

Multifunctional Composites by Self-assembly of Monodisperse Iron Oxide Nanoparticles and Nanolamellar MoS₂ Plates

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1. Experimental Section

1.1 Materials

Ethyl 2-bromoisobutyrate (98%), CuCl (99%), triethylamine (TEA, >99%), 1,1,4,7,10,10-hexamethyltriethylenetetramine (97%), (CH₃)₂SO₄, (99%), oleic acid (technical grade, 90%) were purchased from Sigma-Aldrich and used as received. Sodium sulfide (Na₂S•9H₂O, EM Science) was used without further purification. Iron(III) acetylacetonate (Fe(acac)₃, 99+%), 1,2-hexadecanediol (98%), oleylamine (80-90%), benzyl ether (99%) were purchased from Acros Organics and used as received. Stearyl methacrylate (SMA) technical grade, Sigma-Aldrich) was passed through basic Al₂O₃ (50 – 200 μm, Acros Organics) column. 2-(Dimethylamino)ethyl metacrylate (DMAEM, Sigma-Aldrich, 98%) was distilled in vacuum and stored in the freezer at -18 °C under argon. 1,4-Dioxane (Sigma-Aldrich, 99%) was distilled over Na. Dimethylsulfoxide (DMSO, Sigma-Aldrich, 99.9%) was distilled over BaO under vacuum.

Purified natural MoS₂ powder (DM-1, Scopin factory, Russia) with a particle size (95%) smaller than 7 μm was used as received. The n-butyllithium solution (1.6 M) in hexane was purchased from Sigma-Aldrich. Hexane (95%, Sigma-Aldrich) was distilled over LiAlH₄.

1.2 Synthesis of Iron Oxide Nanoparticles (NPs)

NPs1. In a typical experiment, a three neck round-bottom flask equipped with a reflux condenser, a stir bar, and two septa was loaded with Fe(acac)₃ (0.71 g, 2 mmol), 1,2-hexadecanediol (1.74 g, 10 mmol), oleic acid (2.03 g, 6 mmol), oleylamine (1.61 g, 6 mmol), and benzyl ether (20 mL). The reaction mixture was treated under stirring at 50 °C in vacuum for 30 min for drying and reagent solubilization and then the reaction flask was filled with argon. Then the reaction mixture was heated to 200 °C for 50 min under an argon flow, stirred at this temperature for 70 min, then heated to reflux (~300 °C) with a heating rate of 3.3 °C/min and kept refluxing for 30 min. The dark solution was cooled to room temperature. Ethanol (40 mL) was added to the reaction flask to precipitate the NPs. Then the NPs were separated by centrifugation and washed twice with a mixture of ethanol : hexane=2 : 1. The resultant NPs were dissolved in hexane and the insoluble aggregates were removed by centrifugation. Finally, 9 mL of the stable clear solution with a concentration of 16.6 mg mL⁻¹ of NPs1 was obtained.

NPs2. The NPs2 specimen was obtained as a stable, clear hexane solution (12 mL) with concentration of 11.3 mg mL⁻¹ using the method described elsewhere.¹⁻³

Diameters of NPs1 and NPs2 were obtained from transmission electron microscopy (TEM) images using the ImageJ program and were 5.1 ± 0.4 nm and 11.6 ± 0.8 nm, respectively.

1.3 Synthesis of poly(DMAEM-*co*-SMA)

DMAEM (0.94 g, 5.94 mmol), SMA (1.0 g, 2.97 mmol), 1,1,4,7,10,10-hexamethylenetriethyleneamine (25.5 mg, 0.111 mmol), ethyl 2-bromoisobutyrate (10.8 mg, 55.4 μ mol) and 1,4-dioxane (1.9 mL) were loaded into a Schlenk tube equipped with a magnetic stir bar. The tube was subjected to three freeze–pump–thaw cycles and filled with argon. CuCl (11 mg, 0.111 mmol) was added to the tube under argon flow; the tube content was sealed and stirred for 1 h at ambient temperature. Then it was placed into the oil bath and stirred for 22 h at 75 °C. After cooling to ambient temperature, the tube content was dissolved in methylene chloride, precipitated in tenfold excess of acetonitrile, decanted, washed with acetonitrile, dissolved in a 5 : 1 mixture of methylene chloride : methanol and passed through the column filled with Al₂O₃. After removing the solvents and drying under vacuum at 45 °C for 4 h, 1.77 g (91% yield) of poly(DMAEM-*co*-SMA) copolymer were obtained.

