

Supplementary Material

Synergistic effect of adsorption-photocatalytic reduction of Cr(VI) in wastewater with biochar/TiO₂ composite under simulated sunlight illumination

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Experimental section

Materials and chemicals

All materials were purchased from Aladdin Reagent (Shanghai) Co., Ltd., typically tetrabutyl titanate ($C_{16}H_{36}O_4Ti$), potassium dichromate ($K_2Cr_2O_7$), diphenylcarbazide ($C_{13}H_{14}N_4O$), phosphoric acid (H_3PO_4), sulfuric acid (H_2SO_4), hydrochloric acid (HCl), acetic acid (CH_3COOH), anhydrous ethanol (C_2H_5OH), acetone (CH_3COCH_3), potassium persulfate ($K_2S_2O_8$), ethylenediamine tetraacetic acid (EDTA), benzoquinone (BQ) and methanol (MeOH). All chemicals are analytical grade and used without further purification.

Characterization of materials

XRD data were collected by using an XRD-6100 Advance X-ray diffractometer (Shimadzu, Cu $K\alpha$, $\lambda=1.54060 \text{ \AA}$) at 45 kV and 100 mA. X-ray photoelectron spectroscopy measurements were carried out on a Thermo Fisher Scientific EscaLab 250Xi spectrometer (XPS-Al $K\alpha$ -1486.6 eV) with applied voltage (12 kV) and current (23 mA). The optical properties were measured by UV-Vis absorption spectra (Shimadzu UV-3600). High-resolution transmission electron microscopy (HRTEM-JEM-2100F) with an accelerated voltage (200 kV). Scanning electron microscopy (SEM, Hitachi, SU-8100) with an applied voltage (5.0 KV), and energy dispersive spectroscopy (EDS, Oxford, X-MaxN 80T) were used to detect the content and distribution of elements. The specific surface area and pore size were measured by Brunauer-Emmeter-Teller (BET) (Micromeritics ASAP 2460) at 77 K by nitrogen adsorption-desorption isotherm analysis. The thermal stability test was performed on a thermogravimetric analyzer (TG-DTG, STA-449F5, Netzsch, Germany) at a heating rate of 10 °C/min from 40 °C to 800 °C. Electrochemical impedance spectroscopy (EIS) was measured and recorded on an electrochemical workstation (CHI-660E, Chenhua Instruments Co., Shanghai, China) using a traditional three-electrode system in 1 M Na_2SO_4 electrolyte solution at room temperature of 25 °C. Ag/AgCl, carbon rod and sample-covered nickel foam were used as reference electrode, counter electrode and working electrode, respectively. A working electrode sample was prepared by dispersing 10 mg of photocatalyst in 0.5 mL of anhydrous ethanol and 0.5 mL of deionized water. After ultrasonic treatment for 2 h, 0.1 mL of slurry was repeatedly dropped on the nickel foam substrate (1×2 cm), repeated drying and dropping until the sample droplets were added. The measurements were performed at 1 V with a frequency range of 0.01 Hz to 100 kHz and an AC current amplitude of 5 mV. Zeta

potentials were measured by Nanotracs wave II Zetasizer (Microtrac, Germany) to analyze the surface charge and dispersibility of samples.

Table S1. The XPS peak table of as-prepared TBC-3 sample.

Name	Peak BE	FWHM eV	Area (P) CPS.eV	Atomic %
Ti2p	458.89	2.7	2452419.79	22.2
O1s	530.25	2.65	2484982.05	46.0
C1s	285.08	1.53	672481.52	31.8

Table S2. S_{BET} , pore volume, average pore size and most frequent pore diameter of the as-prepared BC, TiO_2 and TBC-3.

Samples	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Average pore size (nm)	Most frequent pore diameter (nm)
BC	24.6	0.011	8.0	26.7
TiO_2	122.0	0.065	2.1	1.7
TBC-3	306.6	0.450	5.9	8.9

