

Colloidal Template Synthesis of Nanomaterials by Using Microporous Organic Nanoparticles: The Case of C@MoS₂ Nanoadsorbents

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Abstract: The so-called colloidal template synthesis has been applied to the preparation of surface-engineered nano-adsorbents. Colloidal microporous organic network nano-templates (C-MONs), which showed a high surface area (611 m² g⁻¹) and enhanced microporosity, were prepared through the networking of organic building blocks in the presence of poly(vinylpyrrolidone) (PVP). Owing to entrapment of the PVP in networks, the C-MONs showed good col-

loidal dispersion in EtOH. MoS₂ precursors were incorporated into the C-MONs and heat treatment afforded core-shell-type C@MoS₂ nanoparticles with a diameter of 80 nm, a negative zeta potential (−39.5 mV), a high surface area (508 m² g⁻¹), and excellent adsorption performance towards cationic dyes (q_{max} = 343.6 and 421.9 mg g⁻¹ for methylene blue and rhodamine B, respectively).

1. Introduction

MoS₂ materials have received extensive attention from materials scientists.^[1,2] Owing to their unique 2D structural motif, they have been applied to a range of energy materials, including electrode materials for batteries and electrocatalysts for fuel cells.^[2] More recently, MoS₂ materials have been applied to environmental issues, as reviewed by Mi et al.^[1] It is well-known that the surface of MoS₂ materials has a unique negative zeta potential,^[1] and a variety of MoS₂ materials have been applied to the removal of cationic adsorbates.^[3]

Because the performance of an inorganic nanomaterial is critically dependent on its morphological structure, the engi-

neering of its shape and size is an important issue.^[4–6] Over the last two decades, there has been extensive research into the shape- and size-controlled synthesis of inorganic nanomaterials.^[4–6] For example, wet-chemical colloidal synthesis with appropriate surfactants, such as poly(vinylpyrrolidone) (PVP), has led to the successful preparation of high-quality inorganic nanomaterials.^[5] In addition, the atom-economical engineering of functional nanomaterials has been reported in materials science.^[7] For example, when the functionalities of materials originate from their surface structures, core-shell nanomaterials have been engineered with cheap core components.^[7] In colloidal synthesis, nanomaterial precursors are decomposed to form nanoparticles with the help of surfactants (Figure 1). However, the reaction temperature is limited by the decomposition temperature of the surfactants or by the boiling temperature of the solvents. Furthermore, predicting the shape and size of the resultant nanomaterials is relatively hard. Typically, tedious optimization of not only the type of surfactant, but also the decomposition kinetics of the precursors, is required for the tailored synthesis of nanomaterials.^[5b]

In comparison, template synthesis by using a solid template, such as mesoporous silica materials or anionic aluminum oxide (AAO) plates, can result in the predictable and tailored synthesis of nanomaterials (Figure 1).^[6] If the materials can play the roles of both a surfactant and a template, tailored nanomaterials can be more facilely achieved by using wet-chemical synthesis. This method can be termed “colloidal template synthesis” (Figure 1).

Recently, microporous organic networks (MONs) with high surface areas have been prepared through the coupling of rigid building blocks.^[8,9] In addition, the structural morphologies of the MON materials can be controlled by using template and non-template methods.^[10] Owing to their microporosity, MONs have been applied as adsorbents for target molecules, including the precursors of nanomaterials.^[11] Herein, we report

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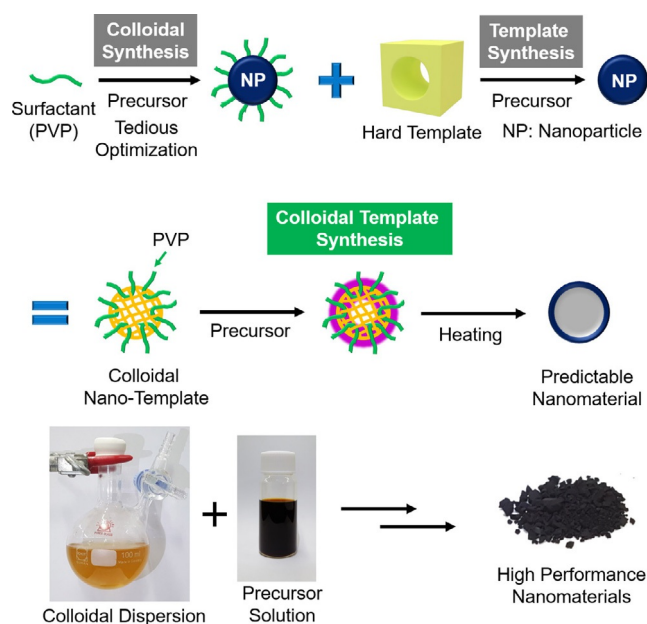


Figure 1. Schematic representations of the colloidal synthesis, template synthesis, and colloidal template synthesis.

the colloidal template synthesis of C@MoS₂ nanoadsorbents, which comprised a carbon core and a functional MoS₂ shell, by using colloidal MON nanoparticles (C-MONs), as well as their adsorption performance for cationic adsorbates.

