Electronic Supplemental Information (ESI)

Hydrophobic monolayered nanoflakes of tungsten oxide: Coupled exfoliation and fracture in a nonpolar organic medium

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Experimental Methods

Synthesis of the precursor layered compounds. The layered cesium tungstate was synthesized by a solid state reaction. The procedure was referred to a previous report. The mixture of tungsten trioxide (WO$_3$, Kanto 99.0 %) and cesium carbonate (Cs$_2$CO$_3$, Kanto, 98.0 %) were calcined at 850 °C for 20 h under air condition. For the ion exchange, 1 g of the resultant Cs$_4$W$_{11}$O$_{35}$ powder was immersed in 100 cm$^3$ of 1 mol dm$^{-3}$ hydrochloric acid (HCl, 35~37 % aqueous solution, Kanto) for 7 to 10 days. The HCl aqueous solution was changed to fresh one by the day. The resultant H-W$_{11}$O$_{35}$ was washed by purified water and then dried.

Intercalation of the alkyl amine for preparation of C$_{18}$-W$_{11}$O$_{35}$. The pH of an aqueous solution containing stearylamine (C$_{18}$H$_{37}$NH$_2$, TCI, 80.0 %) was adjusted to 7.0 with addition of HCl. The concentration of C$_{18}$-NH$_2$ was adjusted to the molar ratio of C$_{18}$-NH$_3^+$/H$^+$=50, where the proton concentration was that in the interlayer space of the H-W$_{11}$O$_{35}$. About 0.2 g of the H-W$_{11}$O$_{35}$ powder was immersed in the aqueous solution containing C$_{18}$-NH$_3^+$ at room temperature with stirring for 10 days. The resultant precipitate, namely C$_{18}$-W$_{11}$O$_{35}$ was washed by an excess amount of the mixed solvent of water and ethanol. The powder of C$_{18}$-W$_{11}$O$_{35}$ was obtained after centrifugation and then dried.

Exfoliation in toluene. About 0.05 of the C$_{18}$-W$_{11}$O$_{35}$ powder was immersed in 20 cm$^3$ of toluene. The dispersion liquid was put in a ultrasonic bath for 1 h and then maintained at 60 °C for 5 days under stirring. The unxfoliated powder was separated by centrifugation at 6000 rpm.
for 30 min. The dispersion liquid of the hydrophobic monolayered nanoflakes was obtained.

**Characterization.** The crystal structure was analyzed by X-ray diffraction (Rigaku Miniflex II and Bruker D8 Advance). The morphologies were observed by field-emission scanning electron microscopy (FESEM, Hitachi S-4700), field-emission transmission electron microscopy (FETEM, FEI Tecnai G2), and atomic force microscopy (AFM, Shimadzu SPM-9600). The dispersion liquid was dropped on a copper mesh supported by collodion membrane for FETEM observation and a cleaned silicon wafer for AFM observation. If the need arises, the dispersion liquid was diluted by toluene for the observation. The contents of the organic amines were analyzed by thermogravimetric (TG, Seiko TG/DTA 7200) analysis and Fourier transform infrared (FT-IR) absorption spectroscopy (Jasco FT/IR-4200).
AFM image and its stereoimage

**Fig. S1.** AFM images (a,b) and size height distribution (c) of the C_{18}W_{11}O_{35} monolayered nanoflakes. (a) AFM image, (b) stereoimage, (c) height distribution estimated from the AFM images in the panel (b).

The flakes larger than 50 nm in the lateral size corresponds to the few-layer objects, such as bilayer and trilayer structures. Fig. S1a is the same image in Fig. 3g. Fig. S1b corresponds to the stereoimage of the Fig. S1a. The objects surrounded by the white circles in Fig. S1a correspond to those indicated by the long white arrows in Fig. S1b. The flakes larger than 50 nm shows the heights larger than 2.5 nm. These observation suggest that the larger few-layer objects, such as bilayer and trilayer structures, were contained. As indicated by the red arrows, the nanoflakes 5-30 nm in the lateral size had the monolayered structures around 2.5 nm in height. The height distribution in Fig. S1c indicates that the main product is the monolayered compounds less than 4 nm in thickness. The few-layered materials thicker than bilayer structures are contained.
XRD pattern of the remaining precipitates after the exfoliation