The number average molecular weight $M_n=27.1$ kDa and $M_w/M_n = 1.13$ were found using GPC method. The numbers of DMAEM and SMA chain segments $l = 88$ and $m = 39$, respectively were calculated, using GPC and ¹H NMR data by measuring the ratio of the NMR signals of 16 methylene groups (32H, $\delta = 1.25$ ppm) of the SMA chain segment to those of the methyl signal (6H, $\delta = 2.27$ ppm) of the DMAEM chain segment. The dimethylamine group content which is equal to 3.23 mmol per gram of the copolymer was calculated in the same manner.

1.4 Synthesis of poly(DMAEMQ-*co*-SMA)

N-methylation of copolymer by Me₂SO₄ to produce positively charged 2-(trimethylammonium)ethyloxycarbonyl methyl sulfate side group in polymer chain was performed in the following way. Poly(DMAEM-*co*-SMA) (1.54 g, 4.97 mmol of dimethylamine groups) was loaded into a three-neck flask equipped with a tube for argon inlet, a reflux condenser and a magnetic stir bar, and was dissolved in 15 mL of dry chloroform. The flask was placed in a water bath and Me₂SO₄ (0.627 g, 4.97 mmol) was added to the copolymer solution upon vigorous stirring. Then the flask content was allowed to stir for 20 min at ambient temperature and 1 h at 50 °C. After cooling, precipitation in 80 mL of dry ethyl ether, washing with ether, filtering and drying under vacuum for 3 h at 50 °C, 2.06 g (95%) of (DMAEMQ-*co*-SMA) was obtained.

1.5 The coating of NPs with copolymer

The coating was carried out according to a modified procedure described elsewhere.⁴ In a typical experiment, 120 mg of copolymer was dissolved in a mixture of 0.6 mL of MeOH and 0.6 mL of CHCl₃ and diluted with 4 mL of CHCl₃. The NP solution in hexane (2.41 mL, 16.6 mg mL⁻¹) and 0.48 mL of DMSO were added to a copolymer solution and the mixture was stirred for 10 min. Solvents were removed from the mixture using rotary evaporator under vacuum for 15-20 min at 35 °C and additionally for 15-20 min at room temperature. Then 18.5 mL of deionized water was added to the viscous residue and the mixture was stirred overnight. After that the solution of the copolymer-coated NPs was sonicated at 60 °C, cooled to room

temperature and separated from insoluble aggregates by centrifugation at 6,000 rpm for 15 min. Usually, the aggregates were absent. Excess of a copolymer was removed by ultracentrifugation for 2 h at 40,000 rpm and 16 °C followed by dissolution in 19 mL of water and repeated ultracentrifugation in the same conditions. Finally 6 mL of the stable clear solution with the concentration of 10.7 mg mL⁻¹ of NPs was obtained. The yield of the purified polymer-coated NPs was 84%. Both NPs1 and NPs2 were coated by this method and designated as NPs1c and NPs2c. The elemental analysis data for NPs1c, found (%): 1.55 N; 28.04 C; 5.05 H; 2.47 S; 31.89 Fe; for NPs2c, found (%): 2.02 N; 36.69 C; 6.55 H; 2.49 S; 22.74 Fe.

1.6 Preparation of MoS₂ single-layer dispersions

The preparation was carried out according to the procedure described elsewhere.⁵

Initially, MoS₂ was intercalated with lithium by treating it with a 1.5-fold excess of a 1.6 M n-butyllithium solution in hexane for one week followed by washing with dry hexane and vacuum drying. Then, the obtained product, Li₁MoS₂, was placed in bi-distilled water, sonicated for 15 min and then stirred on a magnetic stirrer for 30 min to prepare the 1 mg mL⁻¹ aqueous dispersion of MoS₂. This dispersion was used as is or after dilution to 0.2 mg mL⁻¹.