2. Results and Discussion

For the synthesis of the C-MONs, we first grew the corresponding MONs through the Sonogashira cross-coupling reaction between organic building blocks in the presence of PVP. We selected tetra(4-ethynylphenyl)methane^[12] and 1,4-diiodobenzene as representative building blocks and optimized the molecular weight and amount of PVP. Table 1 summarizes the properties of the resultant C-MONs.

In the absence of PVP, conventional irregular MON materials (denoted as MON-1) were obtained with a broad size distribution of 376(±170) nm (Table 1, entry 1). When PVP with a molecular weight (*M_w*) of 10 000 was used, the overall size of the colloidal MON materials (C-MON-1) decreased to 114(±53) nm (Table 1, entry 2). However, the size distribution was still very broad. When PVP with *M_w*=40 000 (PVP-40 000) was used, the size of the MON particles (C-MON-2) further decreased to 82(±9) nm (Table 1, entry 3). Pleasingly, in this case, the size distribution of C-MON-2 was quite uniform. It has been reported that the presence of a surfactant retards the growth of MON materials, possibly owing to the interactions between the surfactant and the surface of the growing MON particles.^[10]

When we decreased the amount of PVP-40 000 from 1.24 g to 0.62 g and 0.31 g, the size distributions of the colloidal MON materials (C-MON-3 and C-MON-4, respectively) gradually broadened to 83(±13) and 93(±16) nm, respectively (Table 1, entries 4 and 5, and the Supporting Information, Figure S1). When we changed the volume of EtOH from 40 mL to 20 mL and 60 mL in the synthesis of C-MON-2, no significant changes

Entry	<i>M_w</i>	PVP [g]	Size [nm]	<i>S_{BET}</i> ^[b] [m ² g ⁻¹]	Name
1	none	–	376(±170)	437	MON-1
2	10 000	1.24	114(±53)	489	C-MON-1
3	40 000	1.24	82(±9)	611	C-MON-2
4	40 000	0.62	83(±13)	632	C-MON-3
5	40 000	0.31	93(±16)	498	C-MON-4
6	360 000	1.24	–	–	C-MON-5

^[a] Reaction conditions: tetra(4-ethynylphenyl)methane (0.10 g, 0.24 mmol), 1,4-diiodobenzene (0.16 g, 0.48 mmol), PVP, [PdCl₂(PPh₃)₂] (17 mg, 0.024 mmol), CuI (4.6 mg, 0.024 mmol), Et₃N (20 mL), EtOH (40 mL), 100 °C, 24 h. ^[b] Surface area was calculated by using BET theory.

in the sizes of the C-MON particles were observed. When we used PVP with *M_w*=360 000, a gel-like material (C-MON-5) was formed (Table 1, entry 6, and the Supporting Information, Figure S1). Disappointingly, C-MON-5 could not be isolated in a powdered form, owing to the small size of the material. Although the size range of the C-MON particles that were prepared in this study was not broad, we suggest that PVP with *M_w*=40 000–360 000 or other polymeric surfactants can be used to extend the size range of the C-MON particles.

Next, we investigated the MON and C-MON materials by using SEM and TEM (Figure 2). SEM analysis of MON-1 showed the presence of relatively large and irregular granules (Figure 2a). Compared with C-MON-1, the size and size distribution of C-MON-2 were smaller and narrower, respectively (Figure 2b,c). The low-magnification SEM image of C-MON-2 showed the overall homogeneity of C-MON-2 (Figure 2d). SEM images of C-MON-3 and C-MON-4 showed similar sizes to C-MON-2, but broader size distributions of the particles (see the Supporting Information, Figure S1). TEM analysis of C-MON-2 showed the adoption of a spherical morphology (Figure 2e).

The surface areas and porosities of the MON and C-MON materials were characterized based on their N₂-adsorption/-desorption isotherms, by using Brunauer–Emmett–Teller (BET) theory. Whilst the surface area of MON-1 was measured to be 437 m² g⁻¹, C-MON-2 showed an enhanced surface area of 611 m² g⁻¹ (Figure 3a). It has been reported that the decrease in the porosity of MON materials can be attributed to the local packing of networks.^[13] Therefore, we suggest that the entrapped PVP retarded the local packing of the networks, thereby enhancing the porosity and surface area of C-MON-2. The pore-size distributions of MON-1 and C-MON-2 were analyzed

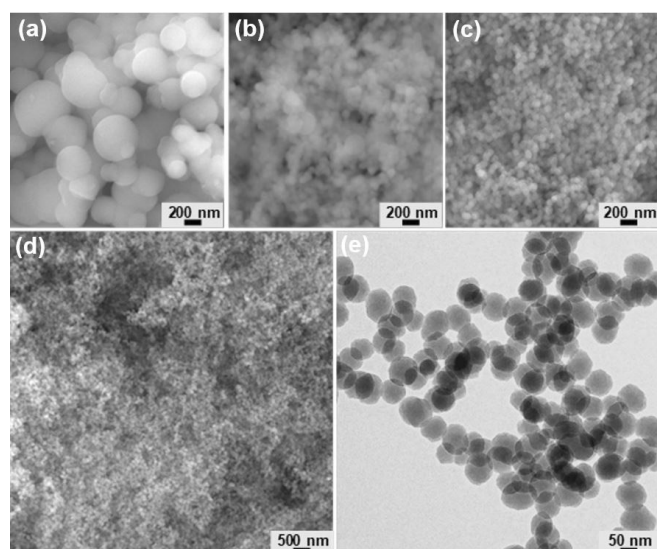


Figure 2. a–d) SEM images of MON-1 (a), C-MON-1 (b), and C-MON-2 (c, d). e) TEM image of C-MON-2.

