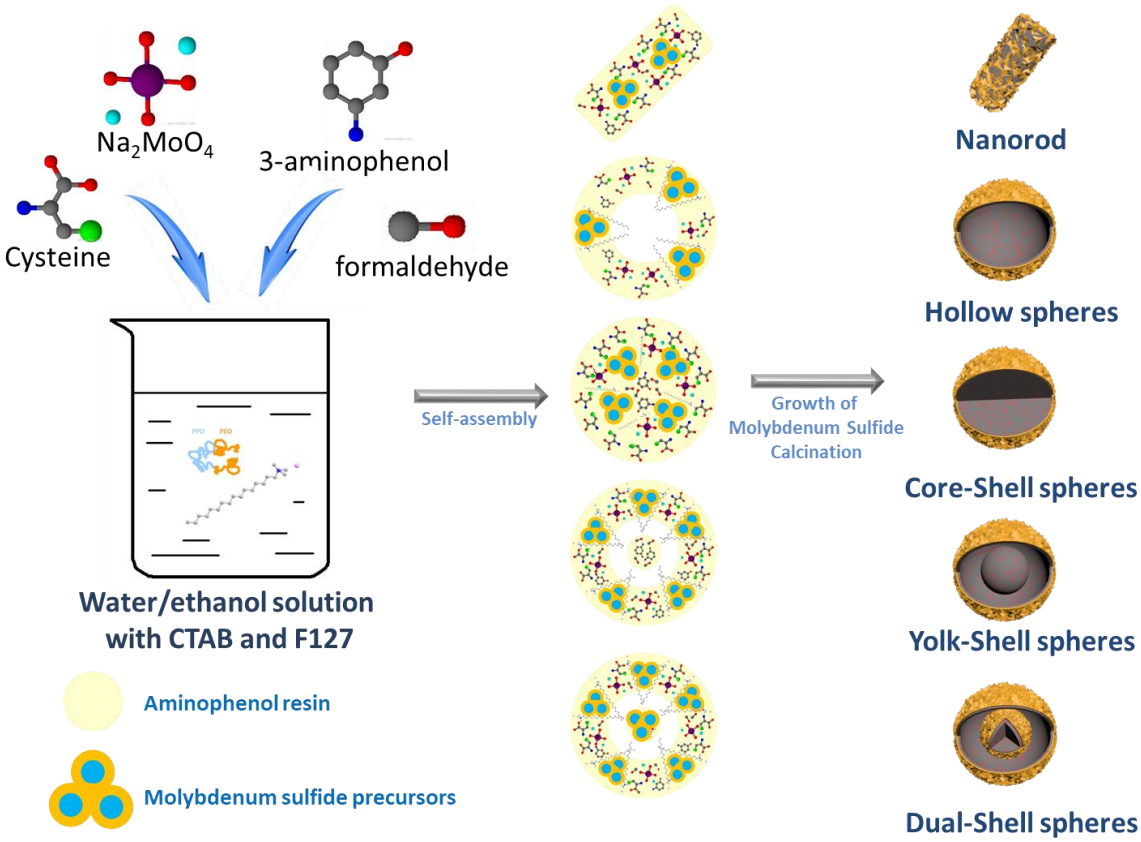
Synthesis of NC-MoS_2 hollow nanocomposites.

0.13 g of CTAB, 0.10 g F127 and 0.30 g cysteine were dissolved in the solution containing 20 mL of water and 8 mL of ethanol. After 30 minutes stirring at 30 °C, 0.05 g of sodium molybdate dihydrate ($Na_2MoO_4\,2H_2O$) was added, and subsequently 0.20 g of 3-aminophenol and 0.28 mL of formaldehyde solution were added in every 10 minutes. The suspension was kept at 30 °C for 24 h. Then the resulting mixture was transferred into a Teflon-lined autoclave and kept at 220 °C under a static condition for 24 h. The solid product was recovered by centrifugation and washed with water and ethanol for three times each and then vacuum-dried at 80 °C for 6 h. To obtain NC-MoS_2 samples, the sample is pyrolysed under nitrogen flow in the tube furnace using a heating rate of 1°C min^{-1} up to 350 °C, dwelling for 2 h, and resuming heating rate at 1 °C min^{-1} up to 800 °C and then dwelling for 6 h.

