# Supporting information:

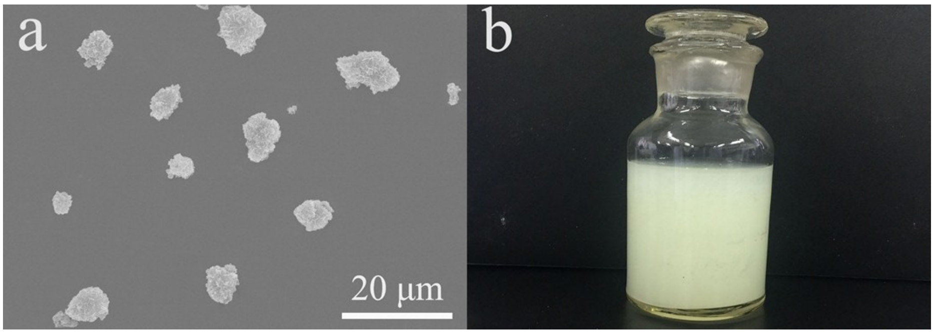


**Fig. S1** (a) The large scale-view SEM image of $NH_2$-MIL-101(Al)@ZIF-8 core-shell nanoflower; (b) The uniform aqueous solution of $NH_2$-MIL-101(Al)@ZIF-8 (the volume of the container is 250 ml ).

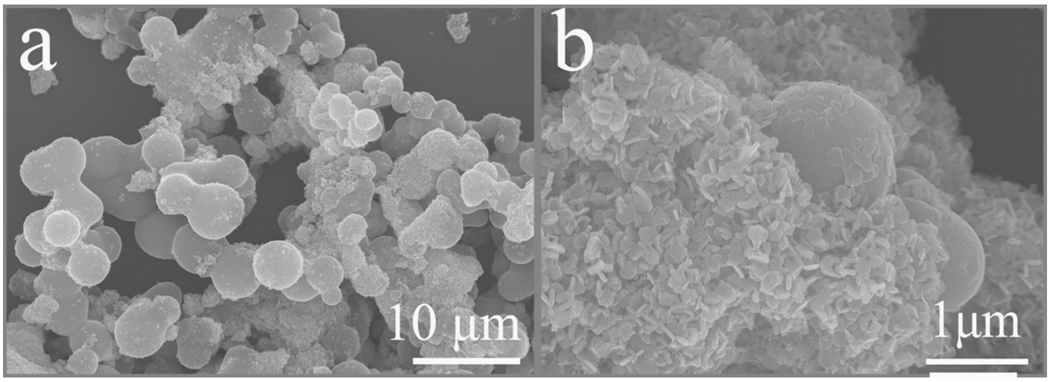


**Fig. S2** (a, b) SEM image of $NH_2$-MIL-101(Al)@ZIF-8 synthesized by the same hydrothermal method without PVP at different magnifications.

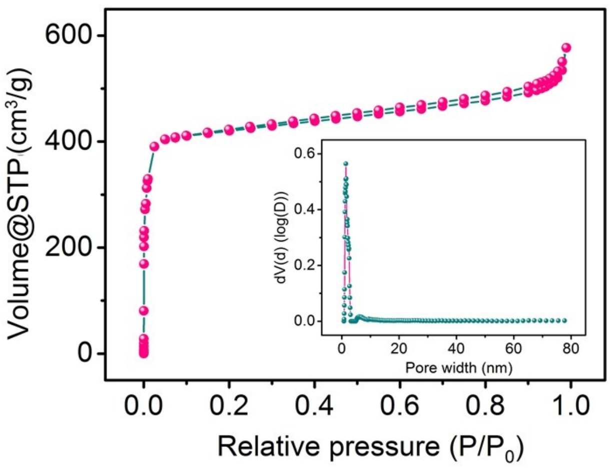


**Fig. S3** $N_2$ sorption isotherms of $NH_2$-MIL-101(Al)@ZIF-8 (inset: the corresponding pore size distribution curve).