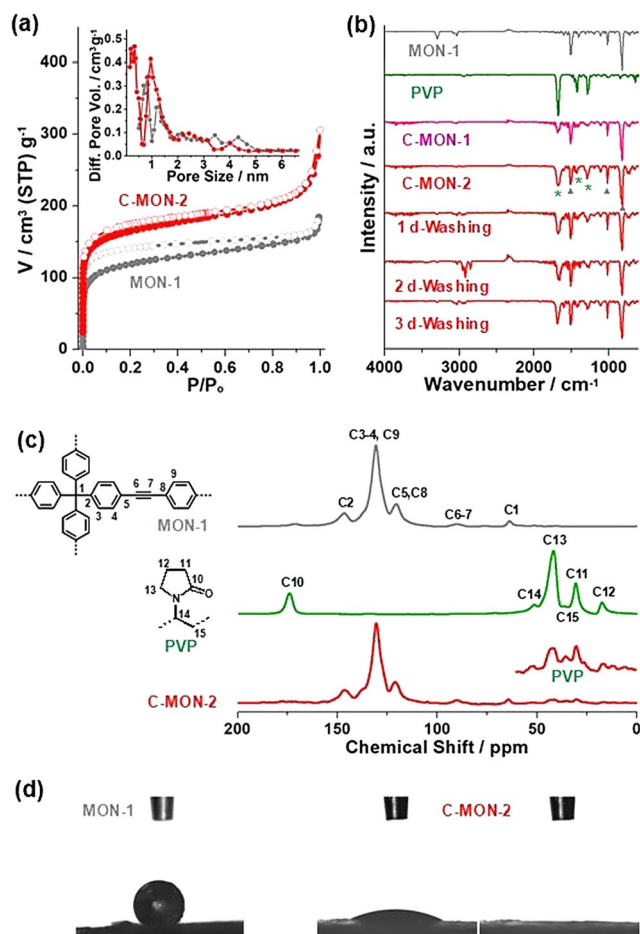


Figure 3. a) N_2 -adsorption/desorption isotherms (at 77 K) and pore-size distributions (by using the DFT method) of MON-1 and C-MON-2. b) IR absorption spectra of MON-1, PVP, C-MON-1, and C-MON-2, as well as the C-MON-2 materials after washing at reflux in EtOH for 1, 2, and 3 days. c) Solid-state ^{13}C NMR spectra of MON-1, PVP, and C-MON-2. d) Water-contact angles of MON-1 and C-MON-2. STP = standard temperature and pressure.

by using DFT calculations. Compared with MON-1, C-MON-2 showed enhanced microporosity and smaller pore sizes (Figure 3a, inset).

The entrapped PVP in C-MON-2 was characterized by using IR spectroscopy (Figure 3b). The MON-1 control material showed two main vibrations at 1507 and 822 cm^{-1} , which corresponded to C=C and C–H vibrations of the aromatic groups, respectively.^[14] By comparison, C-MON-1 and C-MON-2 showed additional vibrations at 1677, 1424, and 1286 cm^{-1} , which corresponded to the C=O, CH₂, and C–N vibrations of PVP, respectively.^[15] The amount of PVP in C-MON-2 was higher than that in C-MON-1, which indicated that PVP-40 000 was more efficient as a surfactant than PVP-10 000. During the work-up of C-MON-2, the materials were sufficiently washed with CH₂Cl₂, MeOH, and acetone. Notably, PVP-40 000 was highly soluble in these solvents, which implied that the PVP-40 000 in C-MON-2 could not be readily removed by using conventional washing procedures, thus indicating that PVP-40 000 was entrapped in the MON networks. Considering that PVP-40 000 was highly soluble in EtOH, we further washed the C-MON-2 materials with excess EtOH at reflux. However, even after washing in EtOH at reflux for three days, C-MON-2 showed almost the same intensity of PVP-40 000 in its IR absorption spectrum, thereby supporting the entrapment of PVP-40 000 in the MON networks (Figure 3b).

The chemical composition of C-MON-2 was analyzed by using solid-state ^{13}C NMR spectroscopy (Figure 3c). ^{13}C NMR peaks for the benzyl carbon, internal alkyne, and aromatic carbon atoms were observed at δ = 64, 86–95, and 121–147 ppm, respectively, which matched well with previous reports for MON materials that were prepared from the same building blocks.^[10d] Compared to MON-1, the ^{13}C NMR spectrum of C-MON-2 showed additional peaks at δ = 18, 31, 42, 52, and 174 ppm, which corresponded to PVP-40 000. According to combustion elemental analysis, the PVP content in C-MON-2 was 13.4 wt.% (N = 1.78 wt.%).

