Atmospheric low temperature plasma for direct post-synthetic modification of UiO-66

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1. Experimental section

2.1 Reagents and Chemicals

All chemicals used in this work were at least analytical grade and used as purchased without further treatment. 18 M Ω ·cm deionized water (DIW) was produced with a water purification system (PCWJ-10, Pure Technology Co. Ltd, Chengdu, China). Zirconium chloride (ZrCl4), terephthalic acid (BDC), hydroxyterephthalic acid (BDC-OH), 2,5-dihydroxyterephthalic acid (2,5-(OH)₂-BDC) and 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) were obtained from Aladdin Reagents Co., Ltd. (Shanghai, China). CrCl₃· $6H_2O$, N, N-dimethylformamide (DMF), HCl, methanol and ethanol were purchased from Kelong Chemical Reagent Co. Ltd. (Chengdu, China), while dimethylsulfoxide-D6 (DMSO-D6) from Cambridge Isotope Laboratories (CIL). Real samples for sensing analysis were collected from filtered local tap water, Lotus pond water and Funan river water, in Chengdu, Sichuan, China. The stock solution (1000 mg L⁻¹ of arsenic) was purchased from the National Research Center of China (NRCC, Beijing, China), with further dilution before use.

2.2 Instrumentation

A Uwave-1000 microwave reactor for the synthesis of UiO-66 was purchased from Sineo Microwave Chemistry Technology Co. Ltd. (Shanghai, China). The powder X-ray diffraction (PXRD) patterns were obtained from an X'Pert Pro MPD (Philips, Netherlands) X-ray diffraction spectrometer using Cu_{ka} radiation. The scanning electron microscopy (SEM) images were recorded with a JEOL JSM-7500F scanning electron microscope at 30.0 kV, and the elemental mapping was accomplished by the energy dispersive X-ray spectroscope (EDS) coupled to the SEM. The UV-Vis absorption spectra were collected with a UV-1750 UV-vis spectrophotometer (Shimadzu, Japan). The photoluminescence (PL) emission spectra were collected with an F-7000 FL spectrometer (Hitachi, Japan) using a 350 nm optical filter with excitation at 320 nm. The ¹H-NMR spectrum was acquired using a BRUKER AVANCE 400 spectrometer (Bruker, Switzerland). In the case of UiO-66, 2 mg of the dry sample was digested in 0.6 mL of DMSO and 20 µL of HF (40% aqueous solution) under ultrasound. The electron paramagnetic resonance spectra were obtained with a EPR spectrometer (EXM, Bruker, Germany). Nitrogen (N_2) gas adsorption-desorption isotherms were obtained using the Brunauer-Emmett-Teller (BET) method on surface area and porosity analyzer Micromeritics ASAP 2460 (4356 Communications Dr. Norcross, GA 30093-2901, USA) at 77 K. The photoluminescence lifetime measurements were performed with a Fluorolog-3 spectrofluorometer (Horiba Jobin Yvon), with a picosecond photo detection module (PPD-850, Horiba Scientific) as the detector.

1.3 Synthesis

UiO-66: 5.4 mmol ZrCl₄ was dissolved in the mixture of 50 mL DMF and 10 mL concentrated HCl under ultrasonication for 20 min. 7.5 mmol BDC and 100 mL DMF were added in and the mixture was left under ultrasound for another 20 min. The obtained mixture was kept in the microwave reactor at the temperature of 100 °C for 1 h, and then cooled down to room temperature. The obtained white precipitate was purified by washing three times with DMF and ethanol, respectively, and then soaked in DMF and ethanol successively for one day to remove trapped guest molecules, such as solvents and unreacted monomers from the pores, followed by being centrifuged (10000 rpm, 10 min) and vacuum dried at 80 °C overnight. Heat treatment at 220 °C under vacuum for 3 h was applied for desolvation of UiO-66 prior to PXRD characterization. Yield: 73 %.

UiO-66-OH: UiO-66-OH was tried to be prepared according to a previous reported method.¹ 41 mg ZrCl₄ was dissolved in the mixture of 5 mL DMF and 0.3 mL concentrated HCl under ultrasonication for 20 min. 32 mg BDC-OH was added, before the mixture was left under ultrasound for another 20 min. The obtained mixture was sealed in autoclaves and heated for 24 h at the temperature of 120 °C, before cooled down to room temperature. The obtained white precipitate was centrifuged at 10000 rpm for 10 min, followed by washing three times with DMF and methanol, respectively, and dried at 80 °C overnight under vacuum.

