

Supporting Information

A “Three-in-one” Water Treatment Material: Nitrogen-doped Tungstic acid **

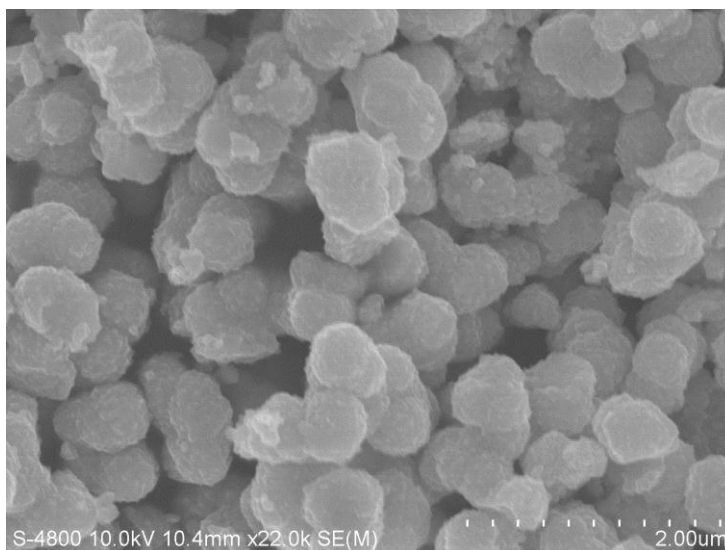


Figure S1 FE-SEM images of the as-synthesized nitrogen-doped tungstic acid hydrate.

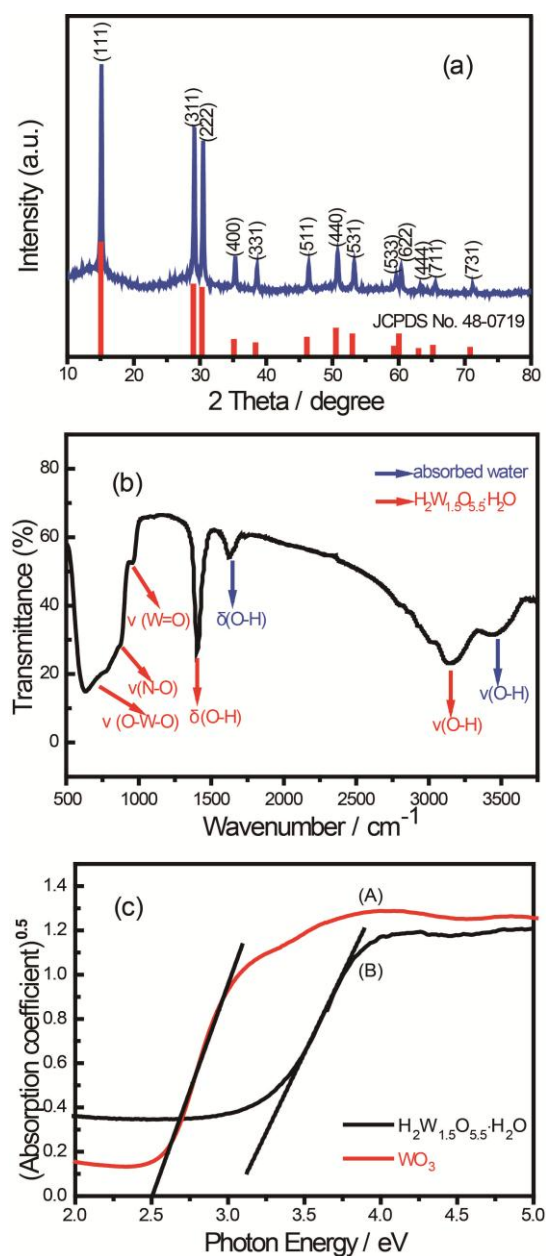


Figure S2 a) XRD patterns and b) infrared spectra of NTAH. c) Tauc plots calculated from the UV-vis reflectance spectra of A) NTAH and B) WO_3 . The as-prepared material is identified as crystalline nitrogen-doped protonated tungsten oxide (NTAH).