As shown in Figure 3d, MON-1 exhibited a water contact angle of 151°, owing to its organic nature. By comparison, C-MON-2 completely absorbed the water drops, thus indicating that the presence of PVP-40 000 in C-MON-2 had changed the surface properties of the MON material. Thermogravimetric analysis (TGA) revealed that C-MON-2 was stable up to 270 °C (see the Supporting Information, Figure S2). According to powder X-ray diffraction (PXRD) studies, MON-1 and C-MON-2 were both amorphous, which is the conventional state of MON materials that are prepared through the Sonogashira cross-coupling of organic building blocks (see the Supporting Information, Figure S3).^[9]

Considering the existence of PVP surfactant molecules on the surface of the C-MON-2 nanoparticles and their excellent dispersion ability in polar protic solvents, such as EtOH (Figure 1, photograph), we tested C-MON-2 as a colloidal template for the synthesis of MoS₂-based nanoadsorbents. First, MoS₂ precursor [Mo(NH₄)₂S₄] was adsorbed onto a dispersion of C-MON-2 in EtOH.^[16] Then, heat treatment of [Mo(NH₄)₂S₄]/C-MON-2 with diameters of 110–130 nm led to the formation of C@MoS₂ core-shell materials with diameters of 75–85 nm

(Figure 4a and the Supporting Information, Figure S4). We prepared three C@MoS₂ materials at different temperatures (C@MoS₂-700, C@MoS₂-800, and C@MoS₂-900, which were obtained at 700, 800, and 900 °C, respectively).

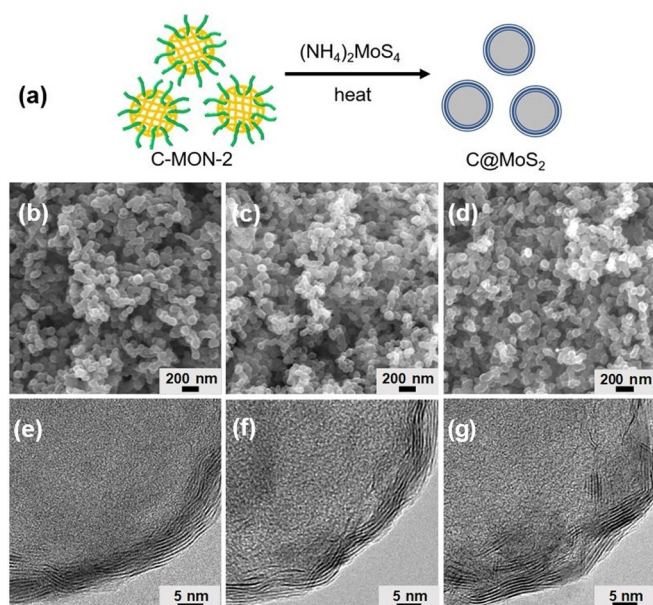


Figure 4. a) Schematic representation of the synthesis of C@MoS₂. b–d) SEM images of C@MoS₂-700 (b), C@MoS₂-800 (c), and C@MoS₂-900 (d). e–g) HRTEM images of C@MoS₂-700 (e), C@MoS₂-800 (f), and C@MoS₂-900 (g).

The sizes (75–85 nm) and shapes of C@MoS₂ replicated those of C-MON-2, thus indicating that C-MON-2 acted as a template in the formation of C@MoS₂ (Figure 4b–d). Careful analysis of the C@MoS₂ materials by using high-resolution TEM (HRTEM) revealed that MoS₂ was present in the outer part of the nanoparticles with thicknesses of 4–6 nm to form core–shell structures (Figure 4e–g). The unique layered structure of MoS₂ was clearly observed in the shells. However, as the heating temperature increased, more-flattened MoS₂ was observed in C@MoS₂, owing to the enhanced crystallinity. Elemental mapping by using electron energy-loss spectroscopy (EELS) confirmed the presence of MoS₂ in the shells and carbon in the cores of the nanostructures (Figure 5a).

X-ray photoelectron spectroscopy (XPS) of the C@MoS₂ materials revealed Mo 3d peaks at 232.33 and 229.18 eV, and S 2p peaks at 163.23 and 162.03 eV (Figure 5b), which matched well with those of previously reported MoS₂ materials.^[3b–j] Raman spectroscopy revealed the presence of D and G bands for the carbon components in C@MoS₂-700 at 1357 and 1587 cm^{−1}, respectively, with an *I*_D/*I*_G ratio of 0.82. The D and G bands in C@MoS₂-800 and C@MoS₂-900 were shifted to 1360 and 1592 cm^{−1}, respectively, whilst the *I*_D/*I*_G ratios of C@MoS₂-800 and C@MoS₂-900 were 0.83 and 0.85, respectively (see the Supporting Information, Figure S5). Based on the elemental analysis, the MoS₂ content in C@MoS₂-700, C@MoS₂-800, and C@MoS₂-900 were 57, 56, and 56 wt.%, respectively.

