Supporting Information

Encapsulating Ag Nanoparticles into ZIF-8 as an Efficient Strategy to Boost Uranium Photoreduction without Sacrificial Agents

Pengyan Jiang[‡a], Kaifu Yu[‡ab], Haibo Yuan[‡a], Rong He[b], Mengping Sun[c], Feng Tao[d], Liangbing Wang[*a], and Wenkun Zhu[*b]

[a] *State Key Laboratory for Powder Metallurgy, Key Laboratory of Electronic Packing and Advanced Functional Materials of Hunan Province, School of Materials Science and Engineering, Central South University, Changsha, Hunan 410083, P. R. China*

[b] *State Key Laboratory of Environment-friendly Energy Materials, National Co-innovation Center for Nuclear Waste Disposal and Environmental Safety, Nuclear Waste and Environmental Safety Key Laboratory of Defense, School of National Defence Science & Technology, Southwest University of Science and Technology, Mianyang, Sichuan 621010, P. R. China*

[c] *Hunan Radiation Environmental Monitoring Center, Ecology and Environment Department of Hunan Province, Changsha, Hunan 410014, P. R. China*

[d] *Hunan Nuclear Institute of Geological Survey, Changsha, Hunan 410011, P. R. China*

‡ These authors contributed equally to this work.

*To whom correspondence should be addressed.

E-mail: wanglb@csu.edu.cn, zhuwenkun@swust.edu.cn

Experimental Section

1. Chemicals and Materials

Uranyl(VI) nitrate hexahydrate ($UO_2(NO_3)_2 \cdot 6H_2O$) and silver nitrate ($AgNO_3$) were obtained from the Beijing HWRK Chem Co., Ltd. Arsenazo Ⅲ was obtained from the Macklin Biochemical Technology Co., Ltd in Shanghai. 2-methylimidazole, Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) and other conventional reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. All solvents and chemicals were in analytical grade and used as received without further purification. Deionized water was used exclusively in this study.

2. Preparation of ZIF-8 and Ag/ZIF-8

Firstly, 3.7 g of $Zn(NO_3)_2 \cdot 6H_2O$ and 4.1 g of 2-methylimidazole were dissolved in 500 mL of methanol. After 24 h, the precipitation was collected and washed with deionized water for 5 times. Then, the precipitation was vacuum dried at 60 °C for 8 h to obtain ZIF-8. In addition, 95 mg of ZIF-8 was added in methanol (35 mL) and ethanol (35 mL) mixed solution to prepare a suspension. After that, 7.9 mg $AgNO_3$ of was added to the suspension with stirring for 24 h. Then, the suspension was transferred to a 100-mL Teflon lined steel autoclave and following heated at 160 °C for 5 h to obtain the powder. After washed with deionized water for 5 times, the powder was vacuum dried at 60 °C for 8 h to obtain Ag/ZIF-8. Without adding ZIF-8, pristine Ag nanoparticles (Ag-NP) was also prepared for further comparison.

3. Uranium Enrichment Tests

The U(VI) solution was prepared by dissolving $UO_2(NO_3)_2 \cdot 6H_2O$ with deionized water. The pH values of U(VI) solution were regulated by adding trace HCl or NaOH solution. For U(VI)

photoreduction, 5 mg of samples and 20 ml of U(VI) solution (C_0 = 200 ppm, pH = 5.0) were added into a glass reactor. Subsequently, the glass reactor was irradiated by a Xenon lamp (Perfectlight PLS-SXE300) in air atmosphere for 60 min. For comparison, similar process was performed for U(VI) adsorption without illumination. To test the recycling of Ag/ZIF-8, the first measurement was conducted as described above. The samples were collected at the end of the U(VI) photoreduced experiment, followed by ultrasound for 2 h in 100 mL of 0.1 mol/L Na_2CO_3 solution, and then dried into the next cycle. Moreover, the applicable scope of Ag/ZIF-8 was further investigated. The experiments were carried out in U(VI) solution with different C_0 (pH = 5.0) or different pH (C_0 = 10 ppm). The ion interference experiments were carried out in a 10 ppm U(VI) solution (pH = 5.0) with 10 times interfering ions. As for the experiment in the effect of sacrificial agents, 20 mL of U(VI) solution (C_0 = 200 ppm, pH = 5.0) containing different methanol dosage were obtained to instead of the aforementioned U(VI) solution. Furthermore, the 20 mL of U(VI) solution containing 3 mL of methanol was also used to test the applicable scope of Ag/ZIF-8.