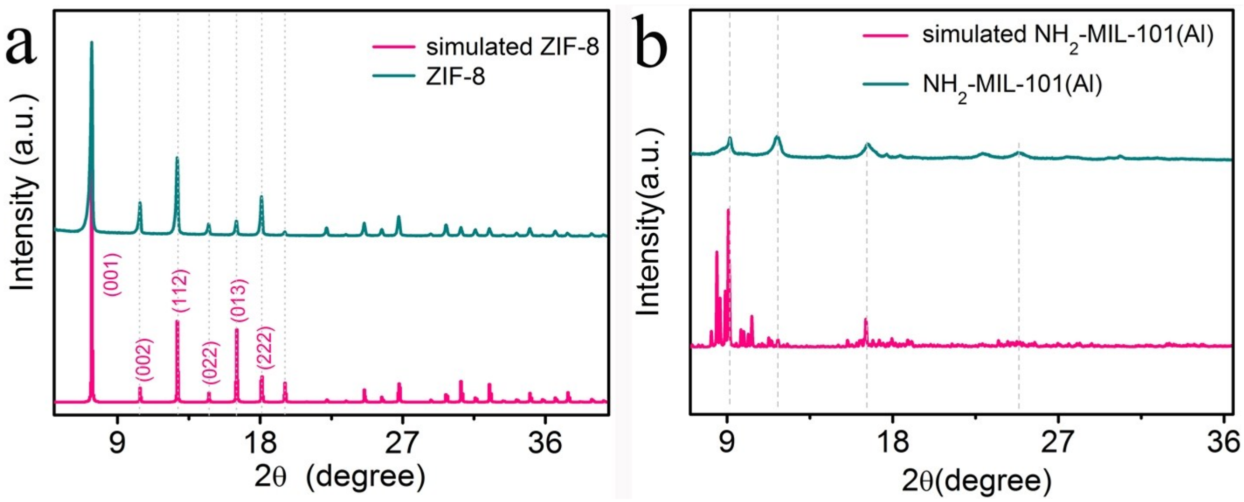


**Fig. S4** (a) the XRD patterns of ZIF-8 and simulated ZIF-8; (b) the XRD patterns of $NH_2$-MIL-101(Al) and simulated $NH_2$-MIL-101(Al).

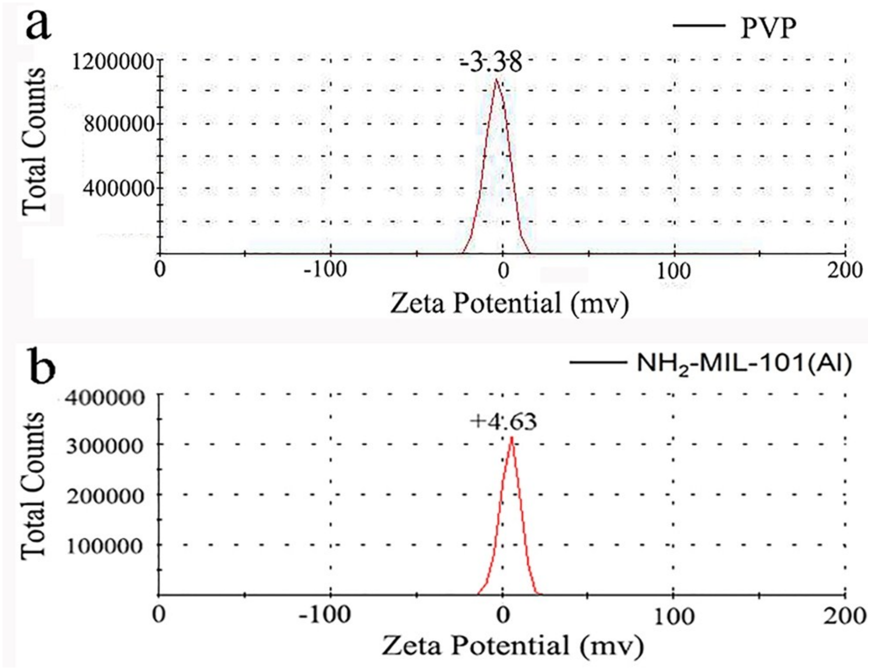


**Fig. S5** (a, b) Zeta potential diagrams of PVP and $NH_2$-MIL-101(Al).

**Table S1.** The parameters of pseudo-first-order kinetic, pseudo-second-order kinetic, and intraparticle diffusion kinetic of Cu(II) adsorption.