1.7 Interaction of copolymer-coated NPs and MoS₂ monolayer dispersion at different component ratios

Experiments were carried out by mixing aqueous 0.2 mg mL⁻¹ dispersions of both polymer-coated NPs and freshly prepared MoS₂ single layers at different weight ratios of the components: NPs(1,2)c : MoS₂ = 10:1 (2 mL + 0.2 mL), 5:1 (2 mL + 0.4 mL), 1:1 (2 mL + 2 mL), 1:5 (0.4 mL + 2 mL), and 1:10 (0.2 mL + 2 mL).

In a typical experiment for preparation of the NPs2c : MoS₂=1:1 nanohybrid used in catalytic experiments, a solution of 20 mg of NPs2c in 6.1 mL of water was added to 20 mL of the MoS₂ single-layer dispersion with a concentration of 1 mg mL⁻¹ (containing 20 mg of MoS₂). The mixture was stirred on a magnetic stirrer for 1 h. The precipitate formed was isolated by centrifugation, washed with 0.001M HCl and then three times with water and dried in vacuum. The elemental analysis data, found (%): C 15.19, H 2.41, N 0.75, Fe 6.8, Mo 29.95. In other experiments, the precipitate was not separated from the supernatant to evaluate the degree of NP incorporation.

Exfoliation of LiMoS₂ directly in the NPs1c solution was carried out by adding 15 mL of the NP solution (1 mg mL⁻¹ concentration) to 15 mg of LiMoS₂ in inert atmosphere. The mixture was sonicated for 15 min and stirred for 1 hr. The isolation and purification procedures were similar to that described above.

1.8 Catalytic oxidation of sulfide ion

Catalytic oxidation of sulfide ion was performed at 25 °C under 1 atm of a molecular oxygen pressure in a 250 mL three-neck flask placed in the temperature controlled water bath. The flask was equipped with a magnetic stir bar, and connected with an oxygen inlet and gas burette. The flask was purged three times with oxygen, filled with oxygen, and then charged with the catalyst and 25 mL of 0.1 M Na₂S aqueous solution under oxygen flow and then sealed. The rates of catalytic oxidation were evaluated under continuous stirring on the basis of the oxygen consumption, which was measured using a gas burette. For reuse of the magnetically recoverable catalyst, it was collected and separated from the reaction using a rare earth magnet placed at the side of the flask followed by solution decantation. The recovered catalyst was washed with water three times and then dried in a vacuum oven overnight.

1.9 Characterization

^1H NMR (400 MHz) spectra were recorded at room temperature on the Bruker AC 400 spectrometer in CDCl_3 as a solvent (tetramethylsilane was used as a reference).

The molecular weight and molecular weight distribution (M_w/M_n) data were obtained by gel permeation chromatography (GPC) at 25 °C with the PL Gel 5 μm MIXED-C Polymer Laboratories column, connected to an Agilent 1100 refractive index detector. The eluent was THF containing 2% of TEA at a flow rate of 1.0 mL min^{-1} . Eight near-monodisperse polystyrene standards (M_p) 100–965 000 g mol^{-1} were used for calibration. The data were analyzed using Agilent Chemstation software.

Transmission electron microscopy (TEM) images were obtained using an electron microscope LEO 912 AB OMEGA (Karl Zeiss) with accelerating voltage 100 kV. Particle analysis was carried out using ImageJ software on at least 300 particles. TEM of hybrid crosssections was performed with a JEOL JEM1010 transmission electron microscope operated at accelerating voltage of 80 kV. The hybrid powders were embedded in epoxy resin and subsequently microtomed at ambient temperature. Images of the resulting thin sections (*ca.* 50 nm thick) were collected with the Gatan digital camera.

X-Ray powder diffraction (XRD) patterns of hybrids were measured on a D8 Advance (Bruker AXS) diffractometer in the Bragg-Brentano focusing geometry using $\text{CuK}_{\alpha 1}$ radiation, angular step was 0.02° , and the scan rate was $0.5\text{--}2^\circ \text{ min}^{-1}$. Powder patterns of NPs were collected on an Empyrean (PANalytical) diffractometer (Cu K_{α} radiation, the step-size was 0.02°). The samples were placed on flat holders.

