Organic superconductor modified NH$_2$-UiO-66 for boosted photocatalytic Cr(VI) elimination under low-power ultraviolet light

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Materials and characterizations

Preparation of NH$_2$-UiO-66@TCNQ composites

The NH$_2$-UiO-66 was synthesized via hydrothermal method according to the previous report with minor

modification. [1] Specifically, 160.0 mg ZrCl$_4$ and 124.28 mg 2-aminoterephthalic acid (NH$_2$-BDC) were dissolved

in the mixed solution with 40.0 mL DMF (N, N-dimethylformamide) and 12.0 mL acetic acid. Then the matrix

was transferred into a 100.0 mL teflon-lined bomb, followed by being heated at 120 °C for 24 h. The NH$_2$-UiO-66

samples were obtained by centrifugation after cooling to ambient temperature and the resulting solid material was

centrifuged and cleaned several times with DMF and methanol solution. Finally, the pale yellow NH$_2$-UiO-66

powders were oven-dried at 60 °C for 12 h.

The NH$_2$-UiO-66@TCNQ composites were prepared by ball-milling treatment (30 Hz, 15 min). The

composites were named as NUxTCy (the letters "NU" and "TC", abbreviated as NH$_2$-UiO-66 and TCNQ. The "x"

and "y" were the mass of NH$_2$-UiO-66 and TCNQ in the composites, respectively).

Photocatalytic Tests

To evaluate the photocatalytic activities of various photocatalysts, 20.0 mg of as-prepared photocatalyst was dispersed in 50.0 mL Cr(VI) aqueous solution under ultraviolet (UV) light irradiation. The aqueous solution, which included 14.14 mg $K_2Cr_2O_7$, was regarded as Cr(VI) model. The required pH values of the solutions ware adjusted by suitable H_2SO_4 or NaOH aqueous solutions. The 10 W LED ultraviolet lamp (PCX50B, Beijing Perfect Light Technology Co., Ltd.) was selected as the light source to provide UV light with a 369 nm wavelength and the selected light spectrum was shown in Fig. S1. The irradiation of 300 ± 50 mW LED visible light (PCX50C, Beijing Perfectlight Technology Co., Ltd) was selected as the light source to provide visible light and the light spectrum was shown in Fig. S1. The equilibrium of adsorption-desorption was achieved with magnetic stirring for 20 minutes in the dark environment, then the system was exposed to UV light. Each 2.0 mL solution was extracted every 10 minutes and filtered using 0.45 μm PTFE membrane to get supernatant. The method of diphenylcarbazide (DPC) (Auto Analyzer 3) was used to determine the concentration of the residual Cr(VI). The picture of Auto Analyzer 3 was given in Fig. S3.

The apparent quantum efficiency test

The apparent quantum efficiencies (AQEs) experiments were performed upon the irradiation of different lights with selected wavelengths originated from 300 W Xe light (Beijing Aulight Co., Ltd) with the aid of different light filters. The AQEs of photocatalytic Cr(VI) reduction and the incident photons were calculated following Eqs. S1 and S2. [2, 3] In addition, the E_g value (band gap energy) was calculated according to the Eq. S3.

$$AQE(Cr)=3 \times [\text{number of reduced Cr(VI)}]/\text{number of incident photons} \qquad S1$$

$$N^i_P=Pt\lambda/hc \qquad S2$$

$$\alpha h\upsilon = A (h\upsilon - E_g)^{n/2} \qquad S3$$

in which, P, t, and λ are the optical power, the irradiation time, and the light wavelength, respectively. h and c

represent Planck constant of $6.62607015 \times 10^{-34}$ J s, and lightspeed of 299,792,458 m s^{-1}.

