Supporting Information

for Small, DOI: 10.1002/smll.202105502

Amyloid Fibril Templated MOF Aerogels for Water Purification

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Materials and Methods

Materials

β-lactoglobulin (BLG) was purified from whey protein isolate (Fonterra, New Zealand). Before fibrilization, BLG monomers were dialyzed through a previous protocol [1]. Zinc nitrate hexahydrate and 2-Methylimidazole were purchased from Sigma Aldrich. Sudan III was supplied by Fluka Chemika. All other reagents employed in this study were of analytical grade and were purchased from Sigma Aldrich.
Preparation of amyloid fibrils

Fibrillation of BLG was performed according to the previously described protocol [2]. Firstly, purified BLG monomer was homogeneously dispersed in Milli-Q water with a concentration of 2 wt%. The pH of the solution was then adjusted to pH 2 by 2 M HCl. Afterward, the BLG solution was incubated at 90°C for 5 h with a magnetic stirring of 350 rpm. During the incubation process, the BLG monomer unfolds, hydrolyzes, and self-assembles into protein amyloid fibrils [3]. Fibrilization was quenched by suspending the system in ice for 30 min. The formation of amyloid fibrils was verified through cross-polarized light to assure the presence of birefringence.

Preparation of amyloid/ZIF-8 hybrid aerogel

2-methylimidazole (0.4466 g) was firstly dissolved in 50 mL of amyloid fibrils solution and stirred for 10 min (300 rpm). Zn(NO₃)₂·6H₂O (0.2038 g) was then dispersed by stirring at 400 rpm. The suspension was incubated at 90°C for 5 h. For aerogels, 2 mL aliquots of the solution were placed in stainless-steel molds and frozen at -18°C, followed by removing the solvent via freeze dryer (FreeZone Plus 4.5, Labconco, United States) for two days.

Characterization of amyloid/ZIF-8 hybrid aerogel

A morphological study of amyloid/ZIF-8 hybrid aerogel was performed using a Hitachi SU5000 scanning electron microscope. Elemental distribution analysis was carried out by an energy-dispersive X-ray spectroscopy. Fourier transform infrared (ATR-FTIR) spectra of samples were obtained using a Varian 640 spectrometer. X-ray diffraction (XRD) tests of samples were conducted using a XRD patterns were recorded with a Bruker AXS D8 ADVANCE diffractometer.
The mechanical properties of aerogels were evaluated using a Z010 (Zwick) through compressive strain-stress curves measurements at a maximum strain of 10%, 30%, 40%, and 70%, respectively.

**Adsorption experiments for heavy metals**

The maximum adsorption capacity ($q_m$) of the hybrid aerogel for each heavy metal ion was calculated with the initial and final concentrations of the metal ions as determined in solution using atomic absorption spectroscopy (AAS) in solution. The initial concentration of each heavy metal ion was 10 mM. The $q_m$ (mg/g) was calculated using equation S1

$$q_m = \frac{C_0 - C_e}{m} V$$

where $C_0$ and $C_e$ (mg/L) are defined as the initial and final concentrations of the heavy metal ions, respectively, $V$ (L) is the volume of the heavy metal ion solution, and $m$ (g) represents the weight of the hybrid aerogel used in this study.

For the isothermic adsorption study, 5 mg of aerogel was utilized, and the concentration of Hg$^{2+}$ solution was varied from 0.1 to 4000 ppm. For all aforementioned experiments, the samples were left with a magnetic stirrer for 24 h. A single binding metal–ligand pair with a single average binding constant was presumed in this approach. For the data simulation of the binding isotherms, equation S2 was used

$$[P \cdot L] = \frac{1}{2} \left( [P_0] + [L_0] + \frac{1}{K_a} \right) - \frac{1}{2} \sqrt{\left( [P_0] + [L_0] + \frac{1}{K_a} \right)^2 - 4 [MP_0][L_0]}$$

where $[P]$ and $[L]$ represent the bound Hg$^{2+}$ and ligand concentration; $[P_0]$ and $[L_0]$ are the initial total Hg$^{2+}$ and ligand concentration, respectively, and $K_a$ is the binding constant.

Adsorption experiments were performed at various time intervals for kinetic studies. Typically,
21.2 mg of hybrid aerogel were added to 20 mL Hg$^{2+}$ solution at a concentration of 10 mM, and 100 μL of supernatant was periodically determined by AAS at different time intervals until adsorption equilibrium. Pseudo-second-order kinetic model (equation S3) was performed to simulate the experimental data of Hg$^{2+}$ adsorption onto hybrid aerogel, as follows

$$\frac{t}{q_t} = \frac{1}{K_{ad} q_e^2} + \frac{t}{q_e}$$

(S3)

in which t represents adsorption time in minutes, $q_e$ and $q_t$ indicate the amount of adsorbed Hg$^{2+}$ at equilibrium and different time intervals, respectively, $K_{ad}$ represents the adsorption rate constants of the pseudo-second-order model.

**Dye removal experiments**

The maximum dye removal capacity was determined using 1000 ppm of each prepared dye. UV-vis spectrometer was used to measure the concentration of each dye before and after treatment with hybrid aerogel. The maximum dye removal capacity was obtained through the same equation (S1) as that for heavy metals.

To evaluate the reusability of hybrid aerogel, crystal violet and malachite green solutions (5 mL, 10 ppm) were employed as model compounds. Their concentrations before and after adsorption by 5 mg hybrid aerogel were measured for 3 consecutive cycles. The regeneration of aerogel was achieved by soaking in methanol anhydrous for 12 h. To understand the influence of pH value, the removal efficiency for crystal violet have been measured with a pH range of 3.5–7.5.