Nitrogen physisorption was conducted at the normal boiling point of liquid nitrogen using a BECMAN COULTER SA 3100 apparatus (COULTER CORPORATION, Miami, Florida). Samples were degassed in a BECMAN COULTER SA-PREP apparatus for sample preparation (COULTER CORPORATION, Miami, Florida), at 120 °C in vacuum for 1 h, prior to the analysis. Brunauer-Emmett-Teller (BET) surface area was used for comparison.

ζ -potential measurements were performed using Malvern Zetasizer Nano ZS. ζ -potential potential was measured at pH 7.4. Data was processed using the absorption of bulk iron oxide, the indices of refraction of iron oxide and solvent, and the viscosity of the pure water. The Smoluchowski approximation was used to convert the electrophoretic mobility to a ζ -potential.

2. Results

The structure and morphology of exfoliated-restacked MoS_2 was previously described in refs.^{6,7}. The sizes of MoS_2 nanoplates and especially the monolayers constituting these plates are hardly visible in TEM images, because of strong tendency of the layered particles to parallel orientation and overlap with each other on a TEM grid. Nevertheless, a close look at the TEM images shows that these particles contain from several to several tens of MoS_2 monolayers, whose sizes range from 10 to 50 nm.⁶ Recent X-ray diffraction analysis of the crystallite sizes in the restacked MoS_2 revealed that the mean thickness is 10.2–12.3 nm (16–20 monolayers of MoS_2).⁸

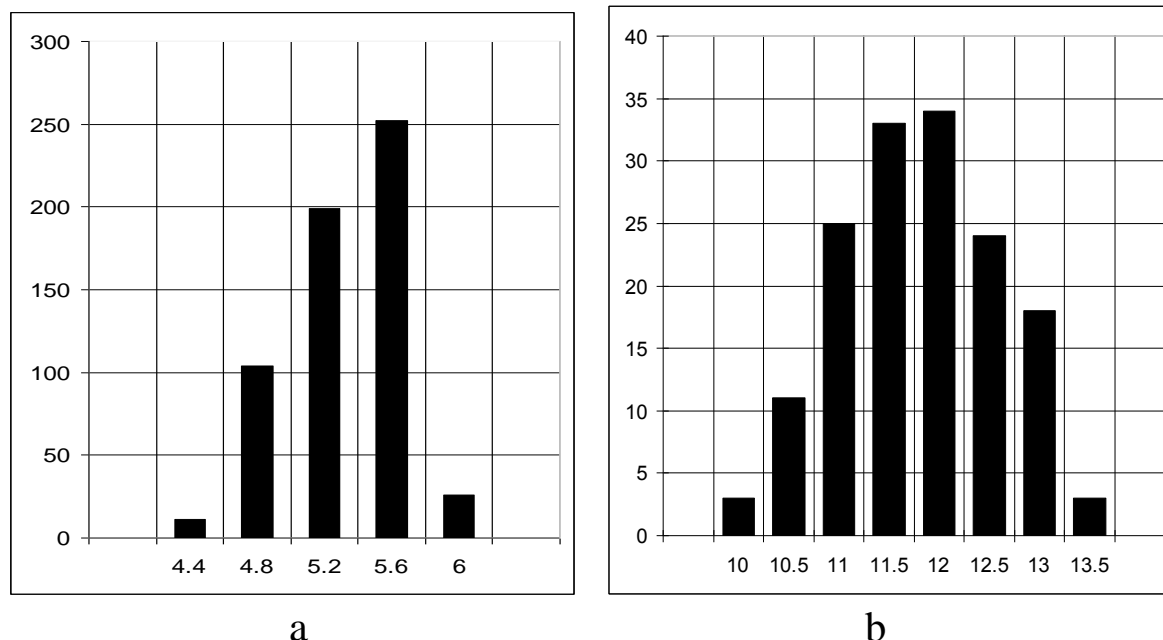


Figure S1. Histograms of NPs1 (a) and NPs2 (b) samples presented in Figure 1a and b.