In addition, the U(VI) enrichment over Ag/ZIF-8 was also directly performed under natural sunlight rather than a Xenon lamp. To be more specific, 5 mg of Ag/ZIF-8 and 20 mL of U(VI) solution (C_0 = 200 ppm, pH = 5.0) were also added into a glass reactor. Then, the glass reactor was placed outside on a sunny day in Changsha, Hunan Province, China. The intensity of natural sunlight was measured by a densitometer.

After separate the solid from the liquid phase, the concentration of U(VI) was analyzed by using arsenazo III spectrophotometric method at wavelength of 652 nm (Figure S18). The limit

of detection was calculated according to international union of pure and applied chemistry (IUPAC) specifications which are summarized below for the readers' convenience :

$$\sigma = \sqrt{\frac{\sum (x_b - \overline{x_b})^2}{n-1}}$$

$$x_l = \overline{x_b} + k\sigma$$

where x_l, n, σ, x_b, and $\overline{x_b}$ represent the limit of detection, the number of replicates (minimum of 20 replicates required), the standard deviation, the blank measurement values, and the mean blank, respectively. k is a numerical factor indicative of the confidence level obtained (here, k = 3 corresponds to 99.86%). Thus, the lowest trusted detection concentration of uranium was calculated at 3.8 ppm. In addition, inductively coupled plasma-mass spectrometry (ICP-MS, PE nexion 2000) was used to measure the concentration of uranium which is less than the lowest trusted detection concentration of uranium via arsenazo III spectrophotometric method.

The U(VI) removal ratio (%) was calculated as $[(C_0-C_e)/C_0] \times 100\%$. The U(VI) enrichment mass (mg/g) was calculated as $(C_0-C_e) \times V/m$. Where C_0 and C_e are the initial and final concentrations of uranium (ppm, mg/L); V is the volume of the solution (L), and m is the mass of samples (g).

4. The detection of O_2

By using He as the internal standard, O_2 was detected by gas chromatography equipped with TCD detector. As shown in Figure S19 and Figure S20, the volumes of O_2 and He were both linearly related to the corresponding peak area. A 100 ml reactor equipped with a gas sample connection was used to detect the resulted O_2 (Figure S21). 5 mg of Ag/ZIF-8 and 20 mL

of U(VI) solution were added into the reactor. The reactor was bubbled with pure Ar (99.999%) for 30 min and then sealed. Next, 1 bar of pure Ar was used to charge and discharge the reactor for three times. We injected 0.1 mL of pure He into the reactor through gas sample connection and then let it stand for 30 min to diffuse the gas. To detecte the amount of O_2 before the reaction, 0.1 mL of gas was extracted from the reactor. Then, the reactor was irradiated by a Xenon lamp for 60 min. During the reaction, 0.1 mL of gas was extracted from the reactor every 20 min. The amount of produced O_2 was obtained by subtracting the amount of O_2 before the reaction from that after the reaction. The amount of O_2 was calculated according to the following formula:

$$V_{O_2} = \frac{A_{O_2} k_{He}}{A_{He} k_{O_2}} \times V_{He}$$

where k_{O2}, V_{O2} and A_{O2} represent the response coefficient, volume and peak area of O_2. k_{He}, V_{He} and A_{He} represent the response coefficient, volume and peak area of He.

5. *In situ* XPS and XANES measurements

In situ XPS and XANES measurements were carried out at the photoemission end-station at beamline BL10B in the National Synchrotron Radiation Laboratory (NSRL), Heifei, China. The photon energies of the beamline are from 100 to 1,000 eV with a resolving power (*E/ΔE*) greater than 1,000. The photon flux of the beamline is 1×10^{10} photons per s. The analysis chamber is connected to the beamline with a twin anode X-ray source and a VG Scienta R3000 electron energy analyser. In addition, the analysis chamber was equipped with a window to allow the irradiation of light during the measurement of XPS and XANES spectra. In the current work, the *in situ* XPS and XANES experiments of Ag/ZIF-8 was firstly conducted without light. Then, the

in situ XPS and XANES spectra were collected again, when the light of a Xenon lamp shone on Ag/ZIF-8 through the window.