According to the N₂-adsorption/desorption isotherms, the surface areas of C@MoS₂-700, C@MoS₂-800, and C@MoS₂-900

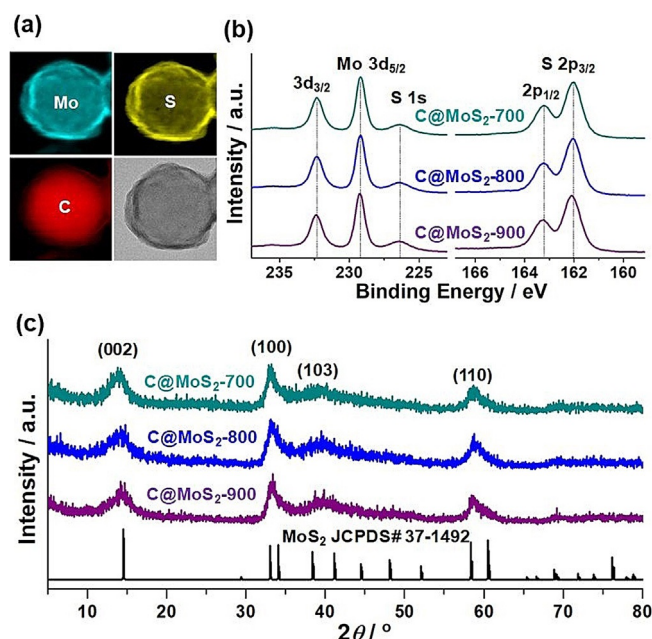


Figure 5. a) EELS elemental mapping images of Mo, S, and C in C@MoS₂-700. b) XPS spectra (Mo 3d and S 2p orbitals) and c) PXRD patterns of the C@MoS₂ materials.

were 418, 423, and 508 m² g^{−1}, respectively (see the Supporting Information, Figure S6). PXRD studies of C@MoS₂-900 showed diffraction peaks at 14.3, 33.1, 38.3, and 58.3°, which corresponded to the (002), (100), (103), and (110) diffraction peaks of MoS₂ (JCPDS#37-1492), respectively (Figure 5c).^[3b–j] As the temperature decreased from 900 °C to 800 and 700 °C, the (002) peaks broadened and gradually shifted from 14.3° to 14.1° (C@MoS₂-800) and 13.8° (C@MoS₂-700), thus indicating the elongation of the interlayer distance in MoS₂, and a decrease in crystallinity.

Next, considering the core–shell structures, nanoscale diameters, and high surface areas of the C@MoS₂ materials, we studied their adsorption performance towards two cationic dyes, methylene blue (MB) and rhodamine B (RhB). In addition, we also prepared MoS₂ nanosheets (MoS₂-NS), submicron-sized C@MoS₂ (S-C@MoS₂), and carbon nanoparticles (C-NP) as control materials (Figure 6a and the Supporting Information, Figures S7 and S8) and tested their adsorption performance (Figures 6 and 7).

Compared with the relatively poor adsorption performance of C-MON-2, MoS₂-NS, S-C@MoS₂, and C-NP, C@MoS₂ showed excellent adsorption towards the cationic MB dye (Figure 6b). Furthermore, the adsorption ability gradually increased from C@MoS₂-700 to C@MoS₂-800 and C@MoS₂-900, possibly owing to the increased surface area. Whilst C-MON-2 exhibited a positive zeta potential of 14.8 mV, C-NP, S-C@MoS₂, C@MoS₂-700, C@MoS₂-800, C@MoS₂-900, and MoS₂-NS all exhibited negative zeta potentials of −13.3, −29.8, −38.1, −38.4, −39.5, and −40.7 mV, respectively (Figure 6c, Table 2, and the Supporting Information, Figure S8). The zeta potentials of previously reported MoS₂-based adsorbents were all within the range −20.6–−36.0 mV (Table 2).^[3b–j]

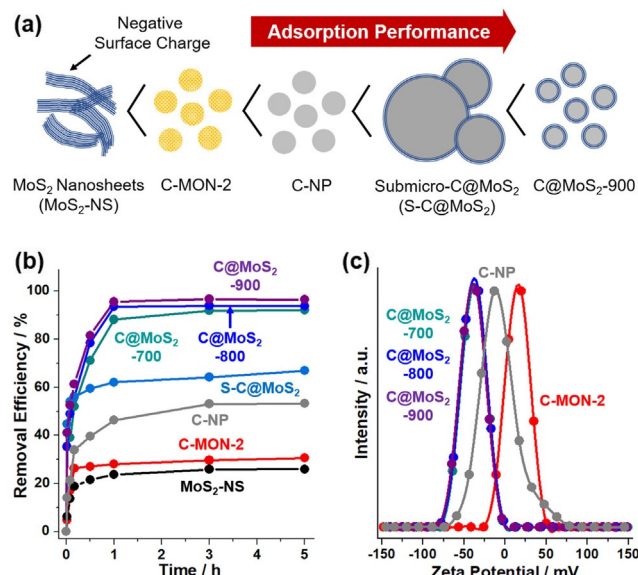


Figure 6. a) Structural comparison of C@MoS₂ with the control materials. b) Adsorption performance of C@MoS₂, S-C@MoS₂, MoS₂-NS, C-NP, and C-MON-2 (5 mg) for methylene blue ($C_0 = 200$ ppm, 5 mL). c) Zeta potentials of C@MoS₂, C-NP, and C-MON-2.