The two copolymers at the monomer ratios SMA : DMAEM equal to 1 : 2 and 1 : 3 were synthesized but only the former one was used in our studies due to the preferable balance between hydrophobic and hydrophilic units. It was sufficiently hydrophobic to coat hydrophobic NPs but could be also transferred to water from an alcohol solution. This allowed easy separation of coated NPs from the copolymer excess by ultracentrifugation in water. The copolymer had $M_n=27.1$ kDa, narrow molecular weight distribution ($M_w/M_n = 1.13$) and the DMAEM : SMA ratio (2.2) close to that in the reaction mixture (2.0). We believe this chain segment relationship is the result of nearly equal reactivity of both methacrylates.

The NP coating was carried out modifying the procedure described elsewhere.⁴ The major feature of this method is addition of DMSO which allows the NP/copolymer mixture to stay in solution before addition of water or buffer, thus avoiding formation NP-copolymer films.⁹⁻¹¹ This modified procedure resulted in 100% coated NP yield without any aggregation. It is worth noting that poly(DMAEMQ-*co*-SMA) is poorly soluble in DMSO indicating that when DMSO is added and hexane is removed, the copolymer has already capped the NPs.

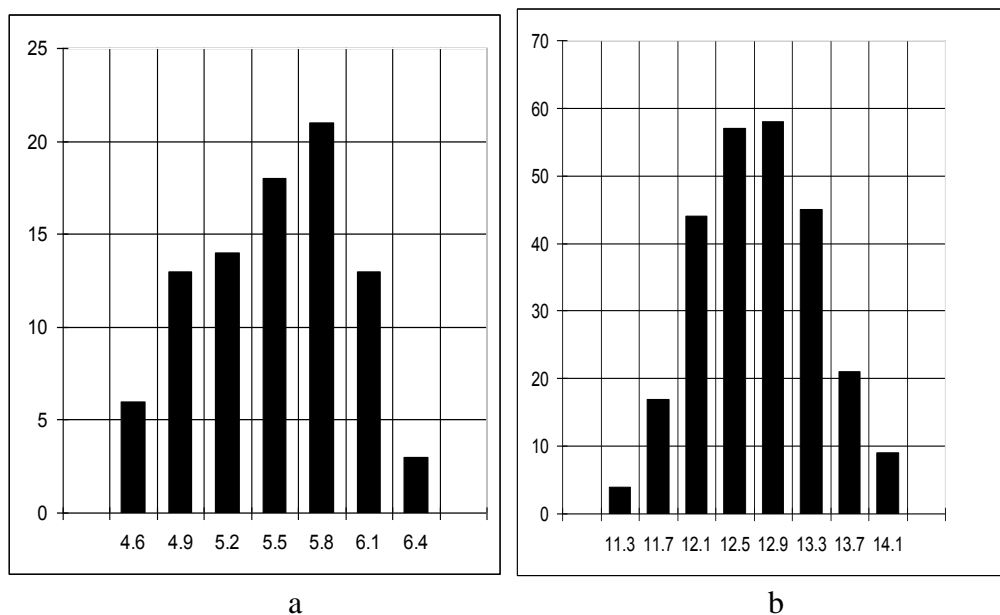


Figure S2. Histograms of NPs1c (a) and NPs2c (b) samples presented in Figure 2a and b.

From the nitrogen content obtained from the elemental analysis for both coated NPs and the copolymer (3.33 wt.%), the copolymer contents in NPs1c and NPs2c were found to be 47% and 62%, respectively. Results in close agreement were obtained from the TGA data presented in Figure S3. The weight losses not associated with adsorbed water, i.e., above 120 °C, were 44% and 55% for NPs1c and NPs2c, respectively. It seems, however, counterintuitive: smaller NPs with a higher surface area are expected to have a higher amount of capping molecules. The opposite trend can be explained by the influence of the NP curvature on the NP coating with poly(DMAEMQ-*co*-SMA). Apparently, on the NP surface with higher curvature (NPs1c) the copolymer attaches less densely, than on NPs with lower curvature (NPs2c). Similar observations were reported in ref.¹².