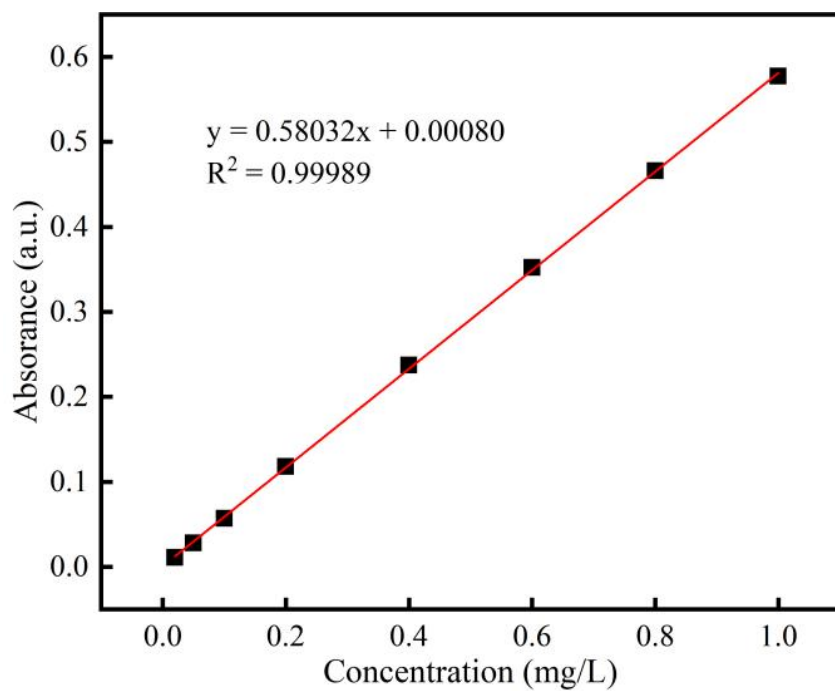


Fig. S1. The linear calibration curve for a series of standard Cr(VI) aqueous solutions.

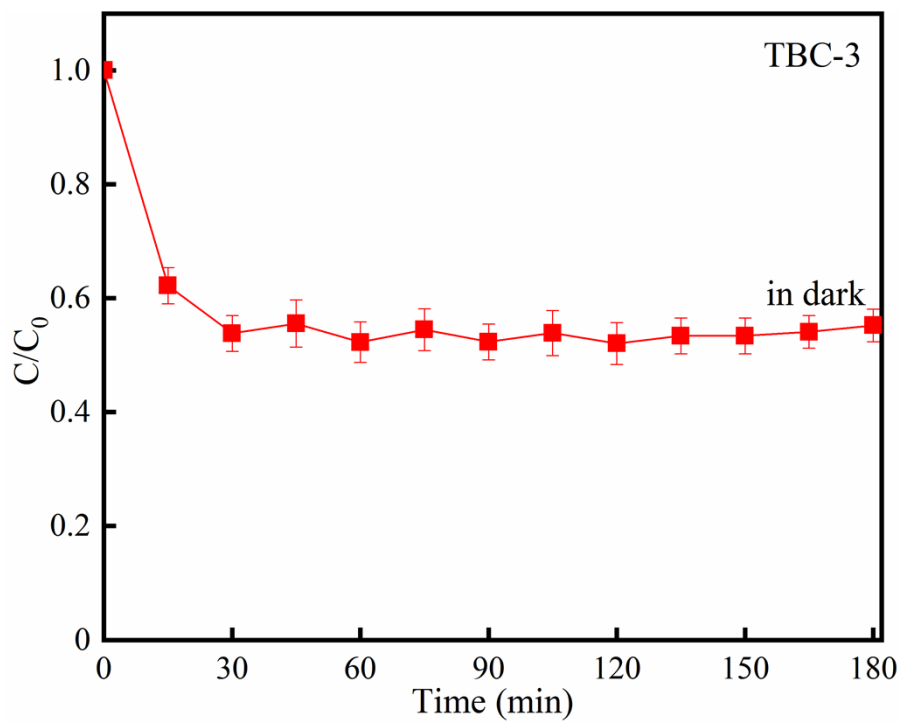


Fig. S2. The adsorption-reduction efficiency of Cr(VI) with TBC-3 sample in dark for 180 min.