The characterizations of the as-prepared NU90TC10

The powder X-ray diffraction (PXRD) patterns were obtained on a DX-2700B X-ray diffractometer using Cu Kα radiation. Fourier transform infrared spectra (FTIR) were measured by a Nicolet 6700 infrared spectrophotometer with KBr pellets. UV-Vis diffuse reflectance spectra (UV-Vis DRS) were tested on a PerkinElmer Lambda 650S spectrophotometer with BaSO$_4$ as the reference. The scanning electron microscope (SEM), transmission electron microscopy (TEM) and high resolution transmission electron microscope (HRTEM) were acquired by SU8020, JEM 1200EX and Tecnai G2 F20, respectively. High-resolution X-ray photoelectron spectra (XPS) measurement was performed on a Thermo ESCALAB 250XI. Photoluminescence (PL) emission spectra were tested on Hitachi F-7000 spectrophotometer and Techcomp FL970 in the range of 300-600 nm a at room temperature with an excitation wavelength of 365 nm. The electrochemical measurements were conducted on a Metrohm Autolab PGSTAT204 electrochemical station. Electron spin resonance (ESR) was measured by a JEOL JES-FA200 instrument using 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) as the spin-trapping agent to detect $\cdot O_2^-$ and $\cdot OH$.
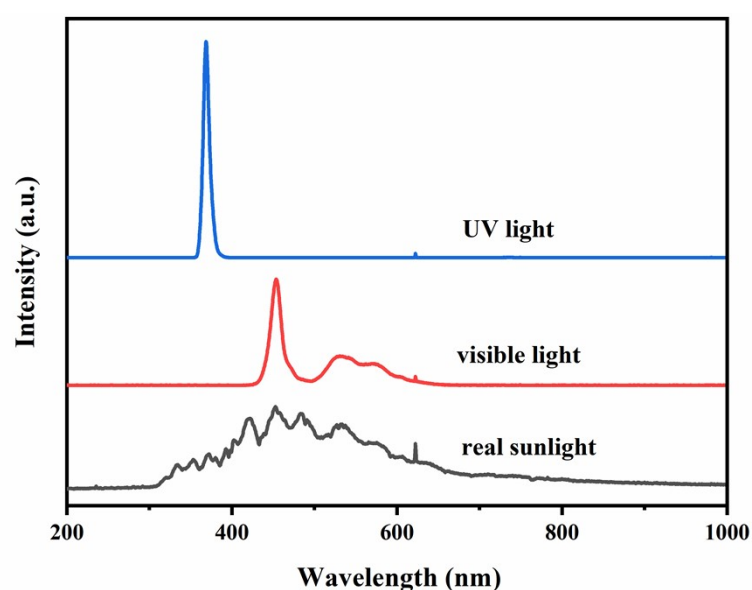
Fig. S1 The spectra of light source of 10 W LED ultraviolet lamp, LED visible light and real sunlight irradiation.

Fig. S2 The picture of Auto Analyzer 3.