| C (mg $L^{-1}$) | Pseudo-first-order | | | Pseudo-second-order | | |
|---|---|---|---|---|---|---|
| | $q_{e,c}$ (mg $g^{-1}$) | $K_1$ | $R^2$ | $q_{e,c}$ (mg $g^{-1}$) | $K_2$ | $R^2$ |
| 10 | 38.61±0.34 | 0.0041±0.0003 | 0.9544 | 39.841±0.05 | 0.0243±0.0043 | 0.9990 |
| 100 | 396.43±10.36 | 0.0040±0.0004 | 0.8966 | 408.175±2.63 | 0.0014±0.0008 | 0.9987 |
| 300 | 459.52±5.84 | 0.0154±0.0015 | 0.9546 | 462.978±3.26 | 0.0012±0.0004 | 0.9979 |

| C (mg $L^{-1}$) | Intraparticle diffusion model | | |
|---|---|---|---|
| | $K_i$ (mg $g^{-1}h^{-0.5}$) | $C_i$ | $R^2$ |
| 10 | 1.087±0.23 | 33.151±0.69 | 0.8753 |
| 100 | 57.330±8.43 | 124.817±25.28 | 0.9378 |
| 300 | 51.432±20.43 | 242.127±61.30 | 0.6400 |

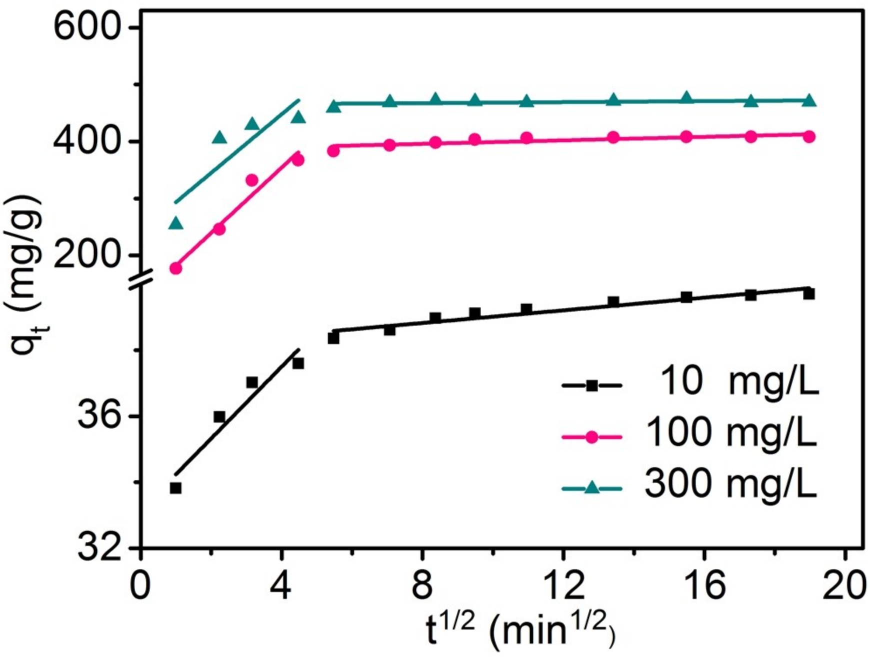


**Fig. S6** The fitting curves of intra-particle diffusion model of Cu(II) adsorption.

**Table S2.** The parameters of Langmuir model and Freundlich model of Cu(II) adsorption

| T/K | Langmuir isotherm | | | Freundlich isotherm | | |
|---|---|---|---|---|---|---|
| | $q_m$ (mg $g^{-1}$) | $K_L$ (L $mg^{-1}$) | $R^2$ | $K_f$ ($mg^{1+n}L^{-n}g^{-1}$) | n | $R^2$ |
| 298 | 325.74±2.11 | 0.252±0.04 | 0.9998 | 91.300±24.43 | 4.013±1.07 | 0.7419 |
| 308 | 440.67±9.57 | 0.264±0.11 | 0.9976 | 52.457±20.54 | 2.145±0.50 | 0.7839 |
| 318 | 526.74±18.36 | 0.137±0.06 | 0.9940 | 62.803±23.22 | 2.139±0.49 | 0.7938 |

