Electronic Supplementary Information

Q-Graphene-Loaded Metal Organic Framework Nanocomposites with Water-Triggered Fluorescence Turn-On: Fluorimetric Test Strips for Directly Sensing Water in Organic Solvents

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Abstract

Supplementary information includes the experimental details including the materials and instruments, the synthesis of QG-loaded MOF nanocomposites, preparation of water test strips, and fluorimetric analysis for water in organic solvents including the evaluation of water in practical samples. Figures are provided for the EDS spectra and element mapping of nanocomposites, the optimization of analysis conditions, and the environmental robustness and storage stability of water test strips.

EXPERIMENTAL SECTION

Experimental section

Materials and instruments

Q-Graphene (QG) nanomaterials were purchased from Graphene Supermarket (Calverton, United States). Melamine (MA), 2-aminoterephthalic acid, and glutaraldehyde (GA) were purchased from Sigma-Aldrich (Beijing, China). Hexadecyltrimethoxysilane (HDS), ethanol, ethylene glycol, N,N-dimethylformamide (DMF), trimethylamine (TEA), dichloromethane (CH_2Cl_2), dichloroethane (DCE), ethyl acetate (EA), isopropanol (IPA) , dimethyl sulphoxide (DMSO), polyethylene glycol

(PEG), acetonitrile (ACN), methanol (MT), butyl alcohol (NBA), tert-butanol (TBA), and aviation gasoline (avgas) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Whatman filter papers used for water test strips were purchased from Sigma-Aldrich (Beijing, China). All of the chemicals are of analytical grade, and all glass containers were cleaned by aqua regia and ultrapure water before usage. Deionized water (18 MΩ) was supplied from an Ultra-pure water system (Pall, USA).

Scanning electronic microscope (SEM) and elemental mapping measurements were conducted for the products using a scanning electron microscope (Hitachi E-1010, Horiba Ex-250) with a microanalysis system (EDAX). UV-3600 spectrophotometer (Shimadzu, Japan) was used to measure the UV-vis spectra of QG-loaded MOF nanocomposites. The fluorescence (FL) measurements were performed by using the Fluorescence spectrometer (Horiba, FluoroMax-4, Japan) on a slit of 5.0 nm, of which a holder was attached for the measurements solid-state FL. Moreover, the photographs of product solutions were taken under UV light at exciting wavelength of 365 nm. Besides, Table centrifuge (Thermo Scientific, Deutschland) was used for the purification of materials. Vacuum drying oven was used for drying the testing strips.

Synthesis of QG-loaded MOF nanocomposites

The QG powder was pretreated by being dispersed in alcohol and further purified by centrifuging, and then dried. An aliquot of QG powder (5.0 mg) was dispersed in 30 mL DMF, followed by the addition of MA (0.2523g). After being stirred for 10 min, BDC-NH_2 (0.3623g) was added. Then, 2 mL GA (25 %) was introduced to be stirred for about 15 min. Further, under the vigorous stirring, an aliquot of Zn $(NO_3)_2$ (1.190g) was added. Next, TEA (1.0 mL) was slowly dropped into the above mixture, and a white precipitate was formed instantly. Moreover, the reaction mixture was stirred for 120 min. Afterwards, the mixture was centrifuged (6000 r/s, 5 min) and washed for five times with DMF (30 mL). The yielded QG-loaded MOF nanocomposites were further dispersed in 30 mL CH_2Cl_2 to be aged for 24 h to exchange the guest molecules of DMF trapped in the MOF framework. After the centrifuging separation, the products were collected and dried in a vacuum oven at 120 ℃ for 12 h to ensure the complete removal of the guest molecules. Finally, the dried products were ground in an agate mortar to obtain the powders of QG-loaded MOF nanocomposites, which were stored in dark for future use.

Preparation of water test strips with QG-loaded MOF nanocomposites

The water test strips were fabricated with the QG-loaded MOF nanocomposites containing highly viscous MA-aldehyde resin according to a modified preparation route reported previously. Typically, filter papers were first cut into the slices of Whatman filter papers test strips (10 mm×10 mm), and then immersed into the suspension of QG-loaded MOF nanocomposites in alcohol (0.20 mg mL^{-1}) for 10 min. After that, the QG-loaded MOF nanocomposites-coated papers were immediately placed onto the super-hydrophobic patterns of HDS to be dried in vacuum for 20 min, which would aid to depress the formidable "coffee ring" effects to achieve uniform coatings of the fluorescent nanocomposites on test strips as described in the previously report [Ref. 23]. The so obtained water test strips were stored in dark for future use.

