Supporting Information

Natural organic matter inhibits aggregation of few-layered black phosphorus in mono- and di-valent electrolyte solutions

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Contents:

14 pages

9 figures

2 tables

Characterization of BPs

BPs concentration was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) (Optima 2000, Perkin Elmer Co.). Natural organic matter (NOM) concentrations in the stock solution and the supernatants of the mixed solution of BPs and NOM after centrifugation were quantified using a total organic carbon analyzer (TOC-L, Shimadzu, Japan). AFM observations were conducted on Bruker Multimode 8 with a Nanoscope V controller after depositing and drying BPs samples onto a mica plate in an Ar-filled glove box. SEM observations were performed using a Hitachi S-3000N scanning electron microscope (Hitachi, Japan) operated at voltage of 15 kV. For XPS analysis, the BPs dispersion was firstly dropped on Si wafer, and then dried in the Ar-filled glove box. XPS spectra were acquired on an ESCALAB 250 spectrometer (Thermo Scientific, UK) using monochromatic Al Kα radiation of energy 1486.6 eV. The zeta potential and hydrodynamic diameter of BPs in various electrolyte solutions were measured using a particle size analyzer (90 Plus Particle Size Analyzer, Brookhaven) at 25 °C. TEM samples were prepared by dropping samples onto carbon-coated grid and drying in the Ar-filled glove box overnight, and characterized using a JEM-2010 FEF microscope (JEOL, Japan). NOM fractions adsorbed onto BPs were characterized by scanning transmission electron microscopy equipped with an electron energy-loss spectrometer (STEM-EELs) at an acceleration voltage of 80 kV (JEM-2100F, JEOL, Japan).

Methods for separation and determination of BPs and NOM

Separation of BPs from NOM stock solution was achieved after centrifugation at 13000 rpm for 30 min at 4 °C by a centrifuge (Microfuge 22 R, Beckmann Coulter, USA), and concentrated BPs at the bottom of centrifuge tube and their amount remained constant with increasing centrifugation time beyond 30 min, indicating that

BPs were completely separated from NOM stock solution.

The solid P in BPs was obtained by the difference between the total P and dissolved P. Briefly, The dissolved P in the stock solution, mainly in the form of species (PO_x) such as PO_4^{3-} and PO_3^{3-}, was quantified based on the sum concentration of PO_4^{3-} and PO_3^{3-} determined by an ion chromatographic system (ICS-3000, Dionex, CA, USA) equipped with an anion-exchange column (IonPac AS19, 4 × 250 mm) after adjusting to adjusting to pH 9 with diluted NaOH and filtration with 0.45 μm membrane filter. The total P in in the stock solution was directly quantified by ICP-OES (Optima 2000, Perkin Elmer Co., USA). Free dissolved NOM in the solution was quantified by a TOC analyzer (TOC-L, Shimadzu, Japan).

Aggregation kinetics of BPs

The aggregation kinetics of BPs dispersion under various solution conditions was measured by time-resolved dynamic light scattering. For each sample, into the cuvette were added 750 μL 5 mg/L BPs suspension and the equal volume of electrolyte solutions containing twice the desired final concentrations of NaCl or $CaCl_2$ without or with NOM. Then the cuvette was immediately placed in the DLS instrument after mixing for 1 s. The size data of BPs were collected every 15 s. The initial aggregation period was defined as the time period from experiment initiation (t_0) to the time when measured D_h values exceeded 1.50 $D_{h,initial}$. The attachment efficiency (α) of BPs aggregated in different electrolyte concentrations was used to quantify aggregation kinetics, and calculated by normalizing the aggregation rate constant obtained in the solution (κ) to that in the diffusion-limited regime (κ_{fast}):

$$\alpha = \frac{\kappa}{\kappa_{fast}} = \frac{\frac{1}{N_0}\left(\frac{dD_h(t)}{dt}\right)_{t\to 0}}{\frac{1}{N_{0,fast}}\left(\frac{dD_h(t)}{dt}\right)_{t\to 0,fast}}$$

(1)

As concentrations of BPs in all samples remain 5 mg/L, α in eq 1 can be calculated by normalizing the initial slope of the aggregation profile in a given solution of interest by the initial slop in the diffusion-limited regime. The critical coagulation concentration (CCC) value of BPs was calculated by extrapolations of the linear regression of α values in both reaction- and diffusion-limited regimes.

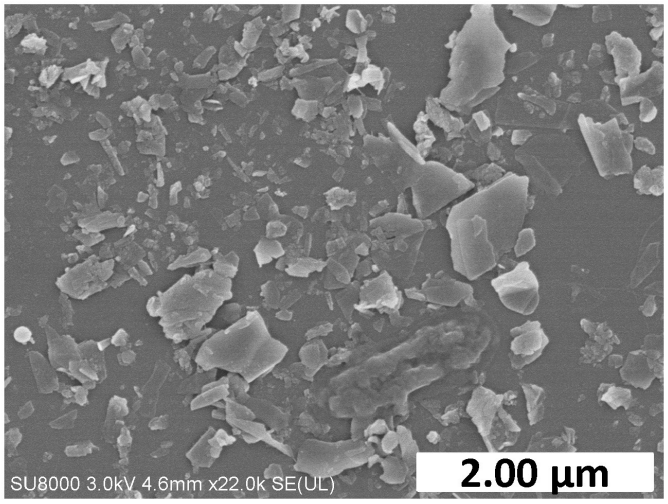

Fig. S1 SEM image of BPs nanosheets.

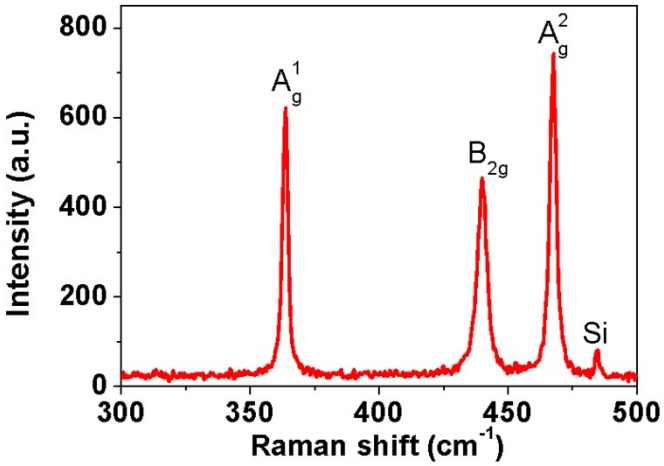

Fig. S2 Raman spectra of bulk black phosphorus.

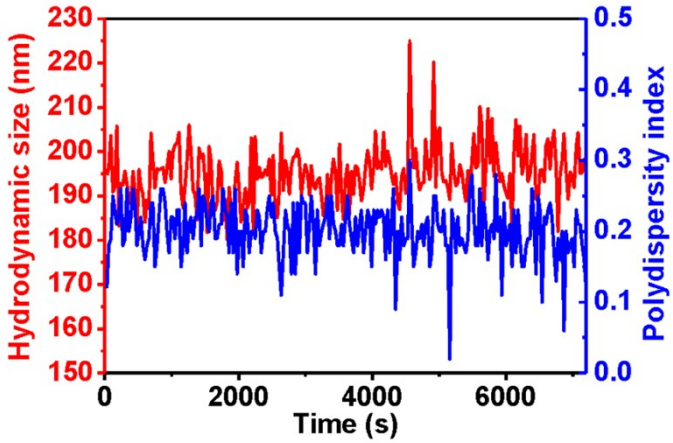

Fig. S3 Evolution profiles of hydrodynamic size (A) and polydispersity index (B) of BPs within 2 h irradiation (658 nm, 35 mW)

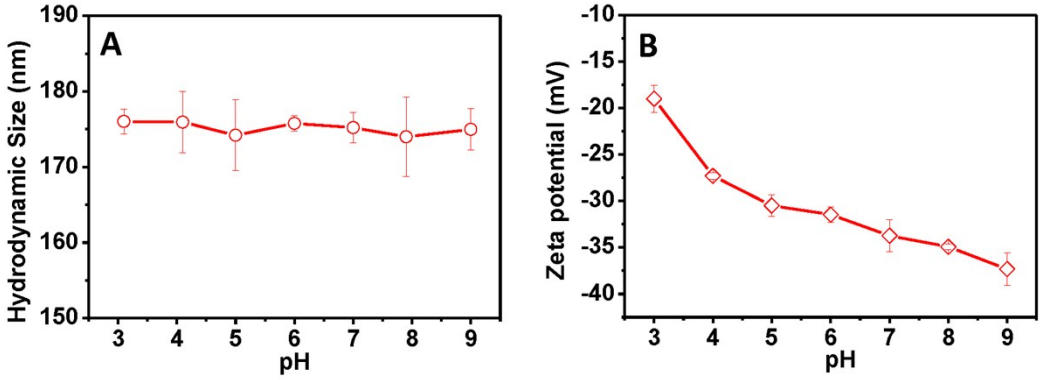

Fig. S4 Hydrodynamic size (A) and zeta potentials (B) of BPs as a function of pH. The error bars represent the standard deviation of at least three measurements..

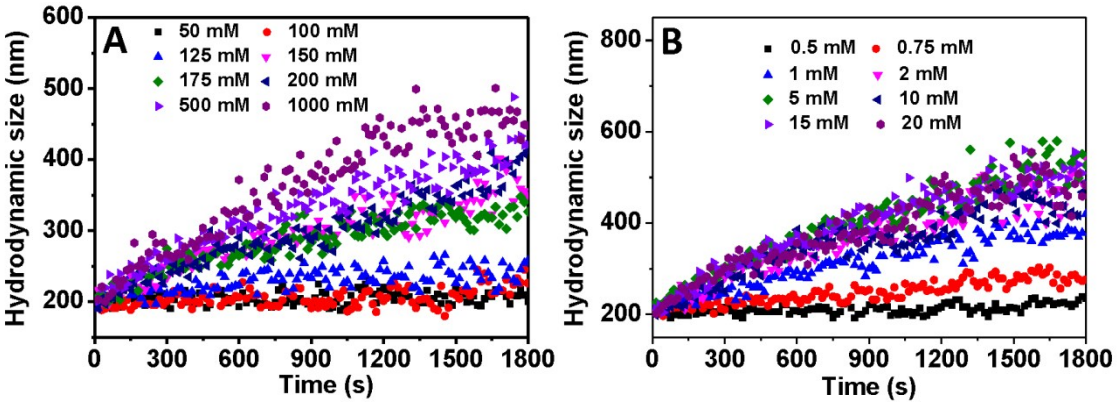

Fig. S5 Representative aggregation profiles of BPs sheets in the presence of various concentrations of NaCl (A) and $CaCl_2$ (B) at solution pH of 5.5.

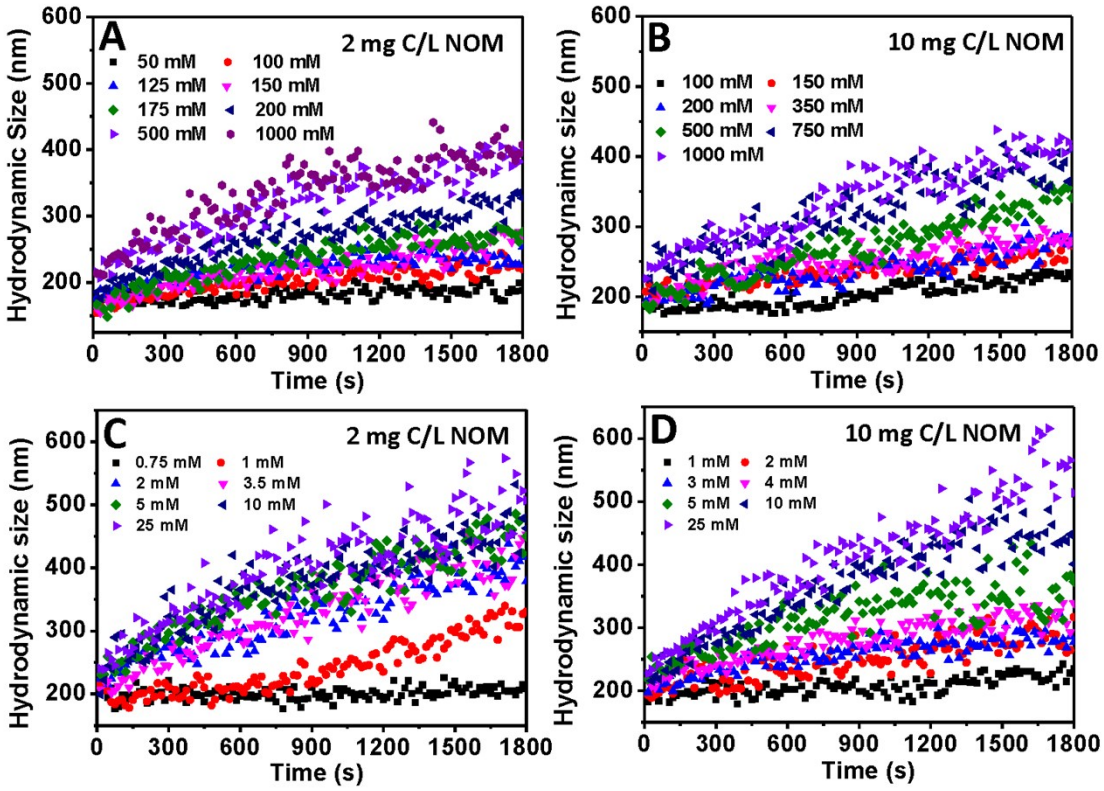

Fig. S6 Representative aggregation profiles of BPs as a function of NaCl (A, B) and $CaCl_2$ (C, D) concentrations in the presence of 2 mg C/L (A, C) and 10 mg C/L (B, D) NOM at solution pH of 5.5.

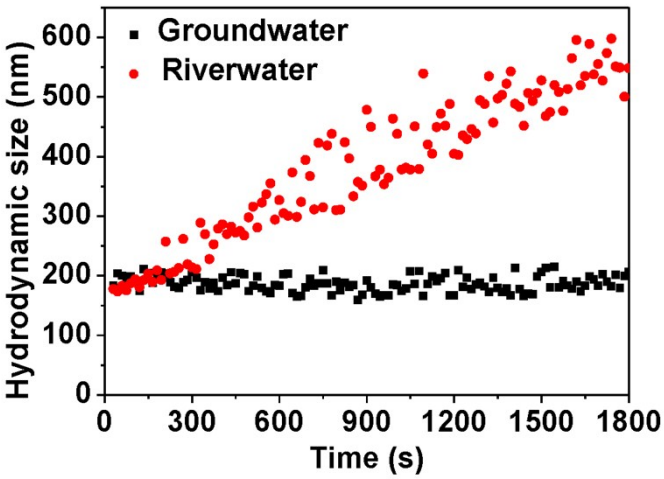

Fig. S7 Aggregation profiles of BPs sheets in groundwater and riverwater samples.