Synthesis of NC-MoS_2 nanorods with different length.

For short NC-MoS_2 nanorods (Figure 2A): 0.13 g of CTAB, 0.10 g F127 and 0.10 g cysteine were dissolved in the solution containing 20 mL of water and 8 mL of ethanol. After 30 minutes stirring at 30 °C, 0.05 g of sodium molybdate dihydrate (Na_2MoO_4 $2H_2O$) was added, and subsequently 0.20 g of 3-aminophenol and 0.28 mL of formaldehyde solution were added in every 10 minutes. The suspension was kept at 30 °C for 24 h. Then the resulting mixture was transferred into a Teflon-lined autoclave and kept at 220 °C under a static condition for 24 h. The solid product was recovered by centrifugation and washed with water and ethanol for three times each and then vacuum-dried at 80 °C for 6 h. To obtain NC-MoS_2 samples, the sample is pyrolysed under nitrogen flow in the tube furnace using a heating rate of 1°C min^{-1} up to 350 °C, dwelling for 2 h, and resuming heating rate at 1 °C min^{-1} up to 800 °C and then dwelling for 6 h.

For long NC-MoS_2 nanorods (Figure 2A), the synthesis process is similar, the only difference is the cysteine amount, 0.20g instead of 0.10 g.



Scheme S1. The possible detail formation mechanism of NC-MoS_2 nanocomposites with different nanostructures through a synergistic self-assembling process.

Table S1. Synthesis parameters of NC-MoS_2 nanocomposites with different nanostructures.

Sample	Cysteine (g)	$Na_2MoO_4 \cdot 2H_2O$ (g)	Mo /APF mole ratio	Cysteine/APF mole ratio
Dual-Shell spheres	0.60	0.40	1.06	2.70
Yolk-Shell spheres	0.60	0.30	0.80	2.70
Core-Shell spheres	0.60	0.10	0.26	2.70
Core-Shell spheres	0.60	0.05	0.13	2.70
Hollow spheres	0.30	0.05	0.13	1.35
Short nanorods	0.20	0.05	0.13	0.90
Long nanorods	0.10	0.05	0.13	0.45

Table S2. Physicochemical parameters of NC-MoS_2 nanocomposites with different nanostructures.

Sample	S_{BET} (m^2g^{-1})[a]	V_t (cm^3g^{-1})[b]	Mo content[c] wt%	N content[d] wt%	C content[d] wt%	MoS_2/C ratio by wt
Dual-Shell spheres	6.4	0.029	35.25	3.38	61.37	0.96
Yolk-Shell spheres	43.7	0.028	27.56	6.68	65.76	0.70
Core-Shell spheres	10.4	0.058	12.37	7.87	79.76	0.26
Hollow spheres	19.9	0.090	9.40	10.05	80.55	0.19
Long nanorods	14.8	0.025	9.74	11.82	78.44	0.21

[a] S_{BET} is the BET specific surface area.

[b] V_t is the total pore volume determined at the relative pressure of 0.98.

[c] The Mo content was obtained by ICP.

[d] The N content was obtained by elemental analysis.