Electrochemical Measurements

The electrochemical tests were carried out on a Metrohm Autolab PGSTAT204 electrochemical station via three-electrode mode adopting 0.2 M Na_2SO_4 solution (pH = 7.0) as the electrolyte. The working electrodes were fabricated on the FTO glasses, which were cleaned by sonication in ethanol and dried in air. And 5.0 mg NH_2-UiO-66, TCNQ or NUxTCy powder samples were mixed with 300.0 μL ethanol/Nafion (v/v = 19/1), which was dispersed by ultrasound treatment. 20.0 μL prepared slurry was dripped onto the surface of FTO substrate (1.0 cm × 1.0 cm), and then dried in air. This operation was repeated five times to ensure the well-distributed coverage of NH_2-UiO-66, TCNQ or NUxTCy samples on the FTO substrate. And the reference electrode and counter electrode were prepared by a saturated Ag/AgCl electrode and a platinum (Pt) electrode, respectively. The Mott-Schottky determination were performed with impedance-potential model. The Nyquist tests were carried out at the frequencies of 500, 1000 and 1500 Hz free of light irradiation.
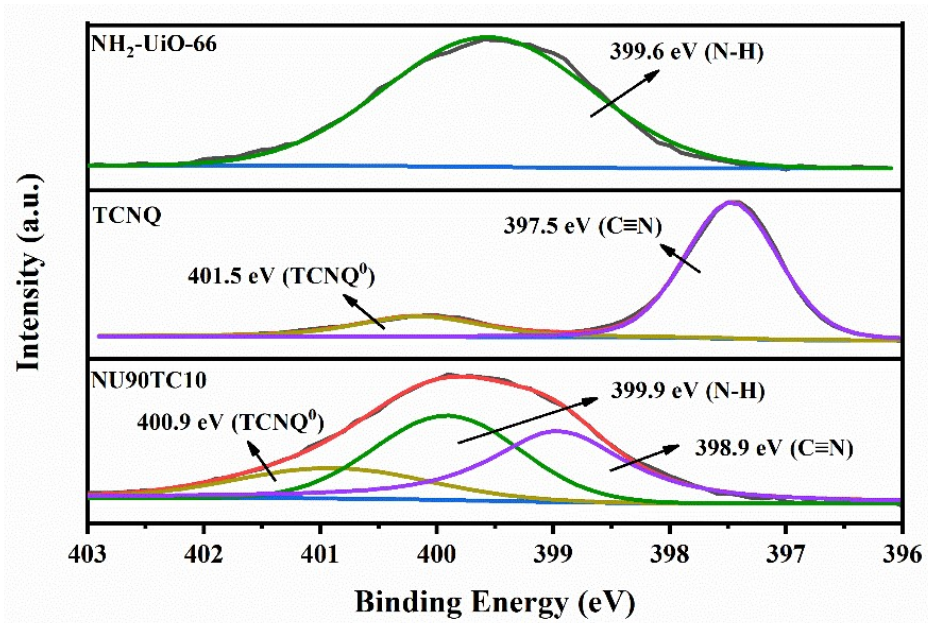
Fig. S3 The high-resolution XPS spectra of N 1s for pristine TCNQ, NH$_2$-UiO-66 and NU90TC10.
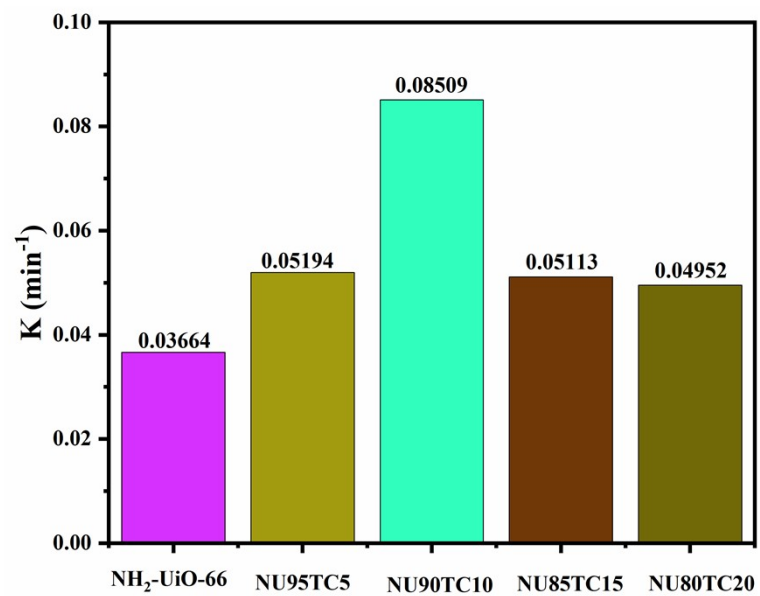