![XRD pattern](image)

**Fig. S2.** XRD pattern of the remaining precipitates after the exfoliation.

All the peaks were assigned to those listed in the ICDD card (00-051-1891). The XRD pattern of the remaining precipitates was not different from that of the precursor \( \text{C}_{18}-\text{W}_{11}\text{O}_{35} \) before the exfoliation. In the \( \text{C}_{16}-\text{MnO}_2 \) and \( \text{C}_{14}-\text{TiO}_2 \) composites, however, the XRD patterns of the remaining precipitates showed no diffraction peaks corresponding to the layered structure (See the pattern (iii) in Fig. 3a for \( \text{C}_{16}-\text{MnO}_2 \) and pattern (iv) in Fig. 4a for \( \text{C}_{14}-\text{TiO}_2 \) in the ref. 8). The results suggest that the exfoliation behavior of \( \text{C}_{18}-\text{W}_{11}\text{O}_{35} \) is different from that of the \( \text{C}_{16}-\text{MnO}_2 \) and \( \text{C}_{14}-\text{TiO}_2 \).
The graft density of alklyamines on the layers

Fig. S3. Structure model of the tungstate layer viewed from the [001] direction. The gray squares and blue circles correspond to \{WO_6\} units and Cs\(^+\), respectively. The red frame represents the unit cell structure of the tungstate.

Based on the TG results, the chemical formula of the layered composite was estimated to be \((C_{18-NH_3})_{0.397}H_{0.603}Cs_{3}W_{11}O_{35}\cdot xH_2O\ (x<0.625)\). In Fig. S3, one unit cell structure, surrounded by a red frame, actually contains 11 \{WO_6\} units \((N_{W,unit}=11)\). The molar ratio of C\(_{18-NH_3}\) to the a \{WO_6\} unit in the unit cell \((R_{C18-NH3+,unit})\) is estimated to be 0.0361. On the other hand, 4 tungsten \{WO_6\} units are exposed on the surface \((N_{W,surf.}=4)\). Therefore, the ratio of the surface-exposed \{WO_6\} units is estimated to be \(R_{W,surf.}=N_{W,surf.}/N_{W,unit} = 0.3636\). The graft density of C\(_{18-NH_3}\) on the surface \{WO_6\} units \((R_{C18-NH3+,surf.}=R_{C18-NH3+,unit}/R_{W,surf})\) is estimated to be 0.09925. In contrast, all the \{MO_6\} (M=Ti, Mn) units were exposed on the surface of the titanate and manganate layers.

The graft density of C\(_{n-NH_3}\) on the surface \{MO_6\} units can be directly calculated by the chemical formula of the layered composites (Table S1). The chemical formulae of these titanate and manganate were referred to our previous report.\(^8\)
Table S1. Relationship between the chemical formulae and graft density

<table>
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<tr>
<th>n in C&lt;sub&gt;n&lt;/sub&gt;-NH&lt;sub&gt;3&lt;/sub&gt;</th>
<th>Chemical formulae</th>
<th>Graft density / –</th>
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<td>14</td>
<td>(C&lt;sub&gt;14&lt;/sub&gt;-NH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;0.12&lt;/sub&gt;MnO&lt;sub&gt;2&lt;/sub&gt;・xH&lt;sub&gt;2&lt;/sub&gt;O (x&lt;0.53)</td>
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<tr>
<td>18</td>
<td>(C&lt;sub&gt;18&lt;/sub&gt;-NH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;0.19&lt;/sub&gt;MnO&lt;sub&gt;2&lt;/sub&gt;・xH&lt;sub&gt;2&lt;/sub&gt;O (x&lt;0.56)</td>
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<td>(C&lt;sub&gt;14&lt;/sub&gt;-NH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;0.517&lt;/sub&gt;H&lt;sub&gt;0.183&lt;/sub&gt;Ti&lt;sub&gt;1.825&lt;/sub&gt;□&lt;sub&gt;0.175&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;・xH&lt;sub&gt;2&lt;/sub&gt;O (x&lt;0.972)</td>
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