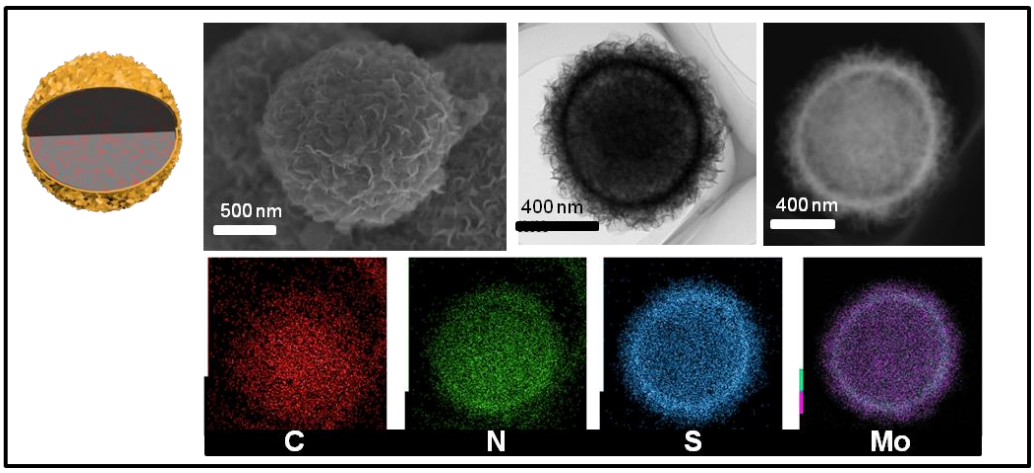


Figure S1. Structural and elemental distribution information of NC-MoS_2 nanocomposites yolk-shell spheres. In this frame, the upper row images are: SEM image (left), TEM image (middle) and dark field TEM image (right), while bottom row images are elemental mapping of C, N, S and Mo of area in dark field TEM image (bottom row).

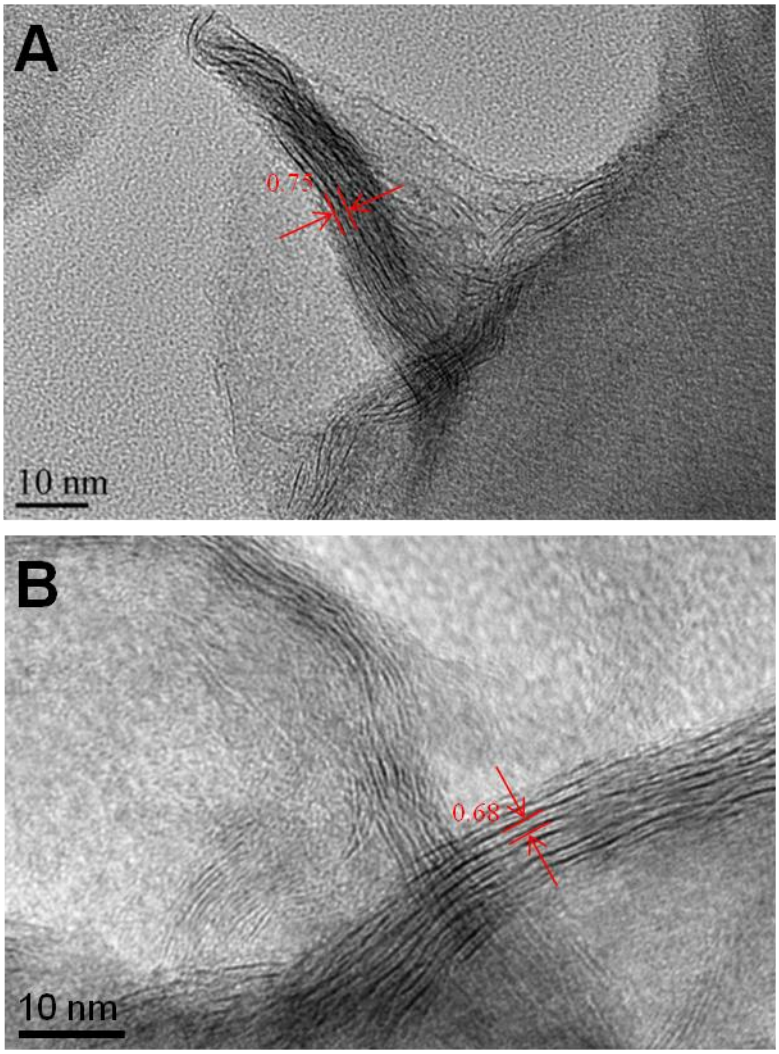


Figure S2. The HRTEM images of the NC-MoS_2 nanocomposites: short nanorod (A) and (B) long nanorod.