6. Instrumentations

HAADF-STEM images were collected on a JEOL ARM-200F field-emission transmission electron microscope with an acceleration voltage of 200 kV. XRD patterns were recorded by using a Philips X'Pert Pro Super diffractometer with Cu-Kα radiation (λ=1.54178 Å). Continuous scans were collected in the 2θ range of 10-80°. ESR spectra were performed by JEOL Jess-FA200 ESR spectrometer at 298 K. The photoelectrochemical experiments were put into effect on electrochemical station of Multi Autolab/M204 at room temperature. We carried out UV-Vis tests on a TU-1901 at room temperature. The XPS and XANES experiments were carried out at the Catalysis and Surface Science End-station connected to the BL10B beamline in the NSRL in Hefei, China. PL signal was collected on a FLS 1000 Edinburgh instrument with excitation wavelength of 325 nm.
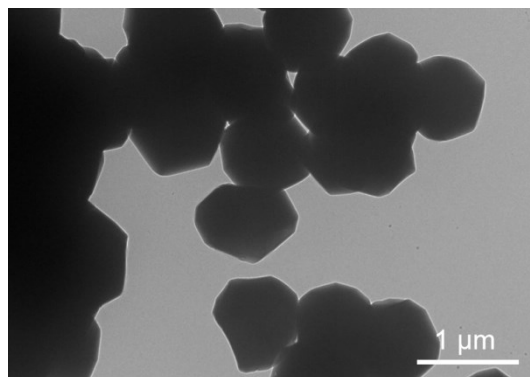
Figure S1. TEM image of ZIF-8.
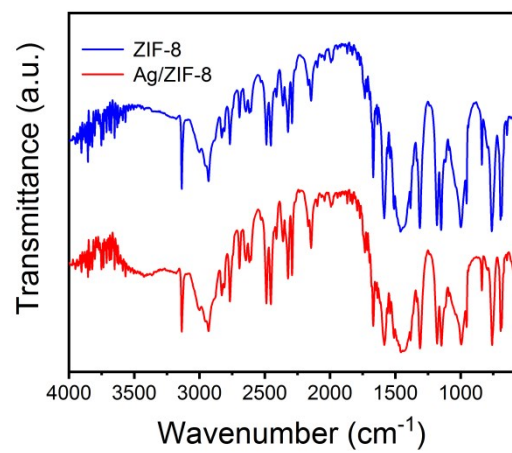
Figure S2. The FTIR spectra of ZIF-8 and Ag/ZIF-8.
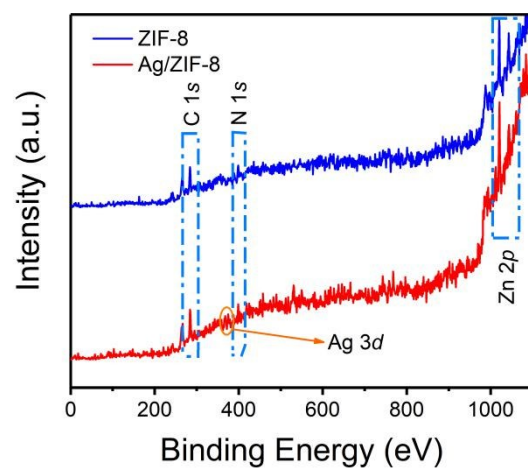
Figure S3. The full XPS spectra of ZIF-8 and Ag/ZIF-8.
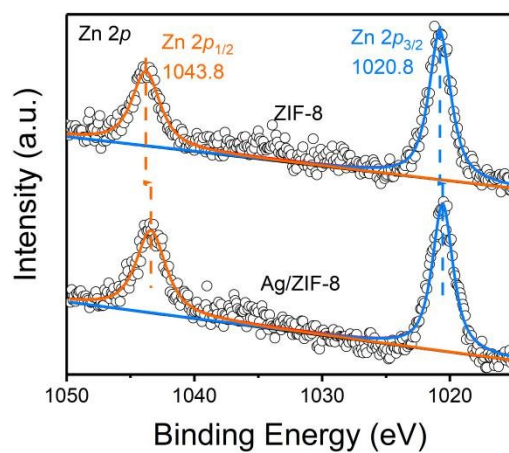
Figure S4. The Zn 2*p* XPS spectra of ZIF-8 and Ag/ZIF-8.
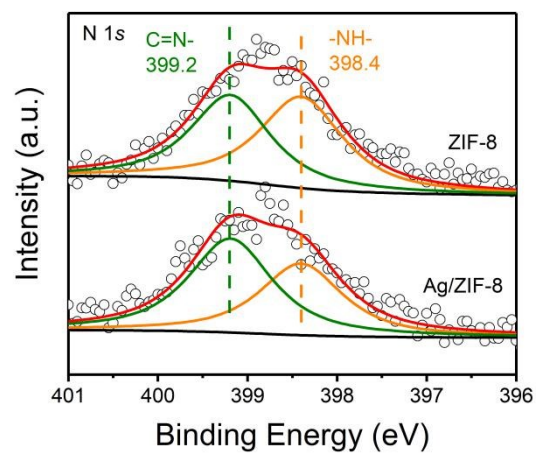
Figure S5. The N 1s XPS spectra of ZIF-8 and Ag/ZIF-8.