Fluorimetric analysis for water in organic solvents using QG-loaded MOF-coated test strips

The detection conditions of the test strips-based fluorimetric assay were first optimized for probing water in alcohol, including the QG-loaded MOF nanocomposites dosages (0.0125, 0.025, 0.05, 0.10, 0.20, 0.50, and 1.0 mg mL^{-1}), pH values (1.0, 3.0 5.0, 7.0, 9.0, 11.0, and 13.0), reaction temperature (4.0, 20.0, 37.0, 50.0, 70.0, and 90.0 ^{o}C), and ionic strengths (0.0, 50, 100, 150, 200, 250, and 300 mM NaCl). Moreover, the control tests for some common organic solvents (5.0 % in alcohol) were carried out including 5.0 % (dichloroethane (DCE), ethyl acetate (EA), isopropanol (IPA) , dimethyl sulphoxide (DMSO), polyethylene glycol (PEG), N,N-dimethylformamide (DMF), acetonitrile (ACN), methanol (MT), butyl alcohol (NBA), tert-butanol (TBA), and aviation gasoline (avgas) were separately conducted. Herein, the FL turn-on efficiencies were calculated according to the following equation: FL turn-on efficiency = $(I - I_0)/I_0$, where I_0 and I refer to the FL intensities of the QG-loaded MOF nanocomposites in the absence and presence of water, respectively.

Under the optimized analysis conditions, the test strips-based fluorimetric assay was practically applied for probing water with different percentages (%, v/v) separately in some organic solvents exemplified as alcohol (0.05, 0.8, 1.55, 2.3, 3.05, 3.8, 4.55, 5.3, and 6.0%), avgas (0.1, 1.6, 3.1, 4.6, 6.1, 7.6, 9.1, 10.6, and 12.1%), and DMF(0.1, 1.3, 2.4, 3.6, 4.8, 6, 7.2, 8.4, and 9.3%). Typically, the

QG-loaded MOF nanocomposites-coated water test strips were separately dipped into the organic solvents containing water of different percentages. The water-induced FL enhanced ratios of the test strips were recorded by the FL spectrometer with a holder for the measurements solid-state FL.