MIL-101(Cr): MIL-101(Cr) was prepared similar to the methods reported earlier.² Briefly, a suspension containing $CrCl_3 \cdot 6H_2O$, terephthalic acid and H_2O with a molar ratio of 1:1:500 was sealed in autoclaves and heated for 24 h at the temperature of 220 °C, before cooled down to room temperature. The obtained light green precipitate was centrifuged at 10000 rpm for 10 min, followed by treating for 1 h at 70 °C with N, N-dimethylformide under ultrasound for purification. After that, the powder was washed thoroughly with deionized water and ethanol, and then soaked in ethanol for 24 h. The solid was finally vacuum dried overnight at 150 °C. Yield: 33 %.

1.4 Plasma treatment

A laboratory-made dielectric barrier discharge (DBD) system was employed to perform the post treatment of UiO-66. The plasma was created with an output power of 40 W by a cylindrical DBD device which was simply consisted of a common glass tube (5 mm i.d.×7 mm o.d.×10.0 cm in length), with a tungsten wire used as the inner electrode and a copper wire tightly wrapped around the outside of the glass tube as the external electrode. The treated samples are denoted as UiO-66-P or MIL-101-P.

Terephthalic acid: 5 mg of terephthalic acid was dispersed in 10 mL of distilled H₂O and 15 μ L of NaOH (1 M) added. Then, the mixture was added to the discharge chamber and discharged at 40 W for 1 h.

UiO-66: 5 mg of UiO-66 was dispersed in 10 mL of distilled H₂O. The sample was discharge at an output current of 1.35 A with AC power source. The resultant UiO-66 was dried at 100 °C overnight before further characterization.

MIL-101(Cr): 2.5 mg of MIL-101(Cr) was dispersed in 10 mL of distilled H₂O. The sample was discharge for 1~2 h at 37 W with AC power source. The resultant MIL-101(Cr) suspension was diluted 5 times with DIW water before the characterization of photoluminescence spectra.

2. Results and discussion



Figure S1. PXRD pattern of UiO-66-OH obtained by using solvothermal method with DMF as solvent.



Figure S2. (a) PXRD patterns of the desolvated UiO-66, as-synthesized UiO-66 and calculated UiO-66, and the calculated pattern was stimulated from Diamond based on the corresponding deposited cif-files under CCDC 837796 (UiO-66); (b) FT-IR spectra of BDC (red line) and as-synthesized UiO-66 particles (black line).



Figure S3. (a) FT-IR spectra of BDC (black line) and BDC-OH (red line). (b) FT-IR spectra of assynthesized UiO-66 (black line), desolvated UiO-66 (red line) and the UiO-66-P (blue line).

As for the as-synthesized UiO-66 (black trace), the intense band at 1583 and 1400 cm⁻¹ is associated to the in- and out-of-phase stretching modes of the carboxylate group, while in the lower frequencies modes (500-1000 cm⁻¹) OH and CH bending are mixed with Zr-O modes. The dominant intense and broad band centred at around 3410 cm⁻¹ was due to physisorbed water condensed inside the cavities. The band at 1655 cm⁻¹ is ascribed to DMF, the solvent molecules retaining in the MOFs. Upon treating with plasma (blue trace), no strong changes occur except the disappearance of the band associated to DMF (1655 cm⁻¹), indicating that the low temperature plasma can not only install of hydroxyl group on the UiO-66 skeleton, but also help to further purify the product. We infer that it is supposed to be the same situation (disappearance of the DMF band) for the desolvated UiO-66 via heat activation, which turns out to be the case (red trace).



Figure S4. (a) The transformation from non-fluorescent terephthalic acid to fluorescent hydroxyterephthalic acid by capturing \cdot OH; (b) fluorescence spectra of terephthalic acid (BDC) and plasma treated terephthalic acid (BDC-plasma).



Figure S5. (a) Fluorescence spectra of plasma-modified UiO-66-P at 1 mg mL⁻¹, 0.5 mg mL⁻¹, 0.2 mg mL⁻¹ and 0.1 mg mL⁻¹, respectively. (b) Corresponding fluorescence intensity at 425 nm.



Figure S6. (a) Fluorescence spectra of UiO-66 treated at discharge current of 0.6 A, 0.8 A, 1.0 A and 1.35 A, respectively. (b) Corresponding fluorescence intensity at 425 nm.



Figure S7. (a) Fluorescence spectra of 0.1 mg mL⁻¹ UiO-66 after plasma treatment with 0 min, 5 min, 10 min, 30 min, 60 min, 120 min, and 180 min, respectively. (b) Corresponding fluorescence intensity at 425 nm.



Figure S8. ¹H-NMR spectrum of terephthalic acid, 2-hydroxyterephthalic acid, and 2,5dihydroxyterephthalic acid. The powder was digested in DMSO-D6 (500 μ L) and HF (20 μ L, 40% aqueous solution) under ultrasound.