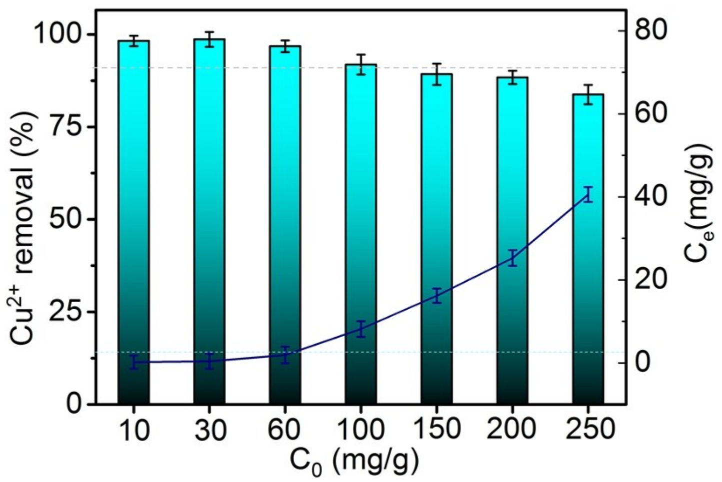


**Fig. S7** The removal rate of Cu(II) at different initial concentrations.

**Table S3.** The pH values of the reaction system before and after adsorption at different initial concentrations.

| $C_0$ (mg $g^{-1}$) | 60 | 100 | 150 | 200 | 250 |
|---|---|---|---|---|---|
| pH (Before adsorption) | 5.21 | 5.16 | 5.14 | 5.07 | 4.95 |
| pH (After adsorption) | 5.32 | 5.26 | 5.27 | 5.16 | 5.05 |

