Supporting Information


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S1. Experimental details.

Synthesis: Briefly, commercial WO₃ (0.232 g, 1 mmol, Wako Chemical Ltd., 99% technical grade), 37% HCl (0.5 ml) and urea (1.8 g, 30 mmol) were added to 40 ml of absolute ethanol. The mixture was loaded into a Teflon-lined autoclave, which was then sealed, maintained at 180 °C for 12 h, and cooled to room temperature naturally. The yellow precipitate was collected and rinsed several times with distilled water and absolute ethanol, respectively. Then the sample was dried at 60 °C for 12 h.

Characterization: Transmission electron microscope (TEM) images were collected using a JEOL JEM 3010F microscope working at 300 kV. A Hitachi S-4800 field emission scanning electron microscope (FE-SEM, Hitachi Co. Ltd. S-4800) was used to investigate the morphology. X-ray powder diffraction (XRD, Rigaku Co. Ltd. Ultima-X) measurement was conducted using filtered Cu Kα radiation. The nitrogen adsorption and desorption isotherms at 77 K were measured using a Micrometrics ASAP 2010 system after the sample was degassed overnight in vacuum at 150 °C. A Shimadzu UV-1601PC spectrophotometer was used to record the UV-Vis spectra in the range of 300-800 nm.

Photocatalytic reduction measurement: In a glass reactor, 10 mg of sample was first mixed with 30 ml of AgNO₃, Pb(NO₃)₂ or K₂Cr₂O₇ aqueous solution (1 mM), respectively, and then the system was illuminated with visible light using a 300 W Xe
lamp (Hayashi Watch-works Co. Ltd.) in conjunction with an optical fiber coupler, a UV cutoff filter (Y43, Asahi Techno Glass Co. Ltd.), and an IR cutoff filter (C-50S, Asahi Techno Glass Co. Ltd.) while simultaneously stirred by a magnetic stirrer at a constant speed. A spectro-radiometer (USR-45D, Ushio Co.) was applied to monitor the visible light intensity which was adjusted to 20 mW/cm². After irradiation for 3 min, the solution was centrifuged, and the precipitates were washed with water to remove the unreacted AgNO₃ or K₂Cr₂O₇. In case of Pb²⁺ ions, the irradiation time was 10 min. The amount of Ag deposited on the sample surfaces, evaluated by Ag weight percentage in the final products, was measured by an Energy Dispersive X-Ray Fluorescence Spectrometer.

S2. The process for the formation of tungstic acid-coated WO₃ octahedra resembles that for Karst topography, happening in two stages: etch and etch-stop. I) Commercial WO₃ particles are etched by ammonia from gradual urea decomposition to form (NH₄)₂WO₄ through reaction: WO₃ + NH₃ → (NH₄)₂WO₄. This corrosive process is similar to Karst process where carbonic acid, formed by the combination of carbon dioxide and water, permeates into the limestone and decays calcium carbonate in the rock (CO₂ + H₂O → H⁺ + HCO₃⁻; H⁺ + CaCO₃ → Ca²⁺ + HCO₃⁻). Without the addition of urea, only commercial WO₃-like irregular-shaped WO₃ particles were observed, suggesting possibly no reactions happened. Urea introduced in the system, besides etching WO₃, may also serve as a capping agent to modify the irregular-shaped commercial WO₃ particles to octahedral-shaped crystals, since urea molecules having amino groups with a high electronegativity can chelate to the W ions.¹,²

The starting materials: commercial WO₃ particles
The as-prepared tungstic acid-covered tungsten oxide octahedra

Products without the addition of urea

II) the yielded (NH₄)₂WO₄ is reversed back to WO₃ via a subsequent reaction with HCl: (NH₄)₂WO₄+HCl $\rightarrow$ H₂W₁.₅O₅.₅⋅H₂O+NH₄Cl+H₂O; H₂W₁.₅O₅.₅⋅H₂O$\rightarrow$H₂O+WO₃, which is also comparable to natural condition where the dissolved calcium carbonate is re-deposited from water to form different type of land forms.

Further investigation shows that the addition of ethanol is essential. When absolute water was used as solvent instead of ethanol, the produced sample showed sheet-like morphologies instead of octahedral shape. This is possibly because that the presence of abundant ethanol can reduce the polarity of the solvent and the deposition rate of W ions, thus preventing homogeneous nucleation growth, which is favorable for the formation of octahedral-shaped particles.³
The above results strongly suggest that urea and ethanol play very important roles in the synthesis of WO$_3$ octahedra. In our previous study, tungstic acid hydrate nanotubes were solvothermally synthesized in WCl$_6$/urea/ethanol system at 180°C,\textsuperscript{1,4} in which urea acted as structure directing agent. However, here the starting materials were modified to be WO$_3$/HCl/urea/ethanol, although synthesis conditions were remained such as growth temperature 180°C, reaction period 12 h. Therefore, different solution chemistry was expected, which was also clearly evidenced by different phases and morphologies of final products observed in the two systems.