Pure BDC, BDC-OH and 2,5-(OH)₂-BDC powder was also measured, respectively, by the ¹H-NMR spectrum as a reference (Figure S8), which turns out that their resonances appear at different chemical shifts and can be clearly assigned. The signal at 7.28 ppm (2H, s) can be assigned to characteristic resonance peak of 2-hydroxy-1,4-benzenedicarboxylic acid. As shown in Figure 4, the 1H resonances of UiO-66 appear at 8.05 ppm (4H, s), which belongs to the characteristic peaks of BDC. In the case of UiO-66-P, the signal at 8.05 ppm (marked by black square) definitely belongs to unreacted terephthalic acid. Beyond that, however, there are three new ¹H resonances peaks (marked by red rhombus), two doublets (δ 7.89 ppm, 1H, d; δ 7.45 ppm, 1H, d) and a singlet at δ 7.44 ppm (1H, s), in the aromatic region of the 1H NMR

spectrum. This signal is in line with the spectrum observed for 2-hydroxyterephthalic acid resulted from the reaction between •OH and terephthalic acid. However, there is no signal assigned to dihydroxy-BDC, demonstrating the selectivity of our PSM method and no dihydroxylation during the plasma treatment.



Figure S9. N_2 adsorption/desorption isotherms of pure UiO-66 (black) and UiO-66-P (red). Solid and open symbols for adsorption and desorption, respectively.



Figure S10. PXRD pattern of plasma-treated UiO-66-P (blue), the desolvated UiO-66 (red) and calculated UiO-66 (black).



Figure S11. The optical excitation and emission of UiO-66-P.



Figure S12. F/F_0 of UiO-66 (left) and UiO-66-P (right) in the presence (red bar) or absence (gray bar) of As at 1 µg mL⁻¹ level.



Figure S13 Scanning electron microscope image of prepared UiO-66-P (a) and the collected powder after incubation of UiO-66-P with 25 μ g mL⁻¹ As for 1 hour (b); Energy dispersive X-ray spectroscope (EDS) results obtained from UiO-66-P (c) and UiO-66-P treated with As (d).



Figure S14 Energy-dispersed X-ray mapping image of Zr, O, C, As obtained from the crystals of UiO-66-P (a) and UiO-66-P treated with As (b).

Based on the EDS spectra of UiO-66-P and the collected powder after incubation of UiO-66-P with arsenic shown in Fig. S13, characteristic peak of arsenic at 1.3 KeV appeared for the UiO-66-P incubated with As, declaring the adsorption of As by UiO-66-P. The elemental mapping of As (Fig. S14) further confirmed the adsorption more intuitively.



Figure S15 (a) FTIR spectra of UiO-66-P and the collected powder after incubation of UiO-66-P with 25 μ g mL⁻¹ As for 1 hour. (b) UV-Vis absorption spectra (inset: partially magnified) of UiO-66-P and UiO-66-P toward various concentrations of arsenic and pure arsenic solution. The samples were all dispersed in DI water. (c) Fluorescence spectra of UiO-66-P and UiO-66-P toward various concentrations of arsenic, and corresponding curves of fluorescence decay of them with black scatter plot of background on prompt (d).

The FTIR spectra was conducted to reveal the interaction between arsenic and the framework of UiO-66-P. After incubation in arsenic solution, the broad As-O stretching vibration bands between 788 and 970 cm⁻¹ appear, confirming the inclusion of arsenic into UiO-66-P. After adsorption, the characteristic absorption peaks at 478 cm⁻¹ corresponding to Zr-O vibration on UiO-66-P shifted to the lower wavenumbers, demonstrating the formation of strong Zr-O-As bonds through the anion-exchange mechanism³ and Zr clusters plays a vital role in arsenic adsorption. Furthermore, a discernible blue shift in the IR absorption occurs for the stretching vibrations of C=O bonds in the arsenic-treated UiO-66-P, might indicating the occurrence of complexation between arsenic and Zr-O clusters which weakening the interaction between the organic ligands and Zr clusters. We also measured the UV-Vis absorption spectra to further provide information on the Zr-O-As interactions. After arsenic treatment, the appearance and gradual increasing of the characteristic peak of arsenic at 309 nm for UiO-66-P also suggested the absorption effect of arsenic. For comparison, there is also signal increasing for arsenictreated BDC-OH, while no significant spectral changes were observed for UiO-66 or BDC (Fig. S16). These results hint that BDC-OH originated from plasma treatment also plays a vital role in this study. More importantly, an obvious red shift in the UV-Vis absorption from 302 to 309 nm occurs for arsenic in the UiO-66-P when compared to free arsenic, which give further evidence that arsenic has coordination interaction with the UiO-66-P, in agreement with the FTIR analysis.