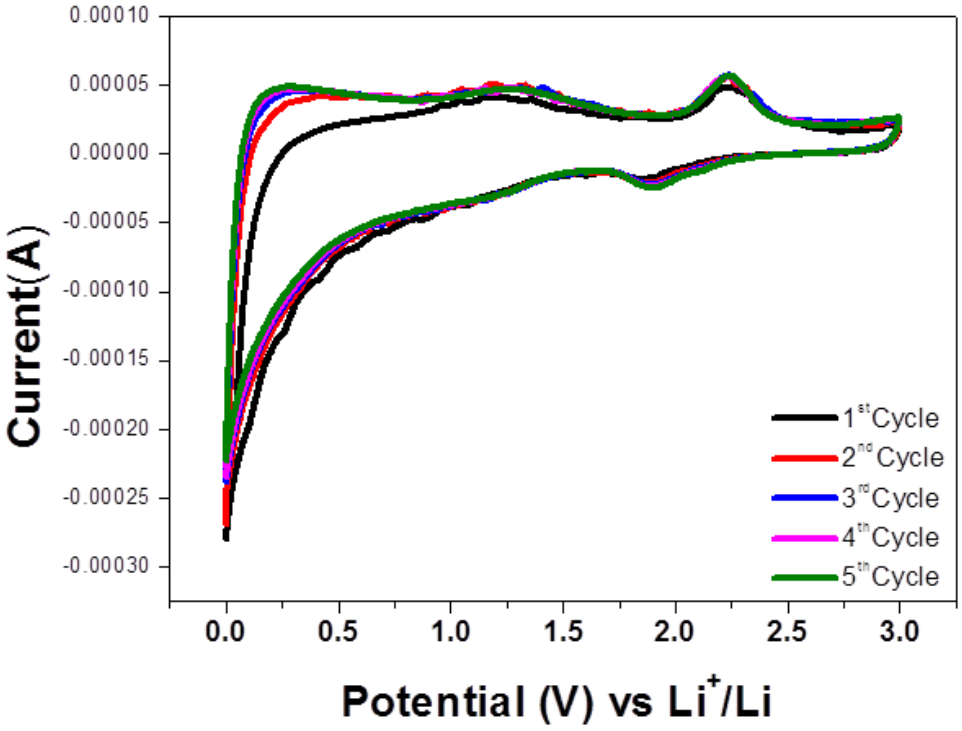


Figure S3. CV curves from 3.0 to 0 V at a scanning rate of 0.1 mV · S^{-1}.

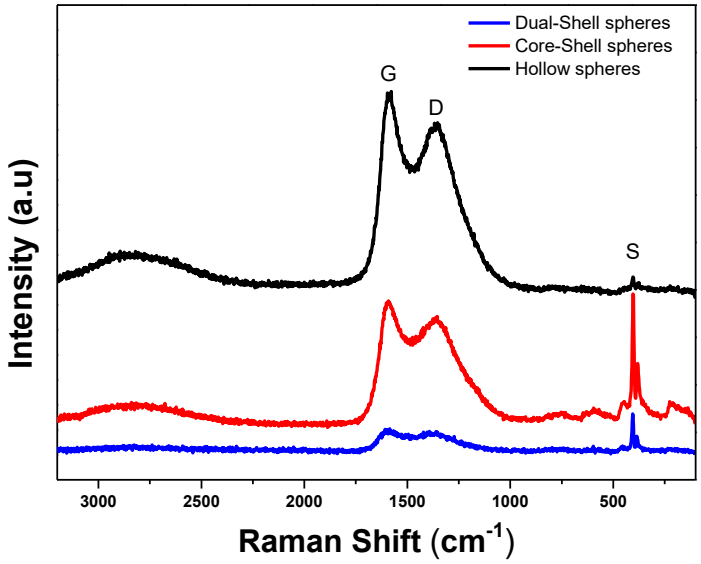


Figure S4. The Raman spectra of NC-MoS_2 nanocomposites with dual-shell, core-shell and hollow nanostructures.