In the previous system (WCl$_6$/urea/ethanol), the solution color was light yellow right after mixing the reagents, while it quickly changed to blue, suggesting the formation of chloride alkoxide tungsten (WCl$_6$+C$_2$H$_5$OH $\rightarrow$ WCl$_6$\textsubscript{x}(OC$_2$H$_5$)$_{x}$(blue)+HCl),\textsuperscript{5} from which tungstic acid was formed by condensation reaction in the following solvothermal process.

Instead, the solution was in yellow color and no color change was observed after mixing the reagents in the current system (WO$_3$/HCl/urea/ethanol), indicative of the absence of WCl$_6$\textsubscript{x}(OC$_2$H$_5$)$_{x}$. Commercial WO$_3$ particles first reacted with ammonia, that was released from urea, to form (NH$_4$)$_2$WO$_4$ (WO$_3$+NH$_3$ $\rightarrow$ (NH$_4$)$_2$WO$_4$). This corrosive process is similar to natural process where carbonic acid, formed by the combination of carbon dioxide and water, permeates into the limestone and decays calcium carbonate in the rock. Then WO$_3$ octahedra with a thin layer of H$_2$W$_{1.5}$O$_{5.5}$H$_2$O on the surfaces were formed via the subsequent reaction of
(NH₄)₂WO₄ with HCl ((NH₄)₂WO₄+HCl → H₂W₁.₅O₅.₅⋅H₂O+NH₄Cl+H₂O; H₂W₁.₅O₅.₅⋅H₂O → H₂O+WO₃), which is also similar to natural condition where the dissolved calcium carbonate is re-deposited from water to form different type of land forms.

**S3.** The H₂W₁.₅O₅.₅⋅H₂O could be converted to monoclinic WO₃ by calcinations at 450 °C for 3 h, as evidenced by XRD observations. After calcinations, only peaks corresponding to WO₃ were left.

The octahedral structure was nearly maintained as well as the overall dimensions with edge length of about 200-400 nm. However the resultant samples without tungstic acid coating displayed surface cracks and fractures, which suggested that the acid layer is critical to the stabilization of the octahedral shape.
S4. Cation Adsorption of Octahedra: We selected methylene blue as indicator because methylene blue is a cationic adsorbate that can be attracted to the WO$_3$ surface. For comparison, commercial WO$_3$ particles and WO$_3$ octahedra after annealing were also tested as adsorbents. S4a shows temporal evolution of the spectral changes occurring during the adsorption process of methylene blue mediated by the three samples (room temperature, 2 h, in the dark). Methylene blue showed a major absorption band at 664 nm, and its intensity can be taken as an indicator of methylene amount left, which is summarized in S4b. In the presence of commercial WO$_3$ particles and WO$_3$ octahedra after annealing, the absorbance decreased by ca. 24 % and 52 % in 2 hours, respectively. However, the absorbance for tungstic acid-coated WO$_3$ octahedra decreased by ca. 88 %, which is almost 3.7 times that of commercial WO$_3$. Hence, among the three samples, tungstic acid-coated WO$_3$ octahedra showed the highest adsorption capacity for methylene blue.
S5. The octahedral shape did not increase the specific area with comparable value with that for commercial WO₃ particles (4.4 m² g⁻¹), regardless of before (6.7 m² g⁻¹) or after calcinations (8.2 m² g⁻¹).

Nitrogen absorption-desorption isotherm plot and Barrett-Joyner-Halenda (BJH) pore size distribution plot of the as-prepared sample. The specific surface area was revealed to be 6.7 m² g⁻¹.

Nitrogen absorption-desorption isotherm plot and BJH pore size distribution plot of the sample after calcination treatment. The specific surface area was revealed to be 8.2 m² g⁻¹.

S6. The UV-Vis spectra indicate that as-prepared octahedra could absorb visible light with a wavelength above 400 nm.
The photocatalytic degradation of Pb$^{2+}$ and Cr$^{6+}$ ions (Cr$_2$O$_7^{2-}$) using the as-prepared octahedra was examined.

Pb$^{2+}$ ions: For a metal ion to be reduced by photocatalysis, the conduction band of the semiconductor must be more negative compared to the reduction potential of the metal ion involved in the system. The conduction band level of WO$_3$ is 0.4 V, and the standard reduction potentials of Pb$^{2+}$ ions is -0.127 V (Pb$^{2+}$ + 2 e$^- = $ Pb $\ldots$ E$_0 = -0.127$ V), consequently the direct photocatalytic reduction of Pb$^{2+}$ ions by the photogenerated electrons in WO$_3$ would be thermodynamically unfavorable. However, using WO$_3$, Pb$^{2+}$ ions can be oxidized into PbO$_2$ under visible-light illumination. In this process, it is considered that oxygen dissolved in the solution or H$_2$O accepts electrons from WO$_3$ while Pb$^{2+}$ ions are oxidized by the positive holes.$^6,^7$ Similar phenomenon was reported for TiO$_2$ particles.$^6,^7$ The appearance of an additional (110) diffraction of PbO$_2$ (2$\theta = 25^\circ$) in the XRD pattern suggested the deposition of PbO$_2$ on the surface of tungstic acid-coated WO$_3$ octahedra after photoirradiation, and efficient photoremoval of Pb$^{2+}$ ions from aqueous solution (Figure a). The amount of PbO$_2$ deposited on the WO$_3$ octahedra was found to be 2.6 and 8.3 times that of commercial WO$_3$ particles and P25, respectively (Figure b). Thus, the photocatalytic removal of Pb$^{2+}$ ions from the solution can also be enhanced on tungstic acid-coated WO$_3$ octahedra. Furthermore, a characteristic peak of tungstic acid at 15$^\circ$ can be
discerned from the XRD pattern of the octahedra after PbO$_2$ photocatalytic deposition (Figure a), which indicates the tungstic acid layer is still left after photocatalytic experiments.