Figure S16. (a) the UV-Vis absorption spectra of UiO-66, and UiO-66 in the presence of $1 \mu g \text{ mL}^{-1} \text{ As}$; and (b) the UV-Vis absorption spectra of BDC, BDC+As, BDC-OH and BDC-OH+As. Note: the suspension of sample was detected with DI water as the dispersant.

Table S1 Photoluminescent lifetime measurement
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Sample	$\overline{\tau}/ns^a$	τ_i/ns^b	f_i	x_R^2
UiO-66-P	1.20	1.96 ± 0.05	0.23	1.15
		6.92 ± 0.04	0.07	
		0.35 ± 0.01	0.70	
UiO-66-P+1 ppm As	1.82	2.31 ± 0.05	0.23	1.08
		8.59 ± 0.03	0.12	
		4.37±0.01	0.65	
UiO-66-P+5 ppm As	2.63	2.57 ± 0.06	0.22	1.02
		$9.19{\pm}0.02$	0.19	
		0.51 ± 0.01	0.59	
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a: The fluorescence decay was fitted to tri-exponential.

b: The retrieved lifetime was calculated with the standard deviation as error.

The average fluorescence lifetime was calculated using the equation:

 $\tau = \sum f_i \tau_i = f_1 \tau_1 + f_2 \tau_2 + f_3 \tau_3$

Where τ_i is the lifetime and f_i is the contribution factor of τ_i to τ , which were collected from the fluorescence lifetime measurements after proper fitting. The data were fitted with the third order exponential decay.



Figure S17. (a) Fluorescence intensity of UiO-66-P in the presence (red bar) or absence (gray bar) of As at 1 μ g mL⁻¹ with different concentrations of 0.01 mg/mL, 0.02 mg/mL, 0.05 mg/mL, 0.1 mg/mL, 0.15 mg/mL, 0.2 mg/mL and 0.3 mg/mL, respectively. (b) F/F₀ value under different concentration in the presence of 1 μ g mL⁻¹ As.



Figure S18. The effect of HEPES concentration on the fluorescent intensity upon the addition of arsenic into the UiO-66-P detection system (arsenic concentration was set at $1 \ \mu g \ mL^{-1}$).



Figure S19. The effect of incubation time on the fluorescent intensity upon the addition of arsenic into the UiO-66-P detection system (arsenic concentration was set at $1 \ \mu g \ mL^{-1}$).

Fluorescent probe	Range (µg L ⁻¹)	LOD (µg L ⁻¹)	Detection matrix	Ref
ZnO QDs	10-100	27	Reference water	4
	100.0000	100	Natural water	-
Zn(cur)O NPs	100-3000	100	Reference water	5
YPO4:Eu ³⁺ NPs	0-100000	10000	Reference water	6
CdSe/ZnS&CdTe QDs- GSH	0.375-2250000	75	Reference water River water	7
Fe-GQDs	5-100	5.1	Reference water	8
Green fluorescent protein	37.5-450	30	Reference water Groundwater	9
1,2,5-dithiazepane	0-633500	11077	Reference water Soil	10
Acf and RhB	40-90	10	Reference water Natural lake water	11
MPA-capped CdTe QDs and R6	1.49-149	45	Reference water, Natural water	12
NH ₂ -MIL-88(Fe)	7.5-3750	4.2	Reference water Tap water Lake water	13
Fluorescent-DNA loaded Fe ₃ O ₄ NPs	0-69500	41.7	Reference water	14
Dihydroxyacetophenone- oxime	0-136770	4089	Reference water	15
CdS-MAA QDs	0.08-1000	20	Sediment sample	16
UiO-66-P	50-1000	28	Reference water Tap water River/Pond water	This work

Table S2 Comparison of various fluorescent sensors for the determination of arsenic

Sample	Concentration (µg mL ⁻¹)	Added (µg mL ⁻¹)	Detected (µg mL ⁻¹)	Recovery (%)	RSD (%) (n=3)
Tap water	nd ^a	0.20	0.19	93	2.7
Lotus water	nd ^a	0.20	0.18	91	1.3
Funan River	nd ^a	0.20	0.22	111	4.8

Table S3 Determination of arsenic in real samples by the proposed UiO-66-P probe.

^a not detected.



Figure S20. (a) PXRD patterns of the as-synthesized MIL-101(Cr) and simulated MIL-101(Cr); (b) Fluorescence spectra of BDC-OH (black dashed and solid lines), MIL-101(Cr) and the plasma-treated MIL-101(Cr).

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