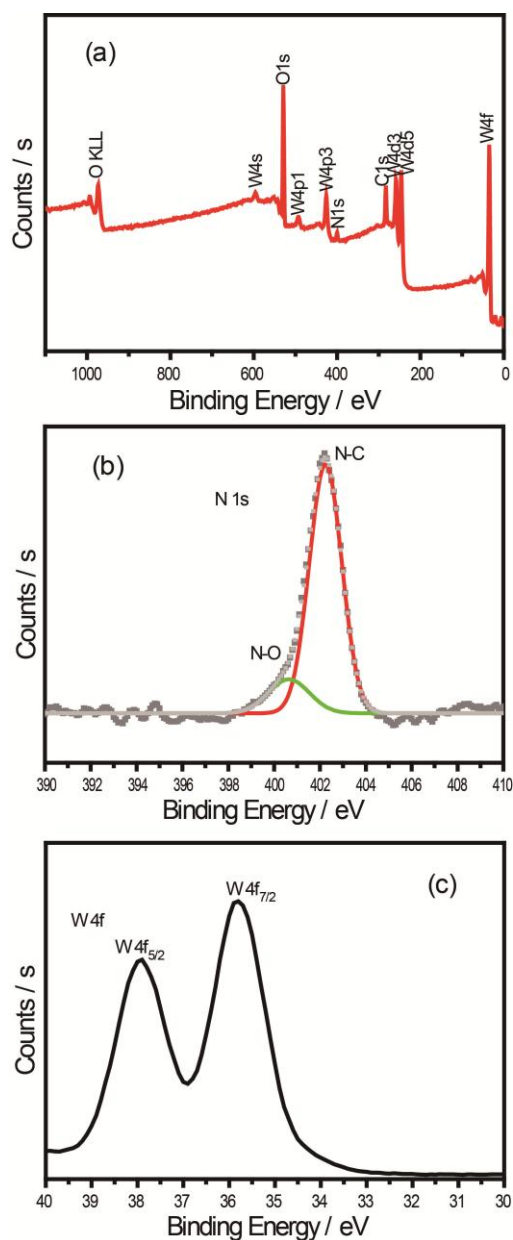


Figure S3 a) XPS survey spectrum of NTAH. XPS High resolution spectra of b) N 1s and c) W 4f peaks for NTAH.

The presence of N and W (VI) in the NTAH is ascertained by XPS spectra.

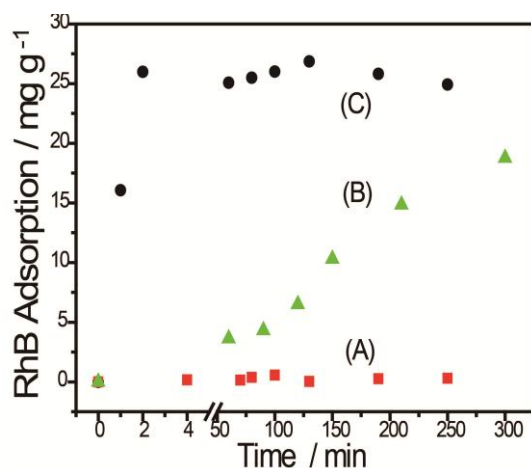


Figure S4 RhB removal efficiency under various contact times in the dark on A) WO₃, B) GAC and C) NTAH. (GAC concentration is 1.0 g L⁻¹, and that of the others are 0.5 mg L⁻¹).

The NTAH shows higher removal rate towards organic dyes compared with WO₃ and granular active carbon (GAC).

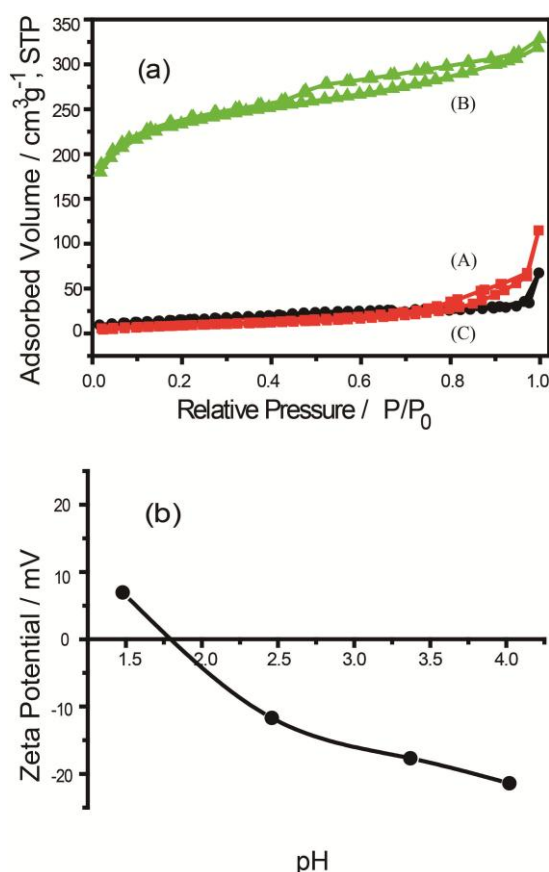


Figure S5 a) Nitrogen adsorption-desorption isotherms of N₂ at 77 K for the samples of A) WO₃, B) GAC and C) NTAH. b) Zeta potential of NTAH as a function of pH.

The higher adsorption capacity of the NTAH could not be attributed to the increase in surface area, but mainly due to the acidic surface generated by protonating and nitrogen-doping.

Experimental section

Chemical reagents.

Tungsten hexachloride was purchased from Aladdin Chemistry Co., Ltd. Rhodamine B (RhB), Victoria blue B (VB), Methylene blue trihydrate (MB), urea, anhydrous ethanol, tungsten oxide and other reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used as received without further purification.

Synthesis of NTAH.

0.397 g of tungsten hexachloride and 0.6 g of urea were added to 40 ml of anhydrous ethanol. The mixture was loaded into a Teflon-lined autoclave, which was sealed, maintained at 180 °C for 12 h, and then cooled to room temperature. The resulting white precipitate was collected and rinsed several times with anhydrous ethanol. It was then dried in an oven at 70 °C for 6 h.

Batch adsorption experiments for cationic organic dyes and metal cations: In order to acquire the pollutant solutions, Rhodamine B, Victoria blue B, Methylene blue trihydrate, and Cupric nitrate trihydrate were dissolved in deionized water and then diluted to the required concentration before use.

Adsorption and photocatalytic degradation experiments.

The adsorption experiments of the dyes were performed at room temperature (25 °C) with constant solution volume of 50 ml. All the experiments were conducted with the same mass of sorbents of 25 mg. The contact time for reaching adsorption equilibrium is 3 h for NTAH and WO₃, while 6 h for GAC. The amount of the dye adsorbed per unit mass of adsorbent, Q_e (mg g⁻¹) was calculated using the following mass balance relationship:

$$Q_e = (C_0 - C_e)V/M \quad (3)$$

Where C_0 and C_e are initial and equilibrium concentrations (mg L⁻¹), respectively. M is the dry mass of the adsorbents (g), and V is volume of the solution (L).

The adsorption experiments of Cu(II) was conducted according to China's National

Environmental Standard HJ 486-2009, Water quality-Determination of copper -2,9-Dimethy- 1,10- phenanthroline spectrophotometric method. The spectra were obtained using the UV-Vis spectrophotometer in the wavelength range from 400-600 nm. An absorption peak at 457 nm was chosen for monitoring the adsorption process since it has been shown that the absorbance of Cu(II) is linear to the concentration in the range from 0.12-1.3 mg L⁻¹ at chosen wavelength (correlation coefficient is 0.99996).

The photocatalytic degradation of RhB was used to estimate the photocatalytic activity of NTAH and WO₃ under light irradiation. The aqueous suspension containing 0.5 g L⁻¹ catalyst and 10 mg L⁻¹ RhB solution (if not otherwise stated) was first stirred for 1h and then irradiated with a 500 W Xe lamp, 515 and 365 nm cutoff filters were used for visible and UV irradiation, respectively. At given intervals, 1 ml of the suspension was withdrawn, centrifuged (10000 rpm, 30 min) and analyzed by UV-vis spectrophotometer. The concentration of RhB was determined from its maximum absorption with deionized water as a reference sample.

Characterization.

The samples were characterized by scanning electron microscopy (FEI Quanta 400 FEG). The X-ray diffraction (XRD) patterns were obtained on a D 8-Advance Bruker-AXS diffractometer using Cu K α irradiation. Fourier transform infrared spectroscopy (FT-IR) was acquired using a Nicolet 6700 FT-IR spectrometer. The absorption spectra were collected using the UV-Vis spectrophotometer (V660, JASCO.). Thermogravimetric analysis (TGA) was conducted in nitrogen (99.999 %) in a Perkin-Elmer Pyris 1. Zeta-potential values were recorded using a HPPS 5001, Malvern Instruments, as a function of pH, 0.1 M NaCl solution was added to each flask to maintain a high background-electrolyte concentration. X-ray photoelectron spectra (XPS) were acquired on X-ray photoelectron spectroscopy (Thermo Escalab 250, a monochromatic Al K α X-ray source). The binding energies obtained were corrected for specimen charging by referencing C 1s to 284.5 eV.