**Table S4.** Estimated total cost for preparing 1 g of adsorbents and corresponding adsorption capacities.

| adsorbent | material | amount used | unit cost (dollar) | Cost (dollar) | total cost (dollar) | Cu(II) adsorption capacity | ref |
|---|---|---|---|---|---|---|---|
| Cd-MOF-74 | $H_2$dhtp (Yield: 56%) | 0.02 | 36.35 | 0.73 | **84.16** | 189.5 | 1 |
| | $Cd(NO_3)_2·4H_2O$ | 0.10 | 0.23 | 0.02 | | | |
| | DMF | 2 | 0.0047 | 0.0094 | | | |
| | ethanol | 100 | 0.0018 | 0.18 | | | |
| UiO-66(Zr)-2COOH | Functionalized $H_2$BDC | 1.80 | 1.14 | 2.05 | **36.53** | 11.3 | 2 |
| | $ZrCl_4$ | 0.87 | 0.92 | 0.80 | | | |
| | benzoic acid | 15.8 | 2.28 | 36.02 | | | |
| | DMF | 30 | 0.0047 | 0.14 | | | |
| $[(Zn_3L_3(H_2O)_6][(Na)(NO_3)]$ | $Zn(NO_3)_2·6H_2O$ | 0.089 | 2.86 | 0.25 | **43.24** | 379.1 | 3 |
| | $H_2L$ | 0.027 | 5.75 | 0.16 | | | |
| | NaOH (0.25 M) | 15 | 0.19 | 2.85 | | | |
| | $CH_3CN$ | 24 | 0.02 | 0.48 | | | |
| | $H_2O$ | 1 | 0.02 | 0.02 | | | |
| Hematite ($\alpha$-$Fe_2O_3$) | $FeCl_3$ | 2.7 | 6.52 | 17.60 | **20.77** | 84.46 | 4 |
| | $H_2O$ | 500 | 0.02 | 10 | | | |
| | HCl | 0.05 | 0.55 | 0.028 | | | |
| $\gamma$ -$Fe_2O_3$ | $H_2O$ | 200 | 0.02 | 4 | **19.00** | 26.8 | 5 |
| | $FeCl_3$ | 5.2 | 6.52 | 33.90 | | | |
| | $FeCl_2$ | 2 | 3.18 | 6.36 | | | |
| | $NH_4OH$ | 1.5 | 0.08 | 0.12 | | | |
| | Tetramethylammonium hydroxide | 1 | 0.23 | 0.23 | | | |
| | 99% Octyl ether | N/A | N/A | N/A | | | |
| $NH_2$-MCM-41 | CTAB | 2 | 13.12 | 26.24 | **15.84** | 85.1 | 6 |
| | NaOH (2 N) | 7 | 0.19 | 1.33 | | | |
| | TEOS | 10 | 1.75 | 17.50 | | | |
| | APTES | 2.1 | 0.52 | 1.09 | | | |
| | ethanol | 100 | 0.0018 | 0.18 | | | |
| | HCl (12N) | 1 | 0.55 | 0.55 | | | |
| $Fe_3O_4$@APS@AA-co-CA MNPs | $Fe_3O_4$ | 1 | 24.44 | 24.44 | **4.36** | 126.9 | 7 |
| | distilled toluene | 190 | 0.03 | 5.70 | | | |
| | APS | 8 | 0.63 | 5.04 | | | |
| | ethanol | 900 | 0.0018 | 1.62 | | | |
| | crotonic acid | 6 | 2.77 | 16.62 | | | |
| | Acrylic acid | 4 | 0.03 | 0.12 | | | |
| | AIBN | 0.05 | 1.27 | 0.06 | | | |
| | DCC | 0.2 | 0.74 | 0.15 | | | |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | distilled THF | 20 | 0.04 | 0.8 | | | |
| S-doped GS | L-cystine | 0.15 | 0.29 | 0.04 | **30.20** | 228.0 | 8 |
| | Graphite | 0.15 | 0.13 | 0.02 | | | |
| | $H_2O$ | 450 | 0.02 | 9 | | | |
| GO membranes | Graphite | 4 | 0.13 | 0.52 | **24.73** | 72.6 | 9 |
| | $NaNO_3$ | 4 | 0.06 | 0.24 | | | |
| | $H_2SO_4$ | 300 | 0.0006 | 0.18 | | | |
| | $KMnO_4$ | 18 | 0.02 | 0.36 | | | |
| | $H_2O$ | 700 | 0.02 | 14 | | | |
| | $H_2O_2$ | 12 | 0.07 | 0.84 | | | |
| | HCl (5%) | 450 | 0.0006 | 0.27 | | | |
| | PVA (0.2 wt%) | 15 | 0.03 | 0.45 | | | |
| | PTFE | N/A | 2.92 | N/A | | | |
| MnOx-loaded BCs | $BC_S$ | 5 | N/A | N/A | **1.92** | 160.0 | 10 |
| | $KMnO_4$ | 0.5 | 0.02 | 0.01 | | | |
| | $H_2O$ | 500 | 0.02 | 10 | | | |
| $SiO_2$@AZOL | CPB | 4 | 0.48 | 1.92 | **4.12** | 260.0 | 11 |
| | $H_2O$ | 800 | 0.02 | 16 | | | |
| | ammonia solution | 35 | 0.03 | 1.05 | | | |
| | n-hexane | 100 | 0.09 | 9 | | | |
| | TEOS | 20 | 0.15 | 3 | | | |
| | methanol | 350 | 0.0018 | 0.63 | | | |
| | HCL (1M) | 5 | 0.0046 | 0.02 | | | |
| | toluene | 150 | 0.03 | 4.50 | | | |
| | APTES | 5 | 0.52 | 2.60 | | | |
| | salicylaldehyde | 4.6 | 0.27 | 1.24 | | | |
| | sodium borohydride | 9.6 | 0.66 | 6.34 | | | |
| | acetic acid | 2 | 0.0046 | 0.0092 | | | |
| | BPPA | 1 | 8.07 | 8.07 | | | |
| THTB (yield: 62%) | acetic acid | N/A | 0.0046 | N/A | **141.85** | 176.3 | 12 |
| | thiosemicarbazide | 9.11 | 0.12 | 1.09 | | | |
| | 5-tert-butyl-2-hydroxy-benzaldehyde | 17.82 | 25.98 | 462.96 | | | |
| | $H_2O$ | 250 | 0.02 | 5 | | | |
| | ethanol | 25 | 0.0018 | 0.045 | | | |
| $NH_2$-MIL-101(Al)@ZIF-8 (Yield:$NH_2$-MIL-101(Al),59% $NH_2$-MIL-101(Al)@ZIF-8, 8.6%) | $NH_2$-$H_2$BDC | 0.56 | 1.72 | 0.96 | **1.58** | 526.3 | **-** |
| | $AlCl_3·6H_2O$ | 0.51 | 0.06 | 0.03 | | | |
| | DMF | 30 | 0.0047 | 0.14 | | | |
| | PVP | 0.02 | 0.13 | 0.0026 | | | |
| | $Zn(NO_3)_2·6H_2O$ | 0.4 | 0.061 | 0.02 | | | |
| | 2-MIM | 0.5 | 0.11 | 0.055 | | | |
| | methanol | 25.6 | 0.0017 | 0.04 | | | |