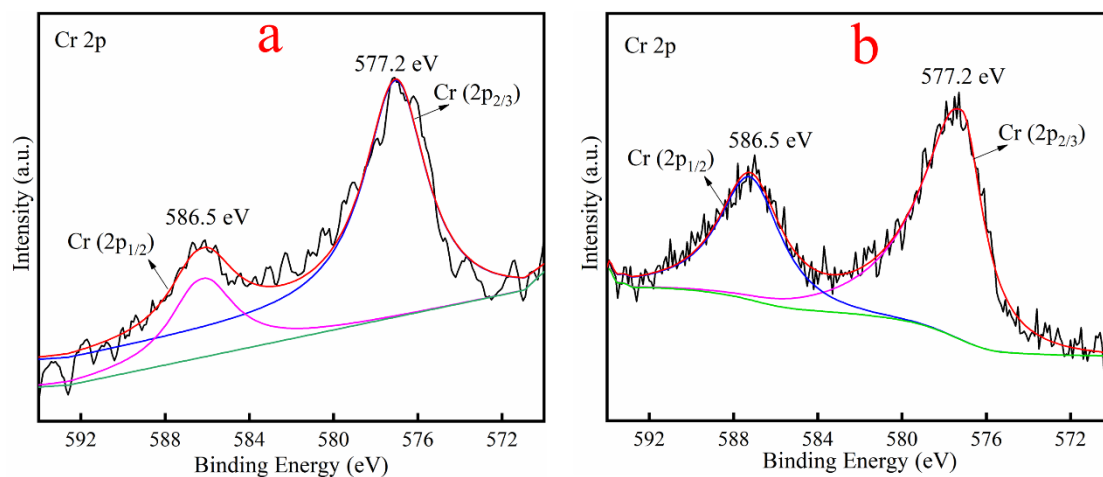


Fig. S3. The XPS spectrum of Cr element on the surface of TBC-3 (a) and in the solution (b) after photocatalytic reaction.

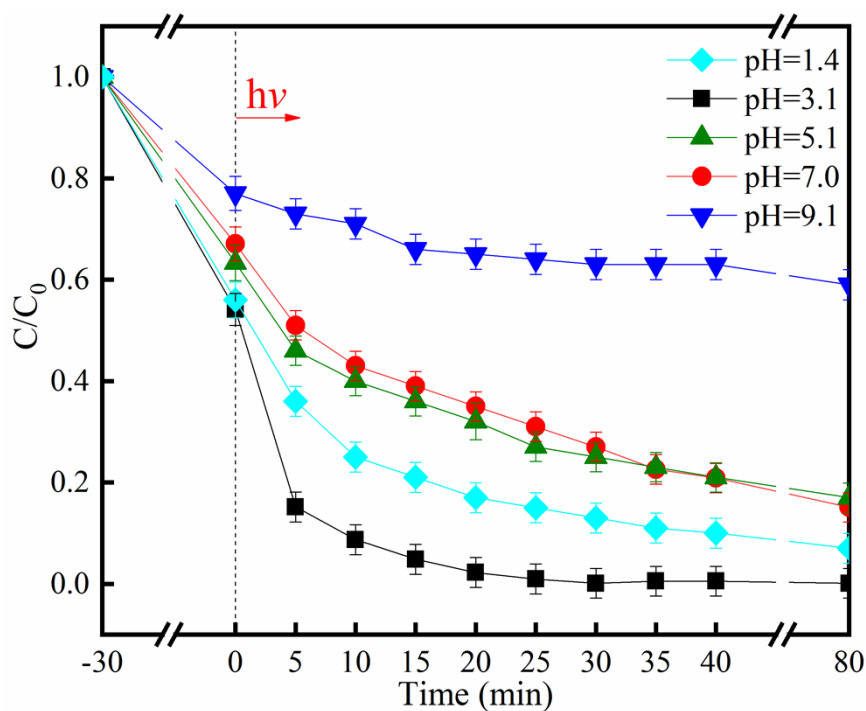


Fig. S4. The adsorption-photocatalytic reduction of Cr (VI) with TBC-3 at different pH values.

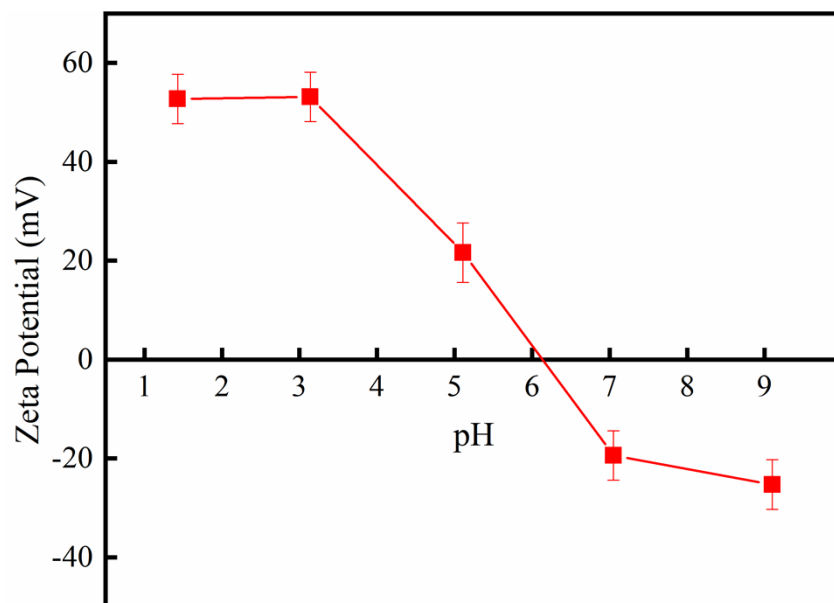


Fig. S5. Zeta potentials of TBC-3 sample at different pH values.