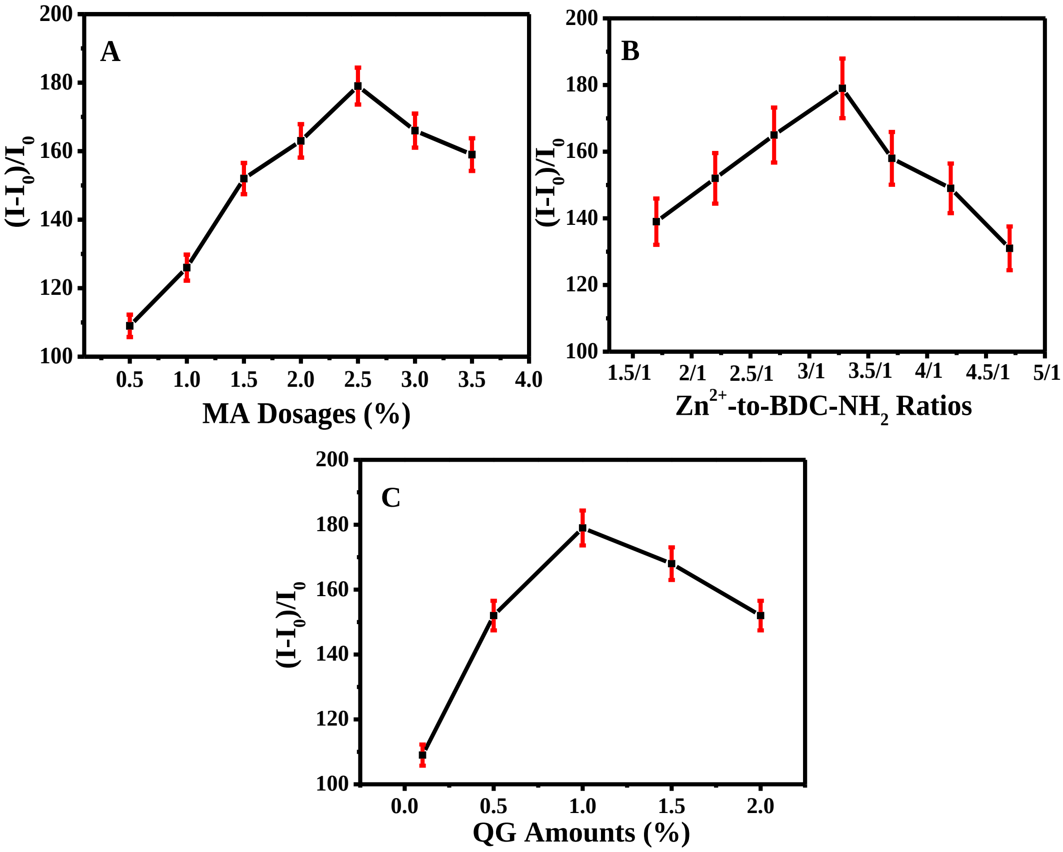
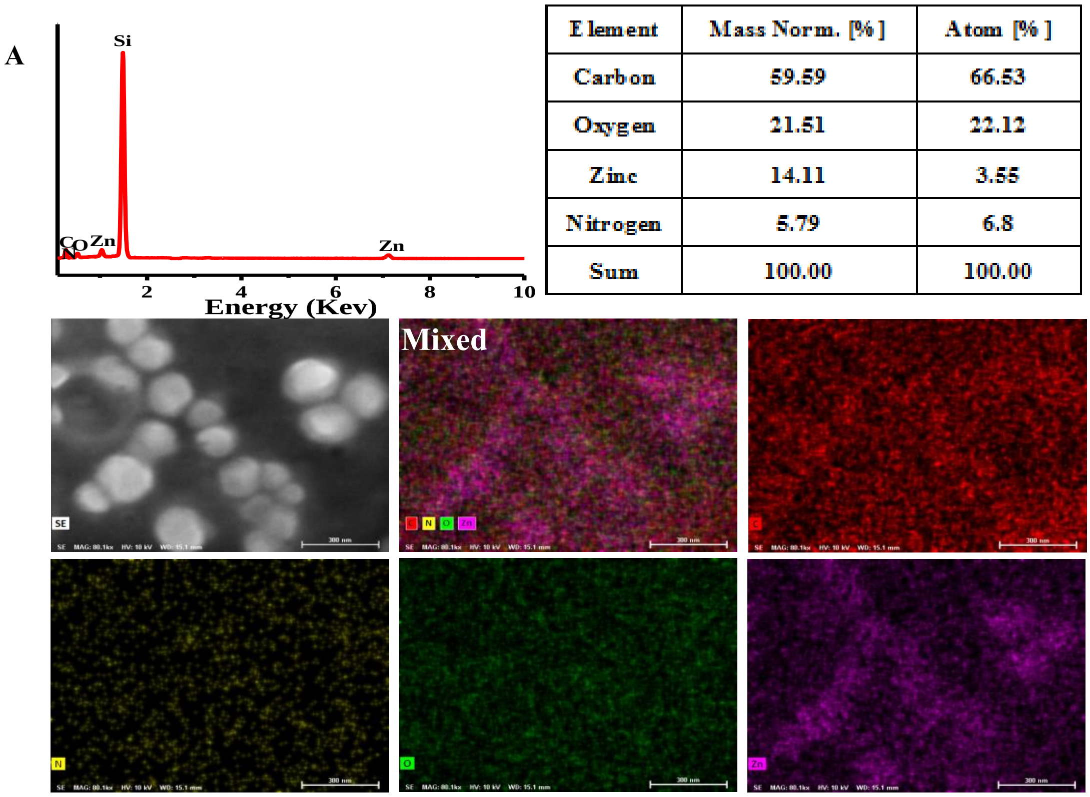