**Table S5.** The concentration of Al(III) and Zn(II) in the reaction system after adsorption at different Cu(II) concentrations.

| $C_0$ (mg $g^{-1}$) | 10 | 30 | 60 | 100 |
|---|---|---|---|---|
| Al(III) (mg $g^{-1}$) | 0.006 | 0.032 | 0.017 | 0.021 |
| Zn(II) (mg $g^{-1}$) | 0.092 | 0.433 | 0.991 | 1. 415 |

**Table. S6** Comparison of Cu(II) detection performance of $NH_2$-MIL-101(Al)@ZIF-8, $NH_2$-MIL-101(Al) and the mixture.

| Materials | $K_{sv}$ ($M^{-1}$) | Range (μM) | LOD (μM) |
|---|---|---|---|
| $NH_2$-MIL-101(Al)@ZIF-8 | $2.94 \times 10^4$ | 1.5-625 | 0.17 |
| $NH_2$-MIL-101(Al) | $1.47 \times 10^4$ | 3.1-625 | 0.35 |
| The mixture | $4.11 \times 10^3$ | 18.7-140 | 12.68 |

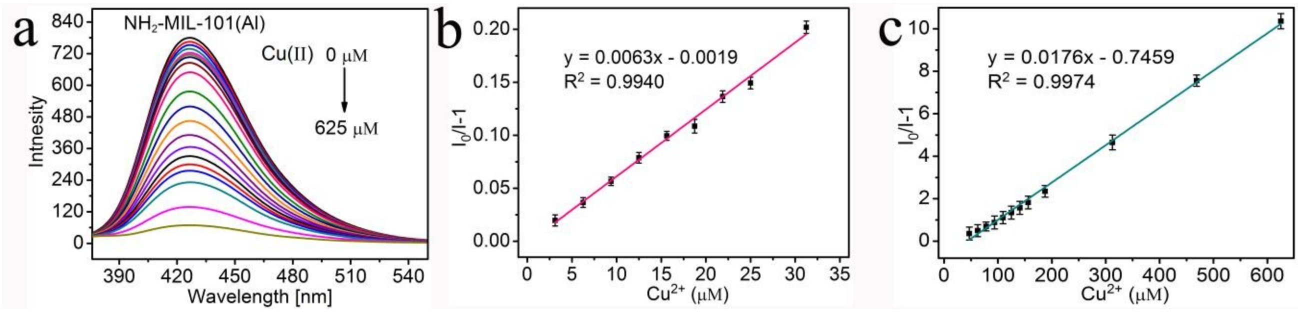


**Fig. S8** (a) Fluorescence emission spectra of the $NH_2$-MIL-101(Al) suspension upon the addition of various concentrations of Cu(II) under excitation at 325 nm; (b, c) the corresponding Stern-Volmer linear fitting curves of $NH_2$-MIL-101(Al) toward Cu(II).

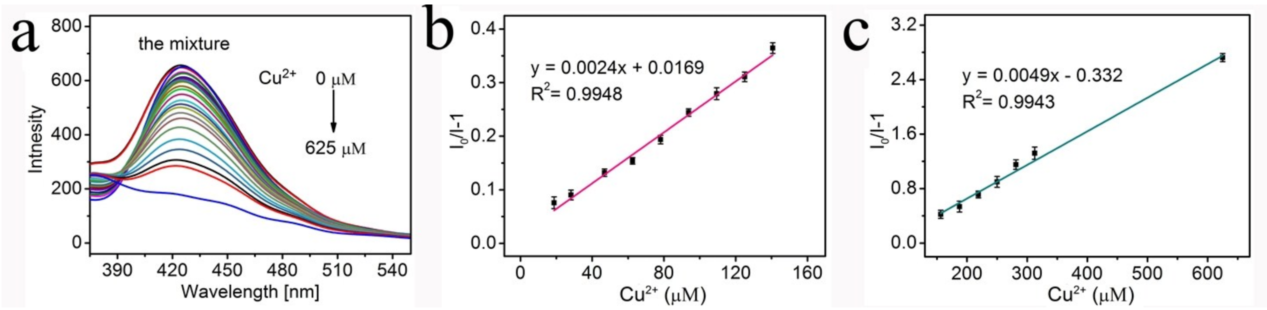


**Fig. S9** (a) Fluorescence emission spectra of the mixture suspension upon the addition of various concentrations of Cu(II) under excitation at 325 nm; (b, c) the corresponding Stern-Volmer linear fitting curves of the mixture toward Cu(II).

**Table S7.** Comparison of the Cu(II) detection properties of $NH_2$-MIL-101(Al)@ZIF-8 with other materials reported in previous article.

| Materials | Range (μM) | LOD (μM) | Reference |
|---|---|---|---|
| Cd-MOF-74 | 78-12500 | 78 | 1 |
| ZnMGO composite | 1-70 | 1 | 13 |
| SiO2@AZOL | 20-100 | 0.22 | 11 |
| [Ce (1,5-NDS)$_{1.5}$(H2O)$_5$]$_n$ | 5-100 | 3 | 14 |
| COF-JLU3 | 0.31-0.4 | 0.31 | 15 |
| ZnO@ZnS CSNPs. | 15-1500 | 15 | 16 |
| THTB | 0.3-1.6 | 0.15 | 12 |
| $NH_2$-MIL-101(Al)@ZIF-8 | 1.5-625 | 0.17 | This work |

**Table S8.** The hetero-atoms content of $NH_2$-MIL-101@ ZIF-8 based on element analysis and XPS.

| $NH_2$-MIL-101 @ ZIF-8 | XPS (at %) | | | | | | | | Element Analysis (EA) (wt %) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | C | N | | | Al | Zn | Cu | C/N | C | N | Al | Zn |
| | | C=N | C-N | Cu-N | | | | | | | | |
| Before adsorption | 58.85 | 3.40 | 19.24 | - | 0.55 | 6.40 | - | 2.59 | 42.09 | 23.84 | 0.69 | 3.91 |
| After adsorption | 26.95 | 1.49 | 3.39 | 5.24 | 0.22 | 2.60 | 9.23 | 2.66 | - | - | - | - |

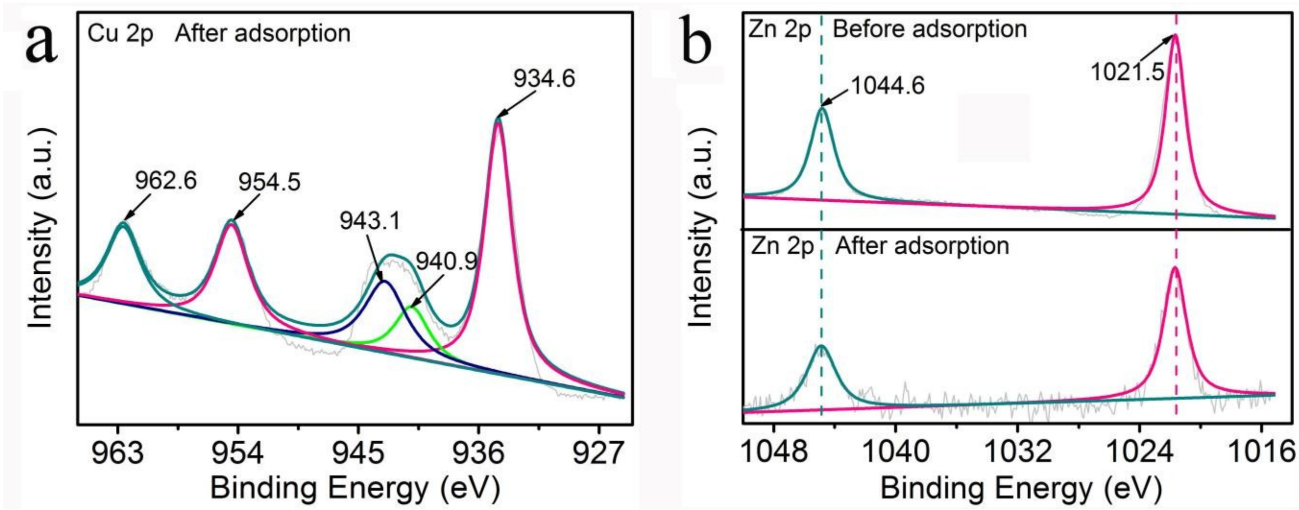


**Fig. S10** (a) XPS spectra of Cu 2p before and after Cu(II) adsorption; (b) XPS spectra of Zn 2p before and after Cu(II) adsorption.

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