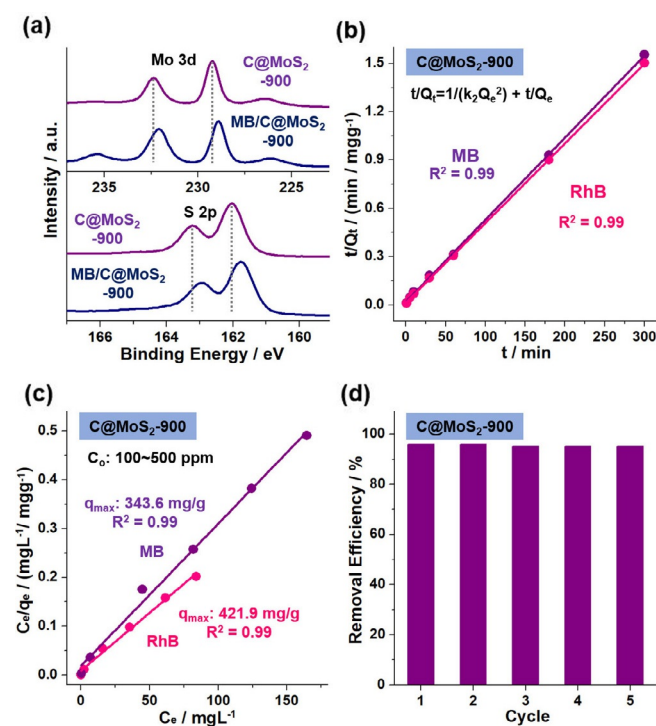


Figure 7. a) XPS spectra of the Mo 3d and S 2p orbital peaks for C@MoS₂-900 before and after the adsorption of MB. b) Adsorption kinetic (pseudo-second-order behavior) of C@MoS₂-900 for MB and RhB. c) Langmuir plots of the adsorption behavior of C@MoS₂-900 towards MB and RhB. d) Recyclability of C@MoS₂-900 (5 mg) for the adsorption of MB ($C_0 = 200$ ppm, 5 mL).

C@MoS₂-900 showed relatively poor adsorption performance for an anionic dye, methyl orange, thus indicating that coulombic interactions between the negatively charged surface of

Entry	Material	Zeta potential [mV]	$S_{\text{BET}}^{[a]}$ [m ² g ⁻¹]	$q_{\text{max}}^{[b]}$	Ref.
1	C@MoS ₂ -900	−39.5	508	343.6 ^[c] 421.9 ^[d]	this work
2	flower-like MoS ₂	−	18.68	49.2 ^[d]	[3b]
3	porous MoS ₂	−	76.85	119.1 ^[c]	[3c]
4	ultrathin MoS ₂	−36.0	15.09	146.4 ^[c]	[3d]
5	MoS ₂ microspheres	−	−	87.4 ^[c]	[3e]
6	flower-like MoS ₂	−20.6	−	231.3 ^[d]	[3f]
7	MoS ₂ sponge	−21.0	26.38	104.8 ^[d]	[3g]
8	PAN-MoS ₂ nanofibers	−	−	77.7 ^[d]	[3h]
9	MoS ₂ -glue sponges	−21.0	−	127.4 ^[d]	[3i]

[a] Surface area was calculated by using BET theory; [b] maximum adsorption capacity was obtained from the Langmuir plots; [c] for methylene blue; [d] for rhodamine B. PAN = poly(acrylonitrile).

MoS₂ and a cationic dye was critical for efficient adsorption (see the Supporting Information, Figure S9). It has previously been reported that the surface of MoS₂ consists of negatively charged sulfide groups and counteranions, such as H⁺, and that the adsorption/desorption of cationic adsorbates onto/from the surface of MoS₂ results from ion exchange between the adsorbates and the adsorbents.^[1,3b–j] According to our XPS studies, the Mo 3d and S 2p peaks of C@MoS₂-900 were red-shifted by 0.25 and 0.28 eV, respectively, following the adsorption of MB, thus indicating the existence of interactions between Mo-2S dipoles and the adsorbates (Figure 7a).^[3b–j]

The adsorption kinetics of C@MoS₂-900 for MB and RhB showed pseudo-second-order behavior, which matched with the conventional results of other previously reported MoS₂-based adsorbents (Figure 7b and the Supporting Information, Figure S10).^[4–11] The adsorption behavior of C@MoS₂-900 towards MB and RhB was well-fitted by the Langmuir model with $R^2 > 0.99$ (Figure 7c). Based on the Langmuir plot, the maximum adsorption capacities (q_{max}) of C@MoS₂-900 for MB and RhB were calculated to be 343.6 and 421.9 mg g⁻¹, respectively (Figure 7c).