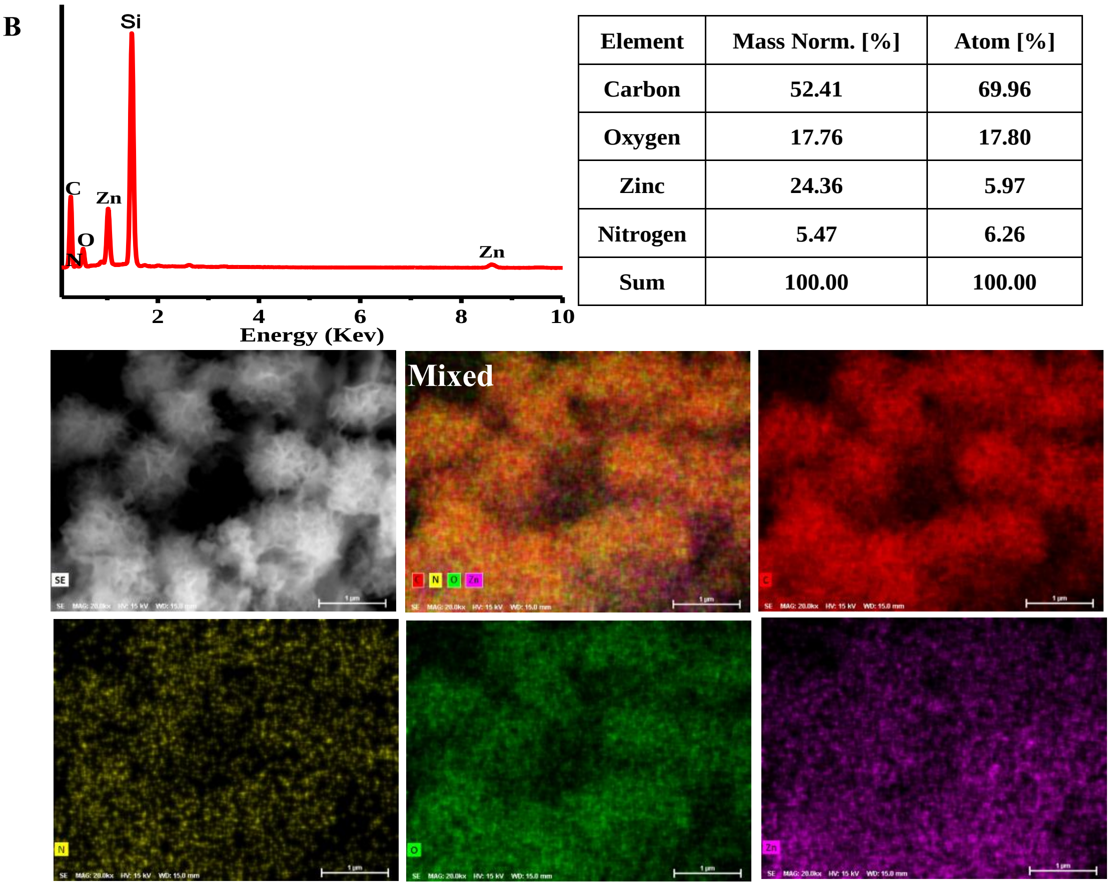