Fig. S4 The Cr(VI) elimination rates (k values) over NH$_2$-UiO-66, TCNQ and NUxTCy under UV light.
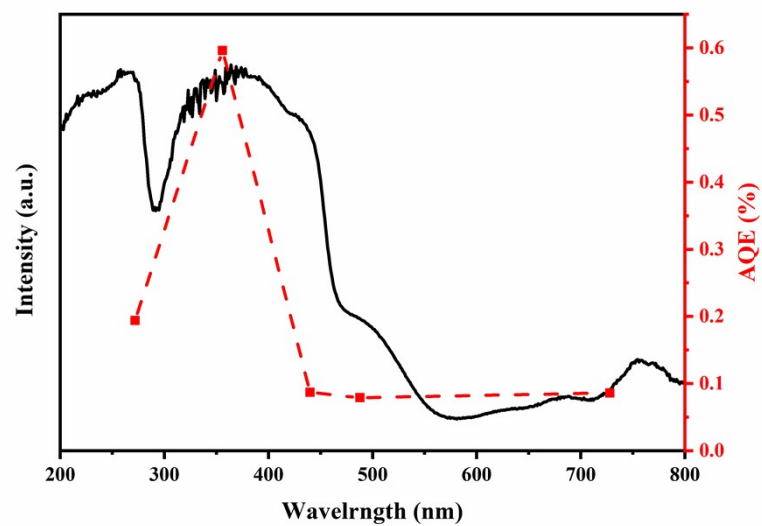
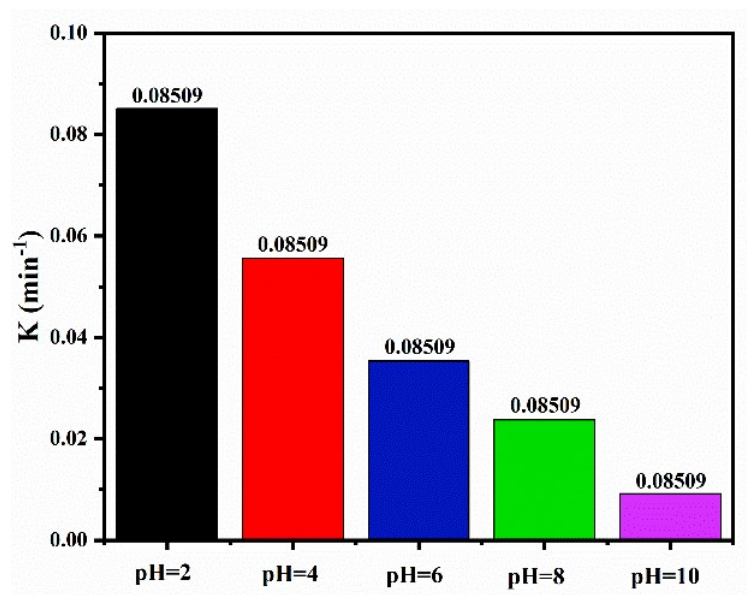**Fig. S5** The AQE of Cr(VI) elimination under the exposure of various lights.

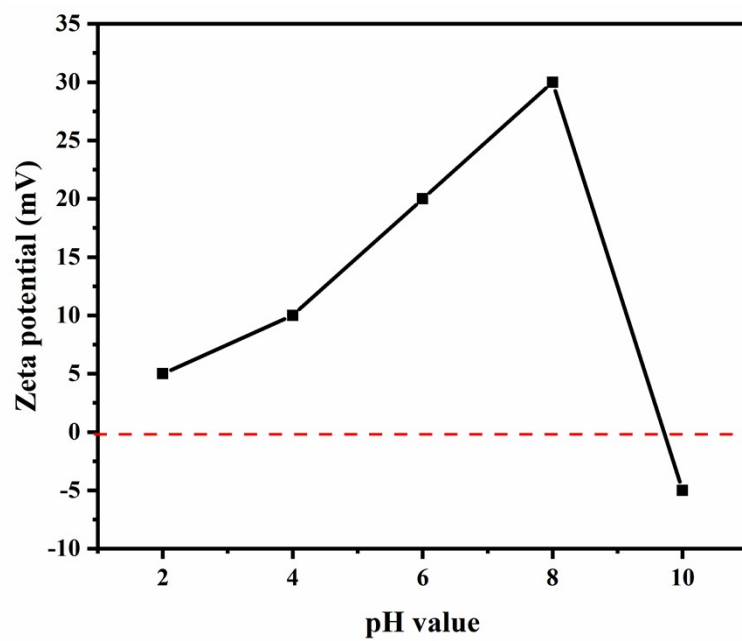**Fig. S6** The influence of initial pH toward the elimination rates (*k* values) over NU90TC10.

Fig. S7 The zeta potential of NU90TC10.