The adsorption performance of C@MoS₂-900 was superior to those ($q_{\text{max}} = 49.2\text{--}231.3$ mg g⁻¹ for MB and RhB, based on the Langmuir plot) of other reported MoS₂-based adsorbents (Table 2).^[3b–j] We suggest that the excellent adsorption performance of C@MoS₂-900 compared with C-MON-2, MoS₂-NS, and S-C@MoS₂ was owing to their size (80 nm), negative zeta potential (−39.5 mV), high surface area (508 m² g⁻¹), and core-shell structure (Figure 6b,c and Table 2). Notably, the diameters and surface areas of other recently reported MoS₂-based adsorbents were within the range 100 nm–2 μm and 15.09–76.85 m² g⁻¹, respectively (Table 2).^[3b–j]

C@MoS₂-900 could be recycled through simple washing with excess protic solvent and maintained its adsorption performance with removal efficiencies of 95–94% for MB over five successive adsorption cycles (Figure 7d). SEM images of C@MoS₂-900 that were recovered after five successive adsorption cycles showed complete retention of the original morphology (see the Supporting Information, Figure S11).

3. Conclusions

The so-called colloidal template synthesis, which is based on the chemistry of microporous organic networks, has been applied to the preparation of C@MoS₂ nanoadsorbents. Colloidal MON nanotemplates that contained entrapped PVP were prepared through the growth of MONs in the presence of PVP and showed excellent dispersion ability in EtOH. Owing to the high porosity of the MON nanotemplates, MoS₂ precursors were readily loaded into the colloidal templates. Heat treatment of the precursor/C-MON materials afforded surface-engineered core-shell nanoadsorbents. The C@MoS₂ materials showed excellent adsorption performance towards cationic dyes. We think that this colloidal template synthesis can be used for the more-efficient preparation of tailored and predictable nanomaterials compared with the conventional colloidal wet-chemical synthesis. In addition, we believe that the colloidal template synthesis as described herein can be readily extended to a variety of other inorganic nanomaterials.

Experimental Section

Characterization

The sizes and morphologies of the synthesized materials were investigated by using SEM and TEM on an FE-SEM (JSM7100F) and a JEOL 2100F, respectively. The surface areas and porosities of the materials were investigated by using N₂-adsorption/-desorption isotherms, which were recorded at 77 K on a BELSORP II-mini and a Micromeritics ASAP2020. The pore-size distributions of the materials were analyzed by using DFT calculations. IR spectroscopy was performed on a Bruker VERTEX 70 FTIR spectrometer. Solid-state ¹³C NMR spectroscopy was performed in cross-polarization-total side band suppression (CP-TOSS) mode on a 500 MHz Bruker ADVANCE II NMR spectrometer at the National Center for Inter-University Research Facilities (NCIRF), Seoul National University, by using a 4 mm magic angle spinning probe. PXRD studies were performed on a Rigaku MAX-2200. TGA was performed on a Seiko Exstar 7300. Combustion elemental analysis was performed on a CEA1110 analyzer. Water contact angles were measured on a Theta Optical Tensiometer (KSV instruments, Ltd.). Elemental mapping images were recorded by using EELS on a JEOL 2100F. XPS was performed on a Thermo VG spectrometer. Raman spectroscopy was performed on a Renishaw inVia Raman spectrometer. Zeta potentials were measured on a Zetasizer ZS90 (Malvern). UV/Vis absorption spectroscopy was performed on a JASCO V-760.

Synthesis of the Colloidal MON Nanotemplates (C-MON)

Tetra(4-ethynylphenyl)methane was prepared according to a literature procedure.^[12] For the synthesis of C-MON-2, [PdCl₂(PPh₃)₂] (17 mg, 24 μmol), CuI (4.6 mg, 24 μmol), and Et₃N (20 mL) were added to a flame-dried Schlenk flask (100 mL) under an argon atmosphere. PVP (1.24 g, M_w = 40 000; Aldrich Co.) was dissolved in EtOH (40 mL), the solution was added to the Schlenk flask, and the reaction mixture was sonicated for 40 min at RT. Then, tetra(4-ethynylphenyl)methane (0.10 g, 0.24 mmol) and 1,4-diiodobenzene (0.16 g, 0.48 mmol) were added and the mixture was heated at 100 °C for 24 h. After cooling to RT, the powder was separated by using centrifugation, washed with CH₂Cl₂, MeOH, and acetone (2 × 50 mL each), and dried under vacuum.

For the synthesis of the control MON material, MON-1 (see Table 1), the same procedure was used without the addition of PVP. For the synthesis of C-MON-1, PVP with M_w = 10 000 (1.24 g) was used instead of PVP (1.24 g) with M_w = 40 000. The other steps were the same as in the synthesis of C-MON-2.