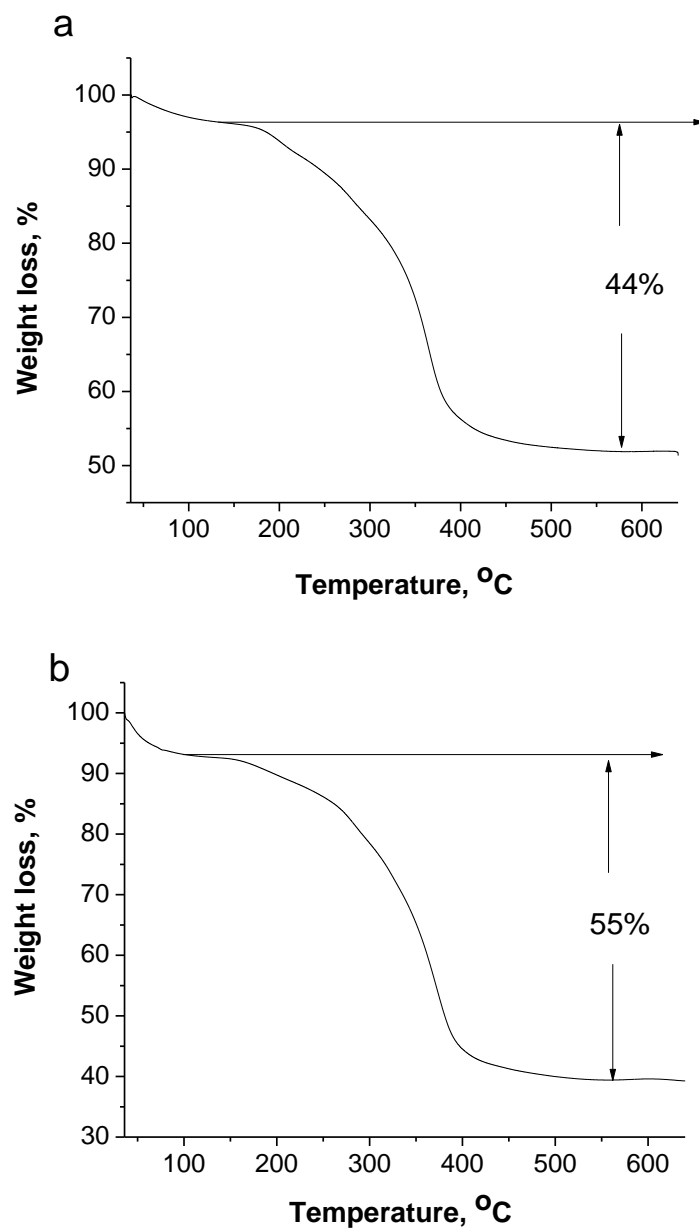


Figure S3. TGA traces of NPs1c (a) and NPs2c (b).

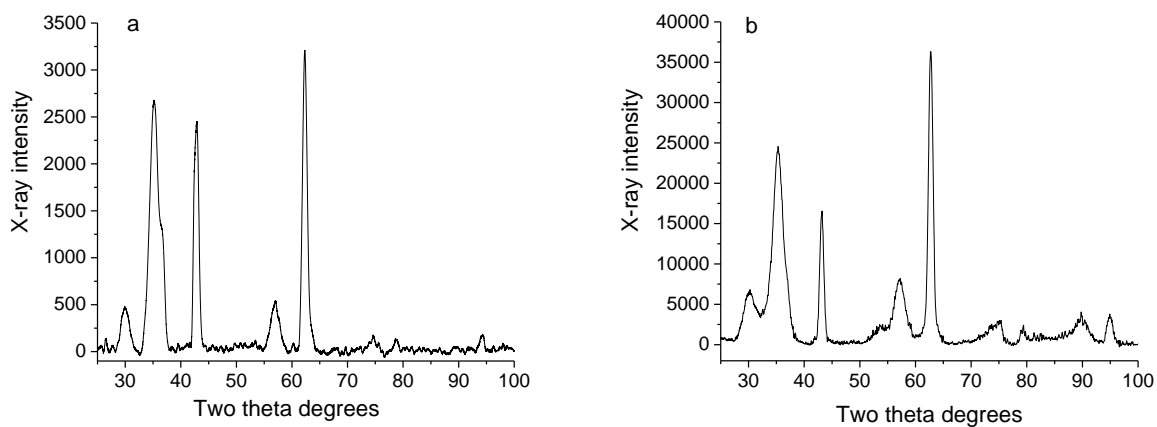


Figure S4. XRD profiles of NPs2 before (a) and after (b) coating.