Fig. S8 The experimental diagram of photocatalytic Cr(VI) reduction under real sunlight irradiation.
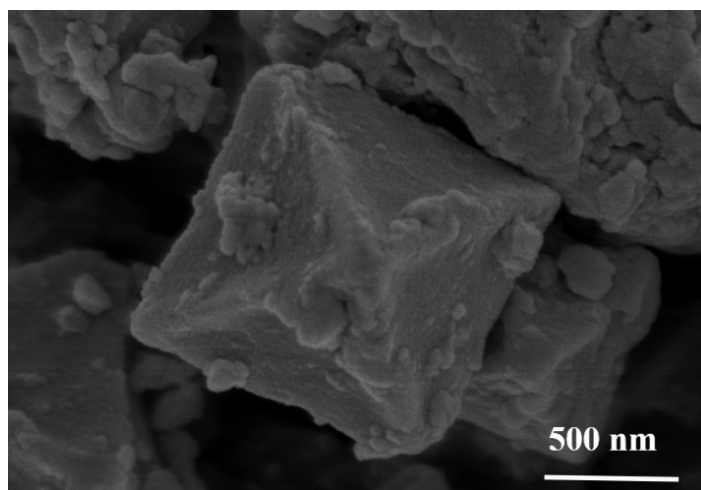
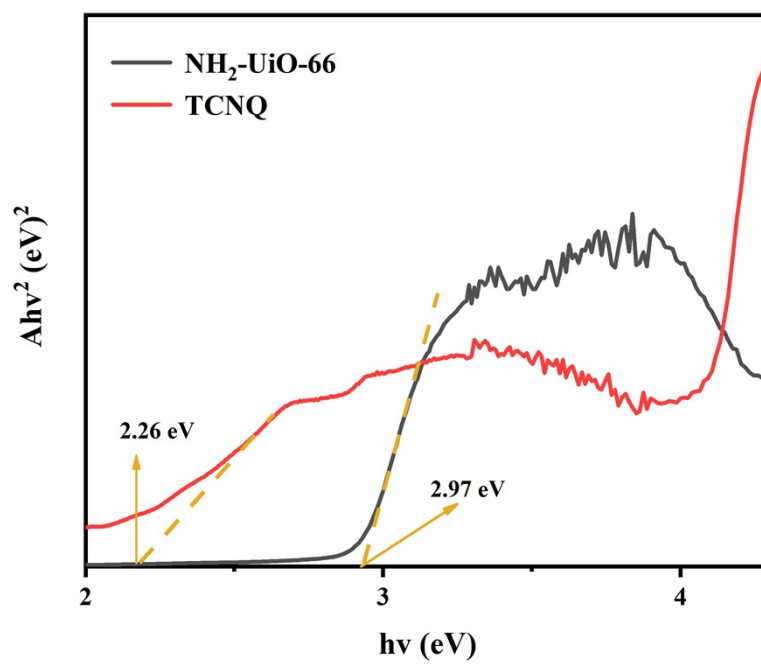**Fig. S9** SEM image of Cr(VI) removal over NU90TC10 before and after the recyclability experiment.

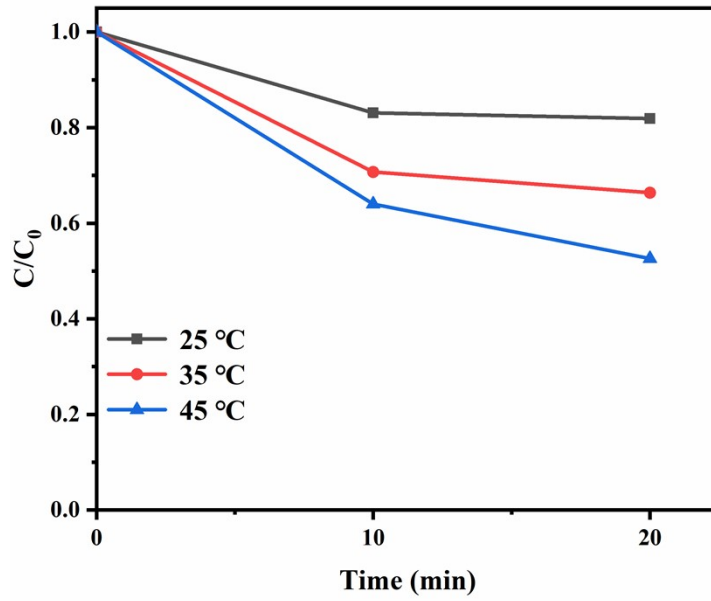**Fig. S10** The E_g plots of NH$_2$-UiO-66 and TCNQ.