**Table S1.** The different catalysts for U(VI) photoreduction in recent literatures.

| Catalyst	Conditions	Electron sacrifice	Removal ratio	Ref.
Ag/ZIF-8	C_0 = 200 ppm, m/V = 0.25 g/L, pH = 5	None	92.8% in 60 min	*This work*
CCNCI/ZnO	C_0 = 200 ppm, m/V = 0.3 g/L, pH = 5	10% Methanol	98% in 60 min	[S1]
SCU-19	C_0 = 400 ppm, m/V = 0.5 g/L, pH = 4	5% Methanol	91% in 2880 min	[S2]
PCN-222	C_0 = 400 ppm, m/V = 0.5 g/L, pH = 4	10% Methanol	97% in 1440 min	[S3]
S-g-C_3N_4	C_0 = 30 ppm, m/V = 0.5 g/L, pH = 7	2.5% Methanol	95% in 20 min	[S4]
CN550	C_0 = 200 ppm, m/V = 0.2 g/L, pH = 5	2 ml Methanol	97% in 360 min	[S5]
g-C_3N_4	C_0 = 20 ppm, m/V = 1.0 g/L, pH = 4	20 ppm Bisphenol A	90% in 30 min	[S6]
$WO_{2.78}$	C_0 = 8 ppm, m/V = 0.25 g/L, pH = 4.8	1 ppm Tannic acid	95% in 120 min	[S7]
BC-MoS_{2-x}	C_0= 8 ppm, m/V = 0.5 g/L, pH= 5.5	25 ppm Tannic acid	92% in 40 min	[S8]