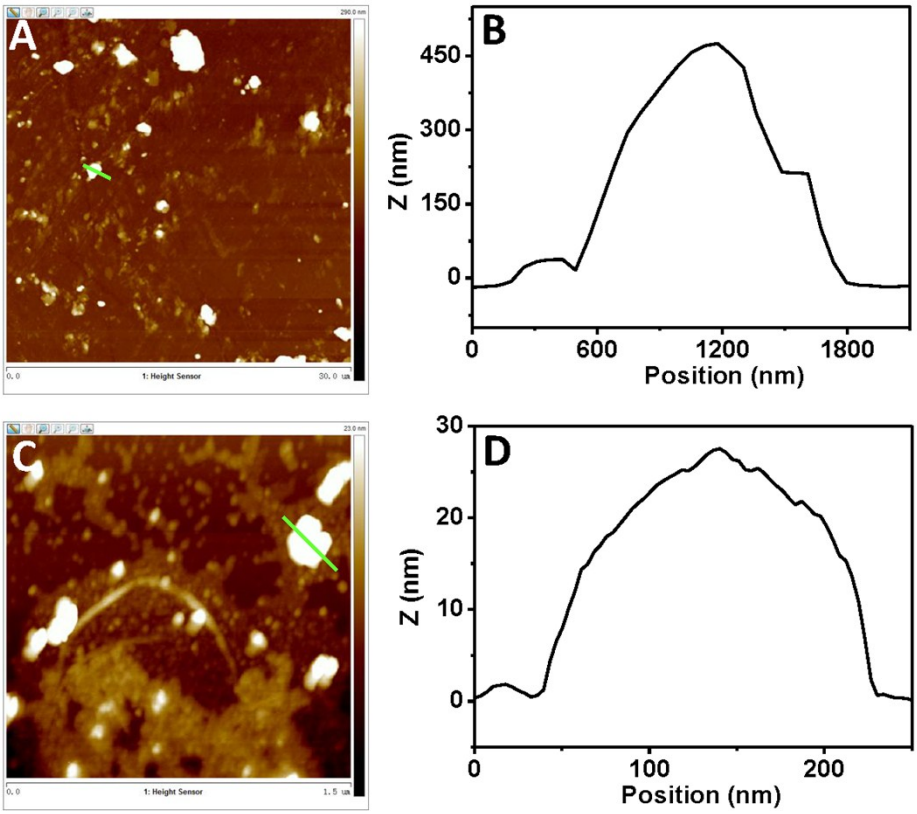

Fig. S8 AFM images of BPs nanosheets in solutions containing 1 mM $CaCl_2$ and 10 mg C/L NOM (A) and 1 mM $CaCl_2$ alone (C). (B) Height images of green lines in A. (D) Height images of green lines in C.

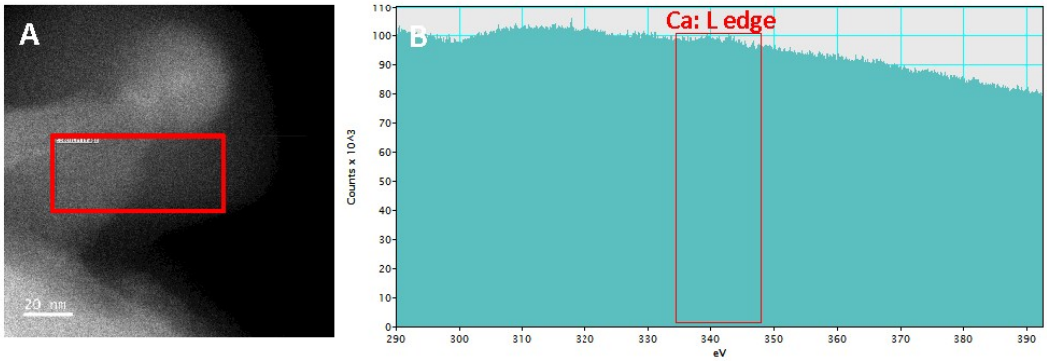

Fig. S9 (A) HAADF-STEM image of BPs incubated with 10 mg C/L NOM and 1 mM Ca^{2+}. (B) EELs spectrum for the edge of BPs surface marked in red solid square in A, demonstrating Ca signal.

Table S1 NaCl and $CaCl_2$ CCC ratio as a function of the concentration of NOM.

	NOM concentration (mg C/L)		
	0	2	10
CCC ($CaCl_2$)	2.5	4.2	7.9
CCC (NaCl)	188.4	268.7	418.7
Ratio	$2^{-6.24}$	$2^{-5.99}$	$2^{-5.73}$

Table S2 Basic physicochemical parameters of groundwater and riverwater samples.

	DOC (mg/L)	pH	Na^+ (mM)	K^+ (mM)	Ca^{2+} (mM)	Mg^{2+} (mM)
Groundwater	1.2	7.7	0.3	0.1	0.4	0.2
Riverwater	4.5	8.2	4.7	0.4	2.3	2.1