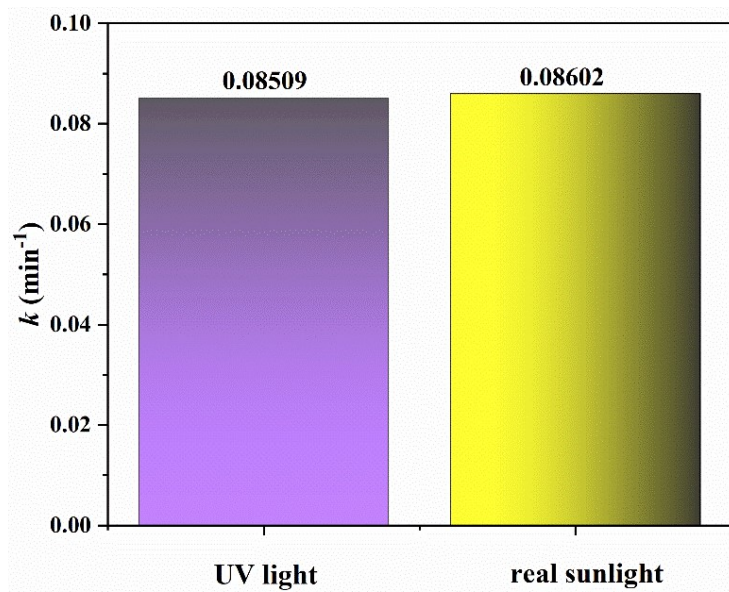**Fig. S11** The influence of temperature of the Cr(VI) elimination performance in dark.

Fig. S12 The elimination rates (*k* values) under UV light and real sunlight irradiation.
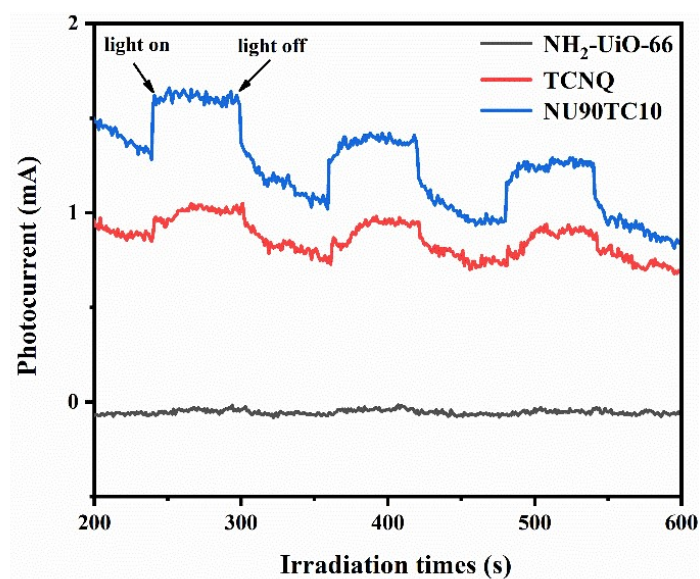
Fig.S13 The photocurrent response densities of NH_2-UiO-66, TCNQ and NU90TC10.

Table S1 The water quality parameters of lake water (sampled from the Ming Lake), tap water in BUCEA DaXing campus.

Quality parameters		K^+	Na^+	Ca^{2+}	Mg^{2+}	Cl^-	NO_3^-	SO_4^{2-}	PO_4^{3-}	COD_{Mn}
Concentration (mg/L)	lake water	4.5	35.6	67.4	32.1	32.0	11.8	174.1	0.4	11.6
	tap water	3.6	26.7	85.6	32.2	58.6	9.5	76.3	NA	1.1

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2. Y.-X. Li, H. Fu, P. Wang, C. Zhao, W. Liu and C.-C. Wang, *Environ. Pollut.*, 2020, **256**, 113417.
3. Y. Li, Y.-H. Li, P. Wang, C. Zhao, C.-Y. Tang, S.-J. Gao and C.-C. Wang, *J. Environ. Chem. Eng.*, 2023, **11**, 109205.