Synthesis of C@MoS₂ and Control Materials MoS₂-NS and S-C@MoS₂

The MoS₂ precursor, [Mo(NH₄)₂S₄], was prepared according to a literature procedure.^[16] For the synthesis of C@MoS₂-800, C-MON-2 (50 mg) was dispersed in MeOH (20 mL) in a flame-dried two-necked Schlenk flask (50 mL) under an argon atmosphere and the mixture was sonicated for 1.5 h. Then, (NH₄)₂MoS₂ (0.114 g, 0.438 mmol) was added and the mixture was heated at 80 °C overnight. Next, MeOH was removed on a rotary evaporator and the solid was dried under vacuum for 8 h. The resultant powder was washed with water (50 mL) to remove any excess (NH₄)₂MoS₂ and dried under vacuum for 12 h. For the preparation of C@MoS₂-800, (NH₄)₂MoS₂/C-MON-2 was heated at 800 °C in a furnace under an argon atmosphere for 3 h. Prior to heating, argon gas was flowed through the furnace for 30 min. The temperature was increased from RT to 800 °C at a rate of 5 °C min⁻¹ and then maintained at 800 °C for 3 h. After cooling to RT, C@MoS₂-800 was obtained. For the preparation of C@MoS₂-700 and C@MoS₂-900, (NH₄)₂MoS₂/C-MON-2 was heated at 700 and 900 °C, respectively, for 3 h.

For the preparation of submicro-C@MoS₂ (S-C@MoS₂), the same procedure was used as for C@MoS₂-900, except that MON-1 (50 mg) was used instead of C-MON-2. For the preparation of MoS₂-nanosheets (MoS₂-NS), the same procedure was used as for C@MoS₂-900, except that PVP-40 000 (6.7 mg) was used instead of C-MON-2. For the preparation of carbon nanoparticles (C-NP), C-MON-2 was heated at 800 °C in a furnace under an argon atmosphere for 3 h. Prior to heating, argon gas was flowed through the furnace for 30 min. The temperature was increased from RT to 800 °C at a rate of 5 °C min⁻¹ and then maintained at 800 °C for 3 h. After cooling to RT, C-NP was obtained.

Adsorption Studies

Methylene blue (MB, 25.0 mg) was dissolved in distilled water to form a 500 mL stock solution (50 ppm) in a volumetric flask, from which 6.25, 5.00, 3.75, 2.50, and 1.25 ppm solutions were prepared through dilution. These solutions were used for the calibration curve of absorbance (at λ = 664 nm) versus concentration of MB.

MoS₂@C-900 (5.0 mg) was added to an aqueous solution of MB (200 ppm, 5 mL) in a vial (10 mL). This process was repeated to prepare seven identical samples. The vials were all wrapped in aluminum foil to prevent the possible photodecomposition of MB and the solutions were stirred at 800 rpm at 23 °C. After a certain time for each sample (1 min, 5 min, 10 min, 30 min, and 1 h, 3 h, and 5 h), MoS₂@C-900 was separated by using a syringe filter. Then, the filtrates were diluted to ratios of 1:20 and 1:10, and the concentrations of MB in the filtrates were analyzed by using UV/Vis absorption spectroscopy, with reference to the calibration curve. The removal efficiency (RE) was defined as RE (%) = [(initial concentration - final concentration) × 100] / initial concentration. The same procedures were used for MoS₂@C-700, MoS₂@C-800, and the control materials (MoS₂-NS, S-C@MoS₂, C-MON-2, and C-NP). For the adsorption of RhB and methyl orange (MO), the same procedure was used as for MB, except that RhB and MO were used instead. For the Langmuir plot,^[17] MoS₂@C-900 (5.0 mg) was added to six separate solutions of MB (100, 200, 300, 400, 450, and 500 ppm;

5 mL each) in individual vials (10 mL). The vials were wrapped in aluminum foil to prevent the possible photodecomposition of MB. After stirring at 800 rpm at 23 °C for 1 h, MoS₂@C-900 was separated by using centrifugation. The concentrations of MB in the filtrates were analyzed by using UV/Vis absorption spectroscopy, with reference to the calibration curve. The adsorption capacity at equilibrium was calculated according to Equation (1), in which C_i denotes the initial concentration of MB, C_e denotes the concentration of MB at equilibrium, V denotes the volume of the solution, and m denotes the amount of adsorbents.

$$q_e = [(C_i - C_e) \times V] / m \quad (1)$$

Next, a Langmuir plot (C_e/q_e vs. C_e) was created, based on the relationship shown in Equation (2), in which $q_{\max}$ (in mg g⁻¹) denotes the monolayer adsorption capacity and K_L (in L mg⁻¹) denotes the Langmuir isotherm constant.

$$C_e/q_e = 1/[q_{\max}K_L] + C_e/q_{\max} \quad (2)$$

The $q_{\max}$ value was obtained from the slope of the Langmuir plot. For the Langmuir plot and the $q_{\max}$ value for RhB, the same procedure was used as for MB, except that RhB was used instead.

For the recyclability tests, MoS₂@C-900 (5 mg) was added to a solution of MB (200 ppm, 5 mL) in a vial (10 mL). Then, the vial was wrapped in aluminum foil to prevent the possible photodecomposition of MB. The solution was stirred at 800 rpm at 23 °C for 1 h and then MoS₂@C-900 was recovered onto filter paper by using a syringe filter, washed with excess water and MeOH under sonication, and dried under vacuum. To maximize the recovery of the material, any residual MoS₂@C-900 on the filter paper was recovered by using sonication in MeOH, centrifugation, washing with MeOH, and drying under vacuum. The recovered MoS₂@C-900 was used directly in the next run.

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Conflict of interest

The authors declare no conflict of interest.

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