g-C_3N_4/GO	C_0= 80 ppm, m/V = 0.1 g/L, pH= 5	25 ppm Tannic acid	91% in 40 min	[S9]
g-C_3N_4/TiO_2	C_0 = 20 ppm, m/V = 0.25 g/L, pH = 7	20 ppm As(Ⅲ)	80% in 240 min	[S10]
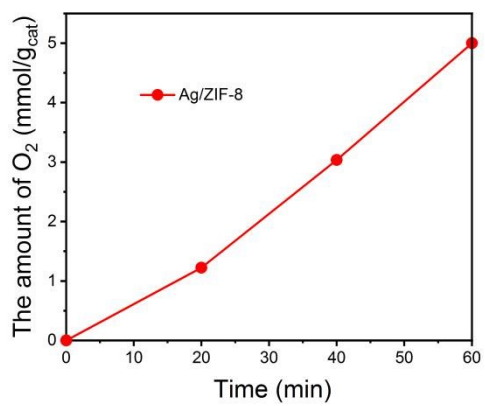
Figure S6. The amount of O$_2$ *versus* time during the process of U(VI) photoreduction in a sealed reactor.
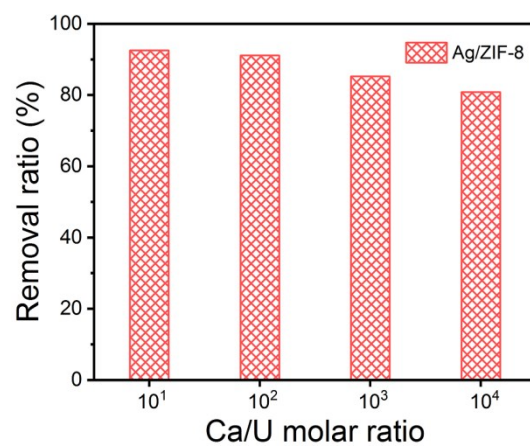
Figure S7. The U(VI) removal ratio over Ag/ZIF-8 in the presence of high concentrations of calcium ions.
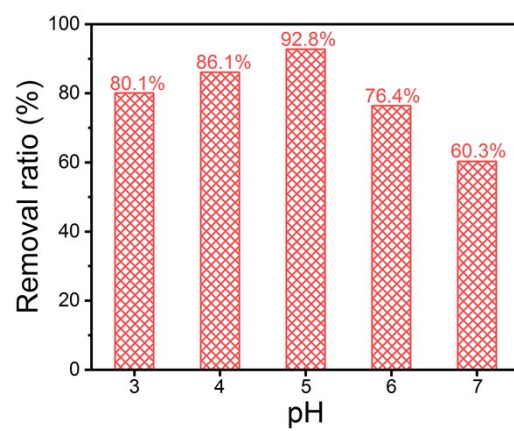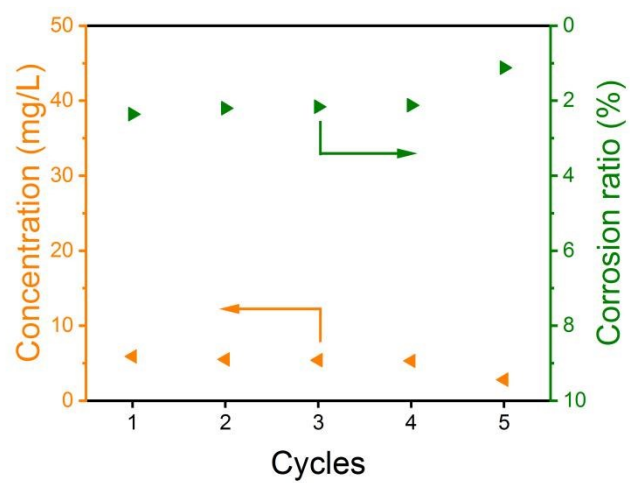
Figure S8. The U(VI) removal ratio over Ag/ZIF-8 under different pH condition.
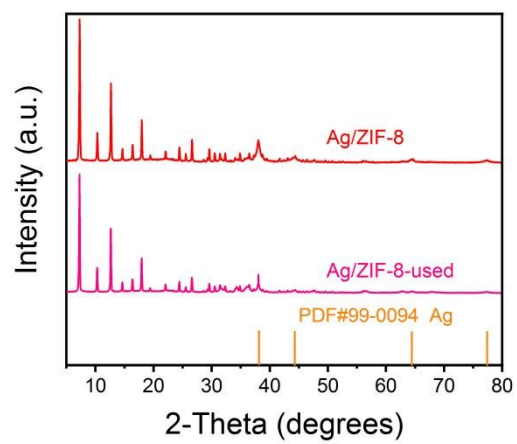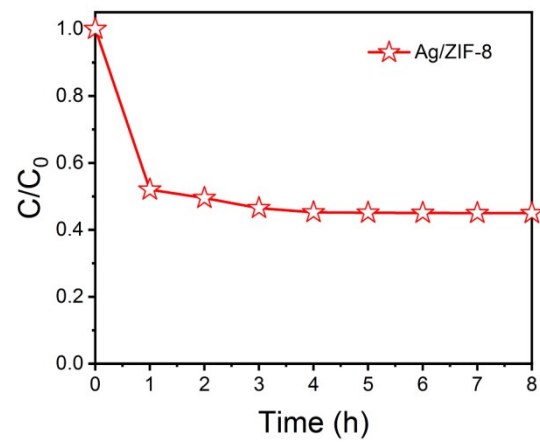
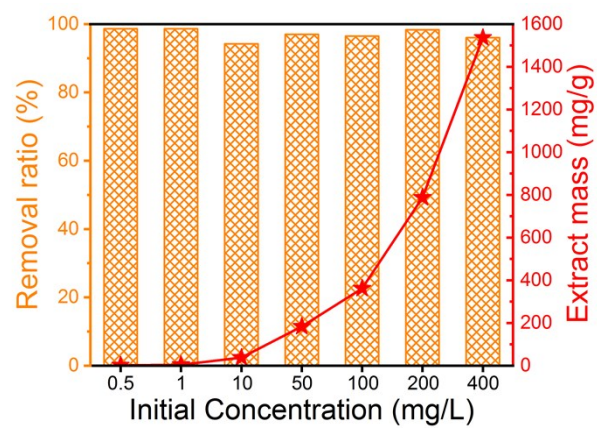**Figure S9**. XRD patterns of Ag/ZIF-8 and Ag/ZIF-8-used.