Fig. S1 Optimization of the preparation conditions for QG-loaded MOF nanocomposites with FL turn-on efficiencies depending on (A) MA dosages, (B) Zn^{2+}-to-BDC-NH_2 molar ratios, and (C) QG amounts.



Element	Mass Norm. [%]	Atom [%]
Carbon	59.59	66.53
Oxygen	21.51	22.12
Zinc	14.11	3.55
Nitrogen	5.79	6.8
Sum	100.00	100.00



Element	Mass Norm. [%]	Atom [%]
Carbon	52.41	69.96
Oxygen	17.76	17.80
Zinc	24.36	5.97
Nitrogen	5.47	6.26
Sum	100.00	100.00

Fig S2. EDS spectra and element mapping of QG-loaded MOF nanocomposites (C, N, O, and Zn) in (A) absence and (B) presence of water.

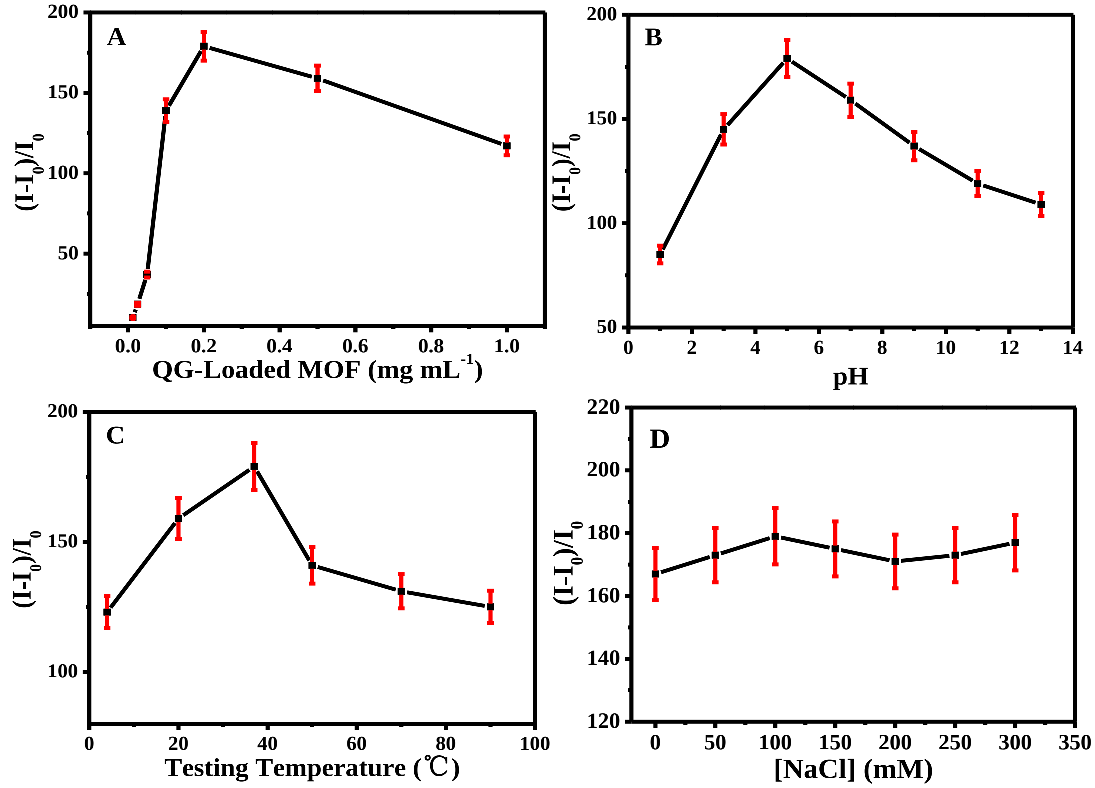


Fig. S3 The FL turn-on efficiencies of water test strips with QG-loaded MOF nanocomposites depending on (A) QG-loaded MOF nanocomposites amounts, (B) pH values, (C) testing temperature, and (D) ion strengths in NaCl concentrations.

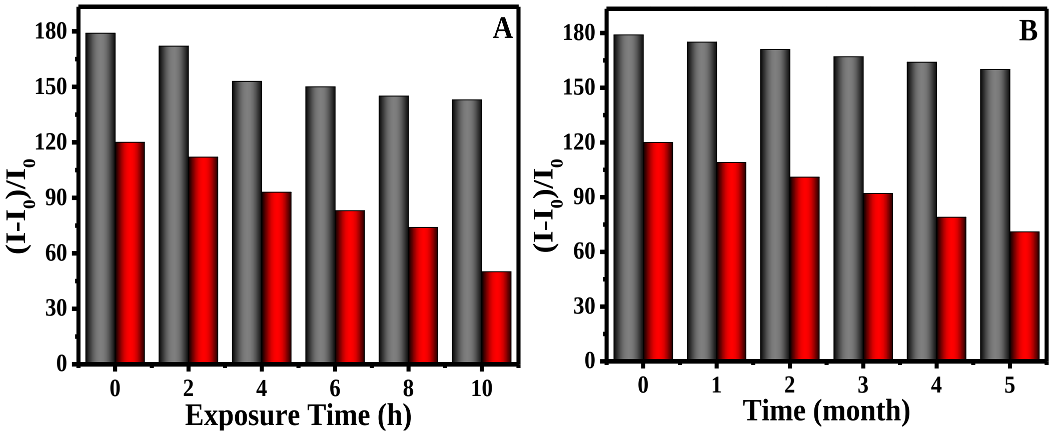


Fig. S4 Comparison of environmental robustness and storage stability between water test strips coated separately with QG-loaded MOF nanocomposites (black) and MOF nanocomposites (red), with the FL turn-on efficiencies changing with different time intervals of (A) exposure under xenon lamp and (B) storage in dark at 4 °C.