Supporting Information

Novel Fe₃O₄ Nanoparticles-based DGT Device for Dissolved

Reactive Phosphate Measurement

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Materials

Hydrochloric acid (HCl, 36%-38%), ammonia solution (NH₃·H₂O, 25%–28%), potassium dihydrogen phosphate (KH₂PO₄), ferric chloride hexahydrate (FeCl₃·6H₂O), ammonium heptamolybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O, sodium nitrate (NaNO₃), sodium hydroxide (NaOH), potassium chloride (KCl), magnesium sulfate (MgSO₄) and calcium chloride (CaCl₂) were purchased from Sinopharm Chemical Reagent Co. Ltd., while ferrous chloride tetrahydrate (FeCl₂·4H₂O) was from Aladdin. All reagents were analytical reagent without further disposal. Deionized water (>18.2 mΩ/cm) was used throughout the experimental procedure. Regenerated cellulose membranes MD 55 (~3500 Da) was purchased from Shanghai green bird science and technology development Co. Ltd.

Synthesis of Fe₃O₄ nanoparticles

 Fe_3O_4 NPs were synthesized via a facile co-precipitation method [1]. To obtain Fe_3O_4 nanoparticles (Fe_3O_4 NPs), 2.703 g (10 mmol) $FeCl_3 \cdot 6H_2O$ and 0.994 g (5 mmol)

FeCl₂·4H₂O were dissolved in 40 mL of deionized water with constant mechanical stirring. Then, 5 mL NH₃·H₂O (28%) was added to the solution under vigorous stirring for 30 minutes at room temperature. The black product was collected by magnetic separation and thoroughly washed with ethanol and deionized water to remove all residual reagents. The final products were drying using a freeze-dryer (SCIENTZ-18N, Ningbo Scieatz Biotechnology, China).

Characterization

The X-ray diffraction (XRD) patterns of the product were obtained using a Philips X'Pert Pro MPD X-ray diffractometer with Cu K_a radiation. Transmission electron microscopy (TEM, JEM-2010, Japan) was used to characterize the morphology of nanoparticles. Their surface potentials and particle size distribution were monitored by zeta-sizer (Malvern Instruments, 3000HS_A, UK). For the surface functional information, Fourier-transform infrared (FT-IR) spectrophotometer (Thermo Nicolet, NEXUS, USA) was used in the region of 400-4000 cm⁻¹. The X-ray photoelectron spectroscopy (XPS) spectra was acquired on an ESCALAB 250 X-ray photoelectron spectrometer (Thermo, America) equipped with Al K $\alpha_{1,2}$ monochromatized radiation at 1486.6 eV X-ray source. The phosphate contents were determined by inductively coupled plasma optical emission spectrometer (ICP-OES, ICP-6300, Thermo Fisher Scientific, USA). UV-Vis spectrophotometer (Shimadzu, UV-2700, Japan) was used for the measurement of phosphate in Nanfei River water to test robustness of Fe₃O₄-DGT. All pH measurements were made with a S220 SevenCompactTM pH meter (Mettler-Toledo Instruments (Shanghai) Co. Ltd., China).

Pretreatment of dialysis membranes

The purchased dialysis membranes (45.0 mm disks with 50 μ m thickness) were pretreated by boiling in a 2% (w/v) solution of NaHCO₃ and a 1 mmol L⁻¹ solution of EDTA·2Na (pH=8.0) at 100 °C for 10 min to remove glycerin and heavy metals. After a final rinse with deionized water, the membranes were stored in a mixed solution of deionized water and ethanol at 4 °C. Dialysis membranes were washed clearly by deionized water and used as the diffusive layer in DGT assembly.

Table S1. The concentration of major cations, dissolved organic carbon (DOC) and pH of collected waters from Hefei Nanfei river water in China

Measured parameters	Value
$[K^+]$ (mg L ⁻¹)	17.90±0.07
$[Ca^{2+}]$ (mg L ⁻¹)	37.72±0.12
[Na ⁺] (mg L ⁻¹)	63.88±0.60
$[Mg^{2+}] (mg L^{-1})$	9.01±0.02
DOC	30.2±0.20
pH	7.5±0.10



Figure S1. Photograph of field deployed DGT devices with a floating-foam pat in Nanfei River in Hefei, China



Figure S2. The main species of phosphate at different pH

References

 H. Zhou, J. Lee, T. J. Park, S. J. Lee, J. Y. Park, and J. Lee, Ultrasensitive DNA monitoring by Au– Fe3O4 nanocomplex, Sens. Actuators, B, 163 (2012) 224-232.