Figure S10. The concentration of Zn^{2+} in the solution after each reaction in five successive cycles for Ag/ZIF-8 and the corresponding corrosion ratio of Ag/ZIF-8.
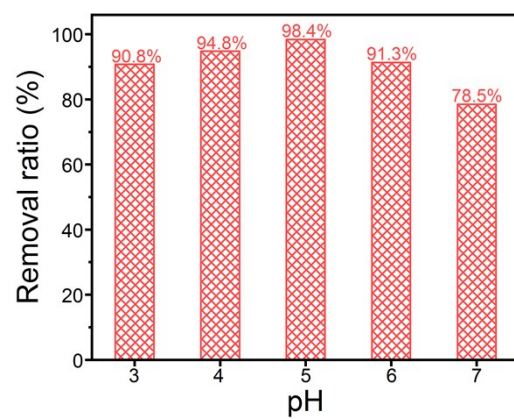
Figure S11. The concentration of U(VI) *versus* time via Ag/ZIF-8 under dark condition.
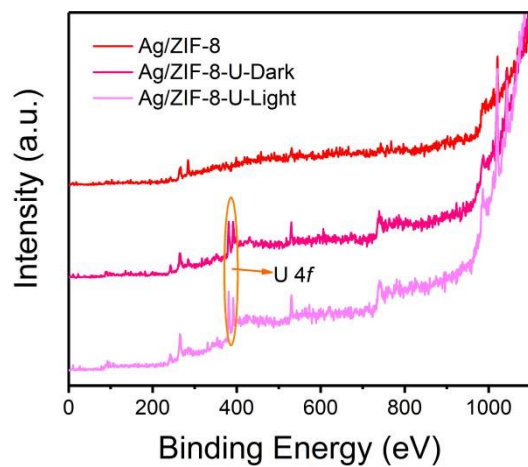
Figure S12. After adding 3 mL of methanol, the removal ratio and extract mass of U(VI) via Ag/ZIF-8 under different initial concentration.
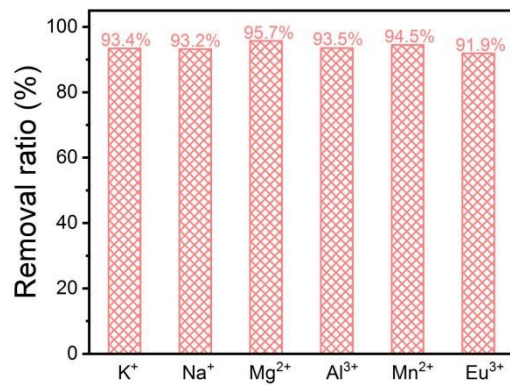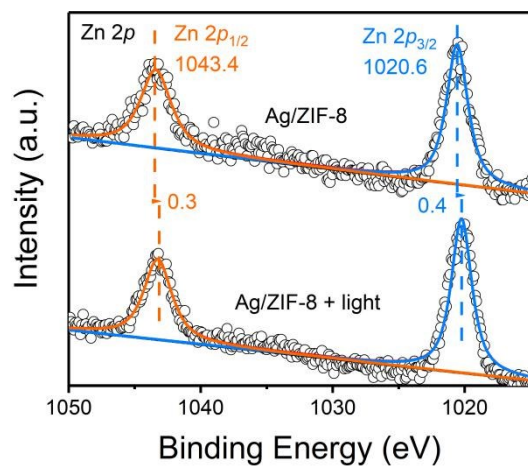
Figure S13. After adding 3 mL of methanol, the U(VI) removal ratio over Ag/ZIF-8 under different co-existing ions condition.
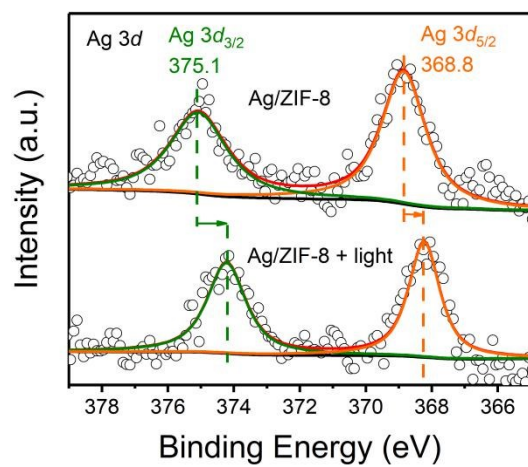
Figure S14. After adding 3 mL of methanol, the U(VI) removal ratio over Ag/ZIF-8 under different pH condition.