Cr$^{6+}$ ions: The toxicity of Cr$^{6+}$ ions is one hundred times higher than that of Cr$^{3+}$ ions. Thus, processes for photocatalytic degradation of Cr$^{6+}$ ions (Cr$_2$O$_7^{2-}$) to Cr$^{3+}$ ions under visible light irradiation are worth developing. The conduction band level of WO$_3$ is 0.4 V, and the standard reduction potentials of Cr$_2$O$_7^{2-}$ ions is 1.330 V (Cr$_2$O$_7^{2-}$ + 14 H$^+$ + 6 e$^- = Cr^{3+} + 7 H_2O \ldots E_o = 1.330 \text{ V} \right)$, therefore thermodynamically the direct photocatalytic reduction of Cr$_2$O$_7^{2-}$ to Cr$^{3+}$ ions by the photogenerated electrons in WO$_3$ would be feasible. The photocatalytic reduction of Cr$_2$O$_7^{2-}$ ions on P25 was almost negligible under visible light illumination. In contrast, Cr$_2$O$_7^{2-}$ ions could be photocatalytically reduced on both tungstic acid-coated WO$_3$ octahedra and commercial WO$_3$ particles, but the two were comparable (Figure c). Since Cr$_2$O$_7^{2-}$ is negatively charged, removal performance on our octahedra was similar to that on the commercial WO$_3$. But the removal performance of WO$_3$ was much higher than TiO$_2$.

Over all, we experimentally confirmed the effective photocatalytic removal of Ag$^+$, Cr$^{6+}$ and Pb$^{2+}$ ions from aqueous solution using our tungstic acid-coated WO$_3$ octahedra under visible light illumination. The photoreduction of Au$^+$ and Hg$^{2+}$ ions with high redox potential values are also expected from thermodynamical estimations (Au$^+$ + e$^- = Au \ldots E^o = 1.691 \text{ V} \right)$; Hg$^{2+} + 2 \text{ e}^- = \text{Hg} \ldots E^o = 0.852 \text{ V} \right)$. Compared with P25, the biggest advantage of WO$_3$ octahedron is that it can utilize part of visible light. For this reason, WO$_3$ octahedron is considered to be a suitable photocatalyst for catalytic removal of heavy ions from wastewater in the presence of sunlight. Compared with commercial WO$_3$ particles, a higher removal rate of metal ions might be achieved on tungstic acid-coated WO$_3$ octahedra, especially for Ag$^+$ and Pb$^{2+}$ ions, which may be due to the existence of tungstic acid sheath on the surface.
(a) XRD pattern of the octahedra after PbO$_2$ photocatalytic deposition; atomic percentage of (b) lead and (c) chromium on P25, commercial WO$_3$, and as-prepared octahedra after photocatalytic degradation.

**S8.** More hints to confirm the presence of tungstic acid in the sample

Figure a shows the thermal gravimetric analysis (TGA) and derivative curves for the tungstic acid layer-coated WO$_3$ octahedra, and demonstrates that the curves for
WO₃ octahedra show two typical steps at ca. 50-150 °C and ca. 150-400 °C with a weight loss of 0.5% and 2.1%, respectively. The weight loss should be associated with the release of the adsorbed water and structural water during dehydration of tungstic acid hydrate. The sample exhibited a slight weight gain of 0.14% between 400 and 1000 °C, indicating the existence of oxygen vacancies in the sample.

Figure b shows typical Fourier transform infrared spectroscopy (FTIR) spectra of the octahedra before and after annealing. The spectra had characteristic infrared bands of crystalline tungsten oxide, namely, strong band centered around 800 cm⁻¹ is discernable, which was assigned as the W–O–W vibration. This band was a doublet, suggesting the presence of two different W–O–W bonds. The main difference in the FTIR curves of the octahedra before and after annealing was the peak near 1402 cm⁻¹, which originated from the bending vibration of structural water of tungstic acid. Heating at 450 °C caused this peak to almost disappear, indicating that the tungstic acid layer turned into tungsten oxide.
(a) TG curve of WO$_3$ octahedra before calcinations; (b) FTIR spectra of WO$_3$ octahedra before and after calcinations.

References:


