

Electronic Supplementary Information

A universal route to fabricate bacterial cellulose-based composite membrane for simultaneous removal of multiple pollutants

Yue Gu,^{a,b} Huaimeng Li,^{a,b} Mengxiang Ye,^{a,b} Xi Zhang,^{a,b} Haimin Zhang,^a Guozhong Wang,^a and Yunxia Zhang^{a,*}

^a *Key Laboratory of Materials Physics, Centre for Environmental and Energy Nanomaterials, Anhui Key Laboratory of Nanomaterials and Nanotechnology, CAS Center for Excellence in Nanoscience, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, China.*

^b *University of Science and Technology of China, Hefei 230026, China.*

Experimental section

Chemicals.

Purified bacterial cellulose (BC) pellicles (thickness: 3.0 mm) with fiber content of ~1% (vol/vol) were provided by Hainan Yeguo Foods Co., Ltd., China. Zirconium chloride ($ZrCl_4$), 1,4-benzenedicarboxylic acid (H_2BDC), L-antimony potassium tartrate ($K(SbO)C_4H_4O_6 \cdot 0.5H_2O$), ascorbic acid, ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), sodium arsenate dodecahydrate ($Na_3AsO_4 \cdot 12H_2O$), thiourea, standard solution of Hg^{2+} (1000 ppm), potassium permanganate powder ($KMnO_4$), urea, bisphenol A and bovine serum albumin (BSA) were purchased from Shanghai Aladdin Reagent Co. Ltd. (China). N, N-Dimethylformamide (DMF), potassium dihydrogen phosphate (KH_2PO_4), ammonium heptamolybdate tetrahydrate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$), lead nitrate ($Pb(NO_3)_2$), cadmium chloride ($CdCl_2$), magnesium chloride hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$) and hydrochloric acid (HCl) were supplied by Sinopharm Chemical Reagent Co. Ltd., China. Deionized (DI) water was obtained through a Barnstead MicroPure (Thermo Fisher). All of the chemicals were directly used as received.

Characterization.

The crystallinity of the obtained products was identified by X-ray diffraction (XRD, Philips X'pert PRO) with Cu $K\alpha$ radiation (1.5478 Å). The morphology and microstructural observations were characterized via transmission electron microscope (TEM, JEOL-2010) and field emission scanning electron microscope (FESEM, SU8020). N_2 adsorption-desorption isotherms were measured using an Autosorb-iQ-Cx analyzer. Nicolet NEXUS FI-IR spectrophotometer was used to FT-IR analysis. UV-vis absorption spectra were recorded on a Shimadzu UV2700 spectrophotometer. The concentrations of As(V), Hg^{2+} , Pb^{2+} and Cd^{2+} after uptake treatment were determined by inductively coupled plasma optical emission spectrometer (ICP-OES, ICP-6300 Thermo Fisher Scientific). The concentration of bisphenol A was analyzed using a high-performance liquid chromatography (HPLC, Waters 1525 Binary HPLC Pump, Waters Corporation, USA) under the UV wavelength of 280 nm.

Synthesis of UiO-66, MIL-88B, MoS₂, MnO₂ and MgO powder.

Synthesis of UiO-66. In a typical protocol, 0.45 mmol of ZrCl₄ and 0.45 mmol of H₂BDC were added to 30 mL of DMF under magnetic stirring, followed by the addition of acetic acid (72 mmol) as modulator. Then, the resulting suspension was put into a Teflon-lined autoclave (50 mL), sealed and heated at 120 °C for 7 h. After cooling down to room temperature, the resultant precipitate was washed using DMF for several times and then activated in methanol at 60 °C for 3 days to remove the trapped DMF molecules. At last, the obtained product was dried under vacuum condition at 60 °C overnight for further use.

Synthesis of MIL-88B. Briefly, 1 mmol of FeCl₃·6H₂O and 1 mmol of H₂BDC were dissolved in 10 mL of DMF under constant stirring to get a homogeneous solution. Subsequently, 2 mL of NaOH solution (2 M) was rapidly injected to the above mixed solution with continuous stirring for another 15 min. The mixture was then transferred into 25 mL of Teflon-lined autoclave and heated without agitation in an oven at 100 °C for 15 h. After cooling to room temperature, the resultant suspension was collected by centrifugation and washed several times with DMF and methanol, respectively. Afterwards, the washed sample was dried at 60 °C for 24 h for further characterization.

Synthesis of MoS₂. Briefly, 3.9276 g of thiourea and 2.1256 g of (NH₄)₆Mo₇O₂₄·4H₂O were dissolved into 60 mL distilled water under vigorous stirring. Then, the solution was transferred into a 100 mL Teflon-lined stainless-steel autoclave and heated at 180 °C for 24 h. After cooling, the obtained products were collected by centrifugation, washed with distilled water for several times to remove any impurities, and then dried at 60 °C under vacuum.

Synthesis of MnO₂. Typically, 160 mg KMnO₄ was dissolved in 80 mL of deionized water and heated to 80 °C. Then, the pH of the solution was adjusted to 2 by adding 1 M HCl and kept for 2 h at 80 °C in an oil bath. The resulting samples were then washed with DI water and dried at 60 °C overnight.

Synthesis of MgO. In a typical procedure, 0.77 g of Mg(NO₃)₂·6H₂O and 0.36 g

of urea were dissolved in 60 mL of ethanol under magnetic stirring. The resulting mixture was then transferred into a Teflon-lined autoclave, sealed and maintained at 180 °C for 12 h. After cooling down to room temperature, the precipitate was collected by centrifugation, rinsed with ethanol and DI water for several times, and calcined in air atmosphere at 400 °C for 2 h.

Fabrication of single-component and multi-component BC composite membrane.

Preparation of BC suspension. In a typical procedure, BC pellicles were cut into small pieces, pulped by using a mechanical homogenizer at a rotation speed of 12,000 rpm for 20 min and then stored at 4 °C. Prior to use, the BC slurry was stirred for 5 min to form the homogeneous BC fiber suspension. Notably, 16.8 mg of dry BC can be obtained after evaporating the moisture of 5 g BC suspension in our case.

Preparation of single-component UiO-66/BC, MIL-88B/BC, MoS₂/BC, MnO₂/BC and MgO/BC composite membrane. UiO-66/BC composite membrane was fabricated by a vacuum filtration method. Typically, 10 mg of UiO-66 nanoparticles were dispersed into 20 mL aqueous solution, and then mixed with 5 g of BC suspension with continuous stirring for 15 min to get a homogeneous suspension. Then, the above suspension was dehydrated via vacuum filtration, subjected to the press of 10 kg weight and dried at 60 °C for 24 h to generate UiO-66/BC composite membrane. Additionally, single-component MIL-88B/BC, MoS₂/BC, MnO₂/BC and MgO/BC composite membrane was also fabricated via a similar procedure using individual MIL-88BB, MoS₂, MnO₂ and MgO as the additional nanoparticles, respectively.

Preparation of multi-component BC composite membrane (UiO-66/MIL-88B/MoS₂/MnO₂/MgO/BC). The multi-component BC composite membrane (MBC) was prepared using a similar vacuum filtration method to single-component BC composite membranes. Briefly, 10 mg UiO-66, 10 mg MIL-88B, 10 mg MoS₂, 10 mg MnO₂ and 10 mg MgO were dispersed in 100 mL aqueous solution under ultrasonication for 20 min, followed by the addition of 25 g of BC suspension under stirring at room temperature. Subsequently, the above mixture was dehydrated via

vacuum filtration, subjected to the press of 10 kg weight and dried at 60 °C for 24 h to obtain MBC.

Assessment of permeability.

Permeability experiments were performed using a cylindrical stirred ultrafiltration cell (Model 8050, Millipore). The MBC with an approximate diameter of 42 mm was placed on the membrane holder, and then sealed with an O-ring. The initial pure water flux was calculated as: $J = V/(A \cdot t)$, where J is the permeation flux ($L \cdot m^{-2} \cdot h^{-1}$), V is the permeate volume (L), A is the membrane area (m^2), t is the collection interval (h) and pressure was fixed at 1 bar. The rejection capabilities of membranes were tested using 1000 mg/L of BSA solution. The concentrations of BSA in the feed and permeate solutions were determined by using UV-vis spectrophotometer at 280 nm. The rejection (R) of BSA was calculated as: $R = (1 - C_p/C_f) \times 100\%$, where C_f is the concentration of the feed solution (mg/L), and C_p is the concentration of the permeate solution (mg/L).

Batch extraction test.

Adsorption experiments of various powdery nanoparticles, bare BC matrix and BC composite membranes were conducted comparatively. The filtration system used in this study consisted of a peristaltic pump (BT-100D, China) and Whatman-Swin-Lok syringe-type reusable membrane filter holder (Whatman, 420400, U.K.) with an effective prefilter size of 42 mm. During each filtration experiment, the feed solutions were pumped through BC composite membrane at a constant permeate flux of 1 mL/min and the time for continuous sequestration was fixed at 12 h. As a consequence, 36 filtration cycles were taken to achieve the adsorption equilibrium for each dynamic purification experiment. All the adsorption experiments were conducted in triplicate and the mean values were recorded. The concentration of phosphate in the filtrate was quantified using the molybdenum blue spectrophotometric method. The concentrations of As(V), Hg^{2+} , Pb^{2+} and Cd^{2+} after uptake treatment were determined by ICP-OES. The concentration of bisphenol A was analyzed using a high-performance liquid chromatography.

Specially, a sheet of UiO-66/BC composite membrane was immobilized in the Whatman-Swin-Lok syringe-type reusable membrane filter holder to explore its adsorption performance with various initial concentration of phosphate (10 ppm and 20 ppm). By contrast, 10 mg UiO-66 nanoparticles were soaked in 20 mL of aqueous solution containing 10 ppm or 20 ppm phosphate. In a similar way, a sheet of single-component MIL-88B/BC membrane was used to remove 5 ppm or 10 ppm arsenate, MoS₂/BC membrane for 80 ppm or 100 ppm Hg²⁺, MnO₂/BC membrane for 20 ppm or 40 ppm bisphenol A, MgO/BC membrane for 20 ppm or 40 ppm Pb²⁺ as well as 10 ppm or 20 ppm Cd²⁺. Comparatively, the adsorption capabilities of corresponding nano-adsorbents and bare BC matrix toward target pollutants were also tested.

Simultaneous removal capability of MBC towards a broad spectrum of pollutants including heavy metals, inorganic anions and organic species was investigated by using Whatman-Swin-Lok syringe-type reusable membrane filter holder. Typically, a sheet of MBC was used to treat 20 mL of mixed aqueous solution containing multiple pollutants, including 20 ppm phosphate, 10 ppm arsenate, 100 ppm Hg²⁺, 40 ppm bisphenol A, 40 ppm Pb²⁺ and 20 ppm Cd²⁺.

Supplementary Figures and Tables

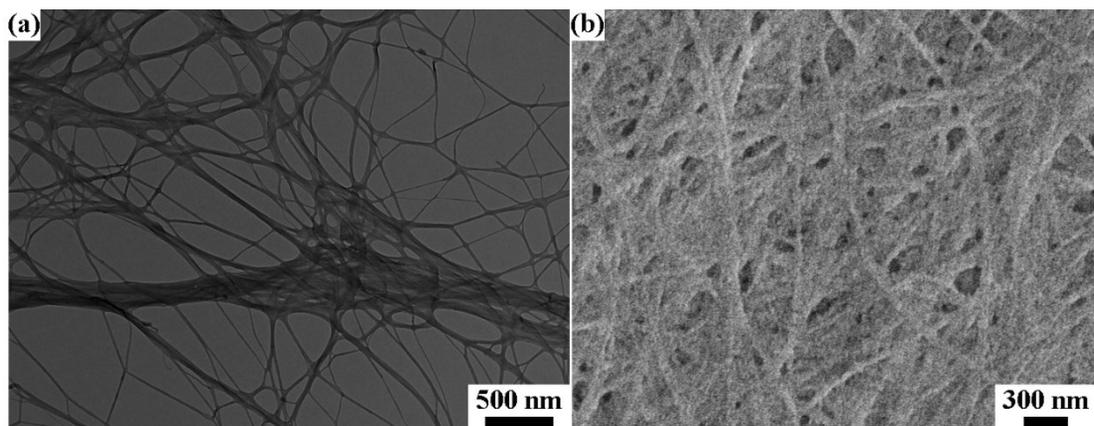


Fig. S1 TEM and SEM images of bacterial cellulose.

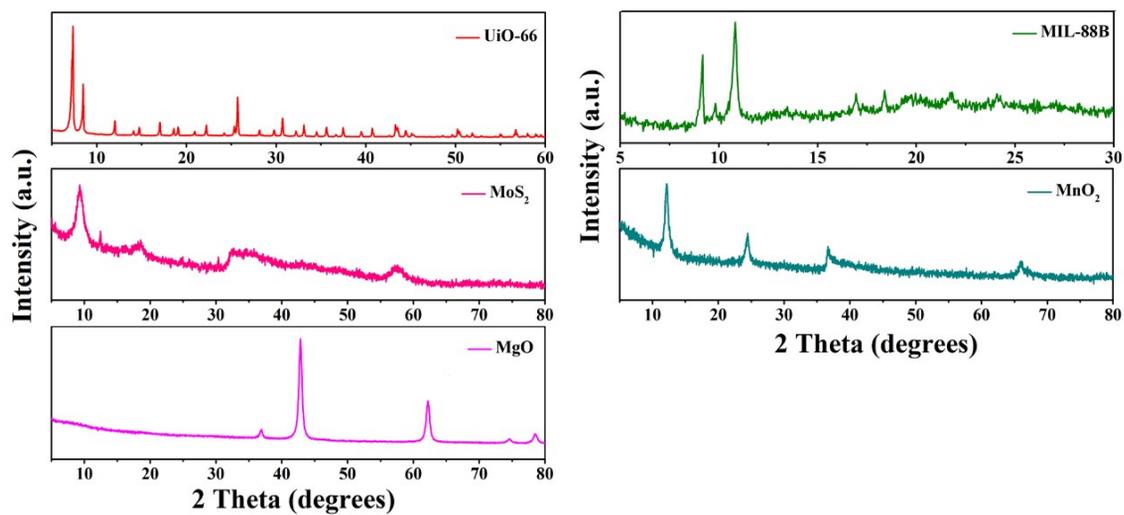


Fig. S2 XRD patterns of UiO-66, MIL-88B, MoS₂, MnO₂ and MgO powder.

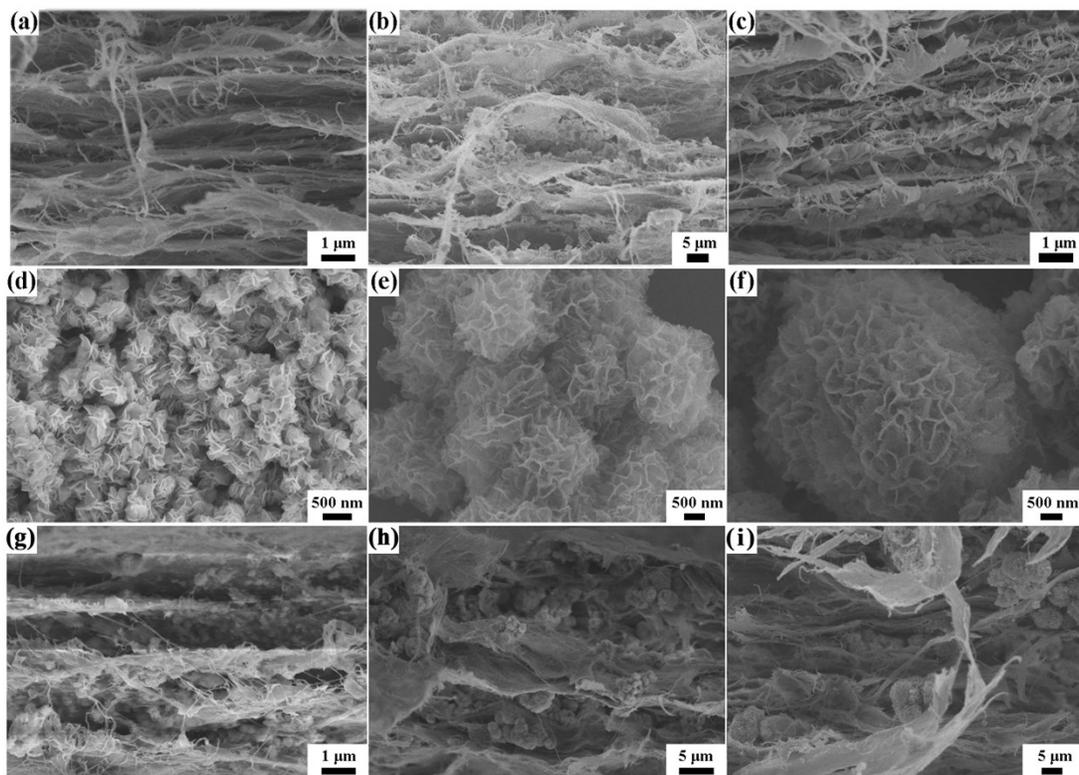


Fig. S3 SEM images of the cross section of (a) bare BC membrane, (b) UiO-66/BC composite membrane and (c) MIL-88B/BC composite membrane; SEM images of (d) MoS₂, (e) MnO₂ and (f) MgO; SEM images of the cross section of (g) MoS₂/BC composite membrane, (h) MnO₂/BC composite membrane and (i) MgO/BC composite membrane.

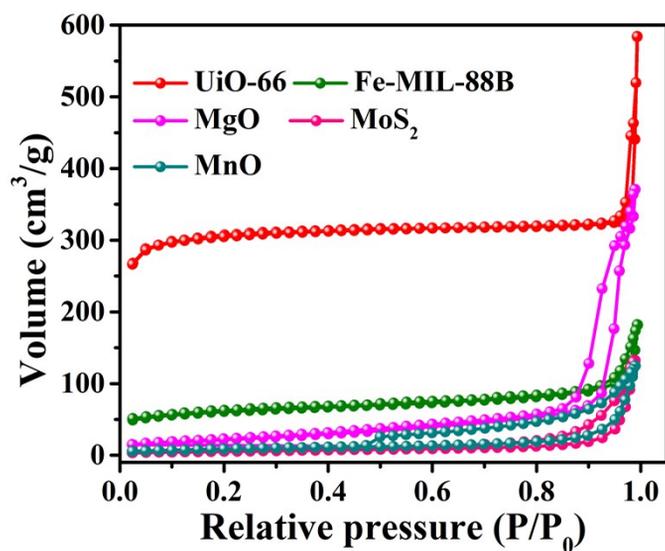


Fig. S4 N₂ adsorption-desorption isotherms of various samples: UiO-66, MIL-88B, MoS₂, MnO₂ and MgO.

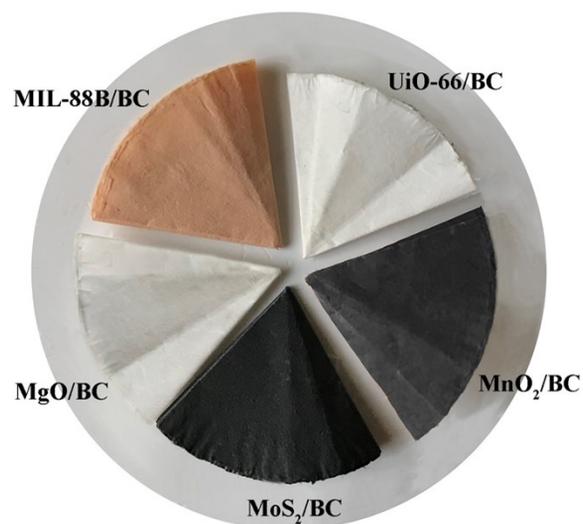


Fig. S5 Photographs of folded UiO-66/BC, MIL-88B/BC, MoS₂/BC, MnO₂/BC and MgO/BC composite membrane.

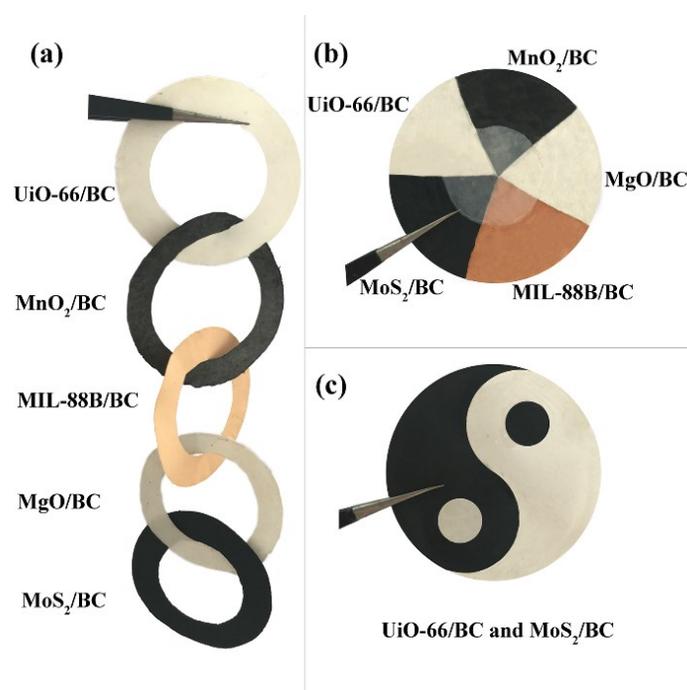


Fig. S6 Photographs of five-ring pattern (a), six-component platter pattern (b) and Chinese Taiji pattern (c) assembled seamlessly by simply splicing wet corresponding membrane.

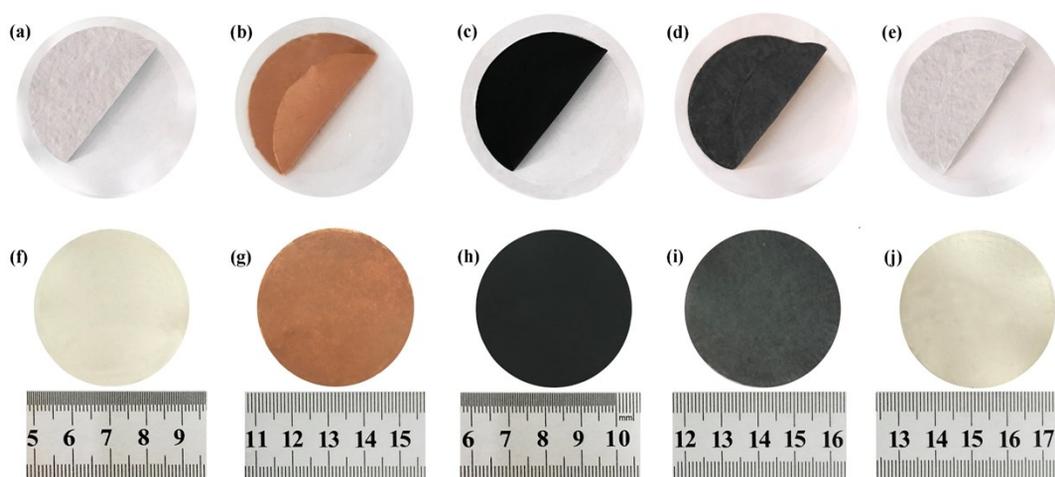


Fig. S7 Photograph illustrations of various single-component BC composite membranes: (a) wet and (f) dry UiO-66/BC composite membrane; (b) wet and (g) dry MIL-88B/BC composite membrane; (c) wet and (h) dry MoS₂/BC composite membrane; (d) wet and (i) dry MnO₂/BC composite membrane; (e) wet and (j) dry MgO/BC composite membrane.

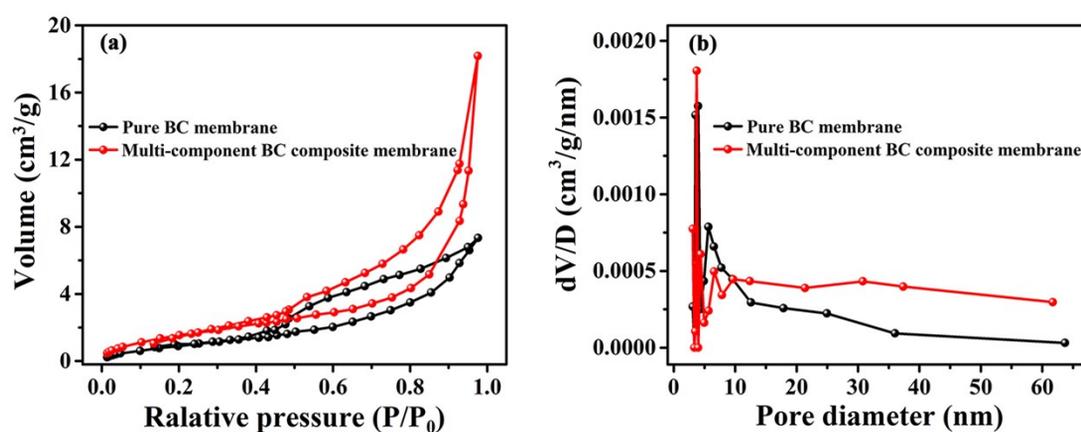


Fig. S8 N₂ adsorption–desorption isotherms (a) and the corresponding pore size distributions (b) of pure BC membrane and multi-component BC composite membrane.



Fig. S9 Filtration setup based on nano-adsorbent/BC composite membrane for the water treatment test.

Table S1 Adsorption capacity of single-component BC composite membranes (SBC), BC matrix portion, nano-adsorbent portion and corresponding powdery nano-adsorbents toward Hg^{2+} , Pb^{2+} and Cd^{2+} at two different concentrations.

	Hg^{2+}		Pb^{2+}		Cd^{2+}	
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Adsorption capacity q_t (mg/g)	80	100	20	40	10	20
SBC	59.63	73.43	14.92	29.79	7.45	14.55
Bare BC matrix portion	0.02	0.10	0.38	1.09	0.34	1.04
Nano-adsorbent portion	159.77	196.66	39.34	78.01	19.39	37.24
Corresponding powdery nano-adsorbents	159.36	164	39.68	76.48	19.99	37.08