Figure S15. Full XPS spectra of Ag/ZIF-8, Ag/ZIF-8-U-Dark, and Ag/ZIF-8-U-Light.
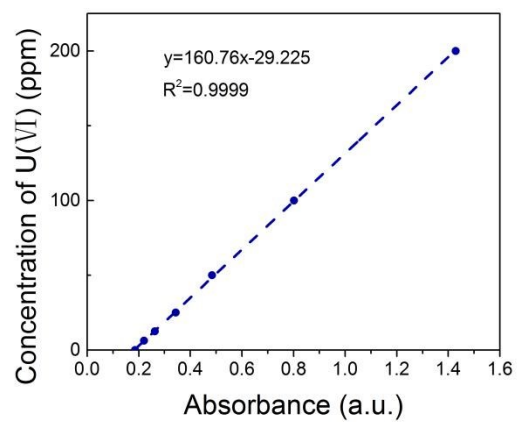
Figure S16. *In situ* XPS spectra of Zu 2*p* in Ag/ZIF-8 with/without light irradiation.
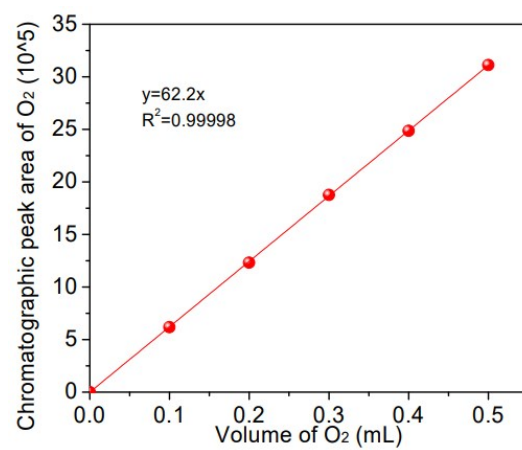
Figure S17. *In situ* XPS spectra of Ag 2*d* in Ag/ZIF-8 with/without light irradiation.

Figure S18. The concentration of U(VI) *vs* the corresponding absorbance at 652 nm.

$y = 62.2x$
$R^2 = 0.99998$

Figure S19. The plot of volume of O_2 gas *vs* the corresponding chromatographic peak area.
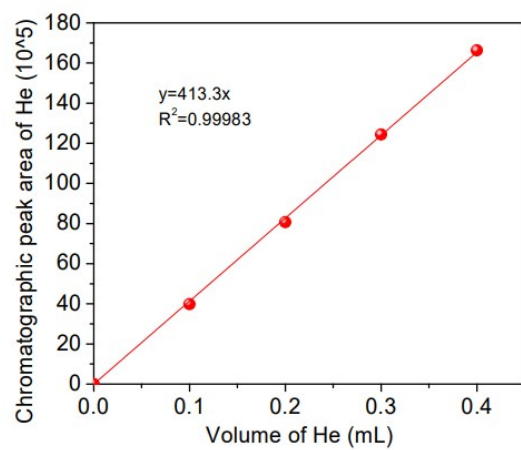
Figure S20. The plot of volume of He gas *vs* the corresponding chromatographic peak area.

1: Gas inlet
2: Gas sample connection
3: Liquid sample connection or gas outlet
4: Condensate inlet
5: Condensate outlet
6: Light position
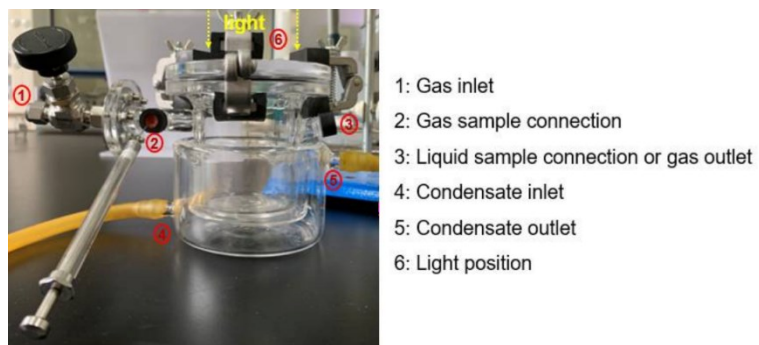
Figure S21. The picture of the 100-mL reactor equipped with gas sample connection.

Reference

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