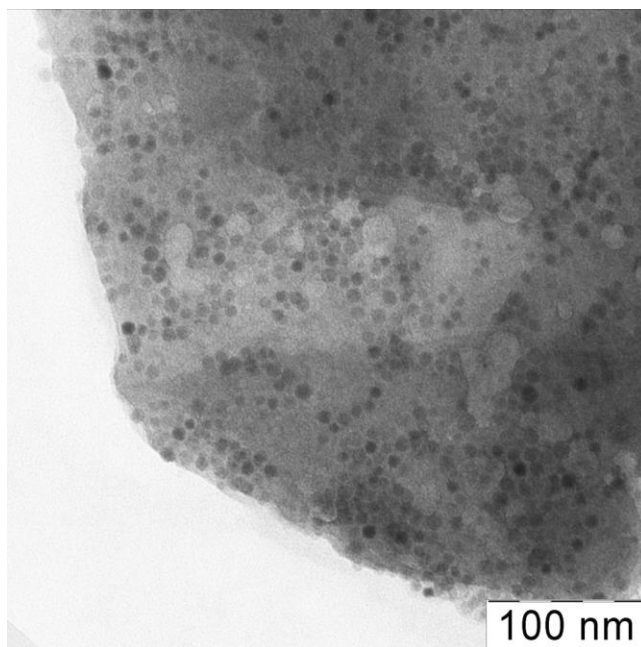


Figure S5. TEM image of the NPs1c/MoS₂ nanohybrid prepared by exfoliation of MoS₂ in the presence of NPs at the equal amounts of two components.

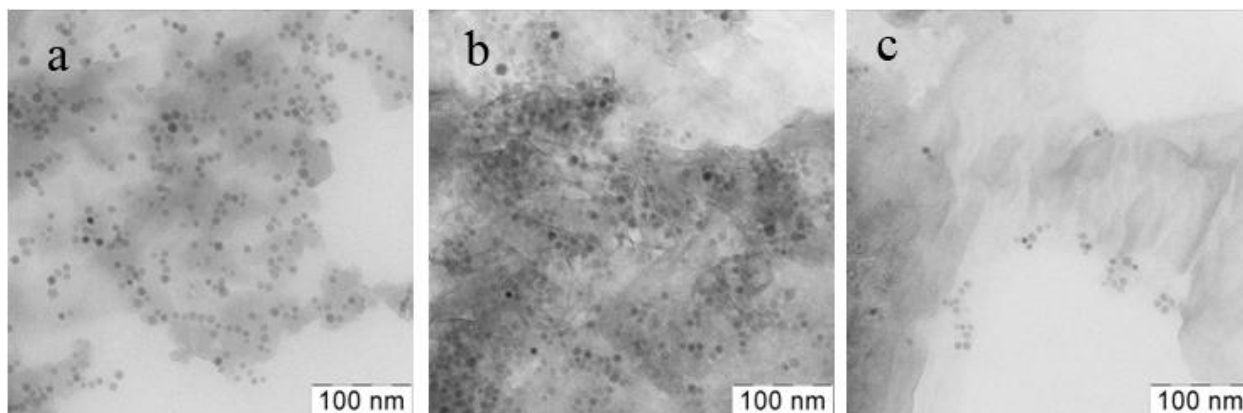


Figure S6. TEM images of the NPs1c/MoS₂ nanohybrids at the NP:MoS₂ weight ratios 1:1 (a), 1:5 (b), and 1:10 (c).

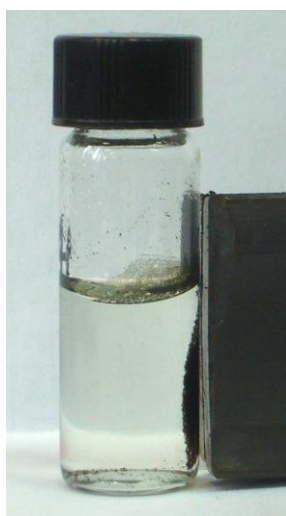


Figure S7. Photograph of magnetic separation of NPs2c/MoS₂ in 30 seconds after sonication.

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