The non-photocatalytic activity of hybrid aerogel was measured by reducing acid fuchsin under dark conditions at room temperature. Typically, 40 mg of aerogel was placed into 10 mL of acid fuchsin solution with a concentration of 25 ppm. The acid fuchsin solution was replaced
periodically to evaluate the continuous removal performance of the catalyst. To explore photocatalytic efficacy, 40 mg of aerogel was immersed in 10 mL of 25 ppm aqueous solution of methylene blue. After 30 min in the dark, the solution was irradiated by using a COB LED lamp (Prolinx GmbH) at 300 W. The lamp was located at a distance of 100 cm above the top surface of the methylene blue solution. The absorbance of the solution was recorded at specific time intervals.

Oils/Organics sorption Experiments

The surface wettability of the hybrid aerogels was quantified by measuring the contact angle of a water droplet placed on a cylinder surface of the aerogel. For organic solvent sorption, droplets of n-hexane (stained with Sudan III) were put on the surface of the water, and 20 mg of aerogel was then gently contacted the organic and subsequently finish the sorption.

The sorption weight gain (%) of hybrid aerogel was measured through a series of sorption experiments toward oily compounds, including acetone, chloroform, isopropanol, t-butanol, cyclohexane, heptane, toluene, hexadecane, peanut oil, and olive oil. In brief, the aerogels were soaked into oils/organics for 20 seconds until reaching sorption equilibrium and then taken out without liquid drip and weighed immediately[^6]. The weight gain ($W_g$) after sorption of the aerogel was calculated by equation S4,

$$ W_g = \frac{m_c - m_0}{m_0} \times 100 \quad (S4) $$

where $m_c$ (g) and $m_0$ (g) were the weight of the hybrid aerogel after and before sorption, respectively. The regeneration of aerogel refers to the complete evaporation of organics was performed at hood under room temperature. The reusability tests of the hybrid aerogel for
oils/organics sorption were repetitions of the same sorption procedure as described above, and calculated after each sorption-evaporation cycle and calculated through a previously described protocol\cite{7}.
Figure S1. Acid and alkaline tolerance profile of amyloid/ZIF-8 hybrid aerogel.
Figure S2. Morphology of hybrid aerogel surface with ZIF-8.
Figure S3. EDX elemental map of the surface of amyloid/ZIF-8 hybrid aerogel.
Figure S4. FTIR spectrum of amyloid and amyloid/ZIF-8 hybrid aerogel.
Figure S5. XRD spectrum of amyloid, amyloid/ZIF-8 hybrid aerogel and ZIF-8.
Figure S6. The effects of pH on Pb^{2+} and Hg^{2+} removal by amyloid/ZIF-8 hybrid aerogel (ion concentration: 3 mM and adsorption time: 24 h).
Figure S7. Fitted binding isotherms for Hg$^{2+}$ removal.

Binding constant: 378 M$^{-1}$
Saturation limit: 12550 μM
Figure S8. a) Adsorption capacities of Hg$^{2+}$ from an aqueous solution over amyloid/ZIF-8 hybrid aerogel. b) Fitted pseudo-second order kinetic model on Hg$^{2+}$ adsorption.
Figure S9. a) Effect of different pH values of crystal violet solutions on maximum absorbance wavelength (100 ppm, 10 times dilution). b) Removal ratio of crystal violet by amyloid/ZIF-8 aerogel under various pH conditions (amount of solution: 5 mL and aerogel weight: 15 mg).
Figure S10. UV-Vis absorption spectra for the continuous degradation of acid fuchsin by amyloid/ZIF-8 hybrid aerogel.
Figure S11. Acid fuchsin aqueous solution before and after the sixth run of amyloid/ZIF-8 hybrid aerogel degradation.
Table S1. Maximum heavy metal ions adsorption performances of various types of MOFs based nanostructures and composites.

| Adsorbents                  | Heavy metal ions | Adsorption capacity | References |
|-----------------------------|------------------|---------------------|------------|
| Cys-UiO-66                  | Hg$^{2+}$        | 350.14 mg/g         | [8]        |
| NENU-401                    | Hg$^{2+}$        | 600 mg/g            | [9]        |
| UiO-66-DMTD                 | Hg$^{2+}$        | 670.5 mg/g          | [10]       |
| PCN-224                     | Hg$^{2+}$        | 843.6 mg/g          | [11]       |
| ZnS@ZIF-8                   | Hg$^{2+}$        | 925.9 mg/g          | [12]       |
| ZIF-8                       | Hg$^{2+}$        | 1271.27 mg/g        | [13]       |
| UiO-66-NH$_2$               | Au$^{3+}$        | 158 mg/g            | [14]       |
| UiO-66-MTD                  | Au$^{3+}$        | 301.5 mg/g          | [15]       |
| UiO-66-TA                   | Au$^{3+}$        | 372 mg/g            | [14]       |
| UiO-66-RSA                  | Pb$^{2+}$        | 189.8 mg/g          | [16]       |
| nFe@ZIF-8                   | Pb$^{2+}$        | 175.43 mg/g         | [17]       |
| MIL-101(Fe)/GO              | Pb$^{2+}$        | 128.6 mg/g          | [18]       |
| ZIF@NiTiO$_3$               | Pb$^{2+}$        | 155 mg/g            | [19]       |
| Zn(Bim)(OAc)                | Pb$^{2+}$        | 253.8 mg/g          | [20]       |
| ZIF-8                       | Pb$^{2+}$        | 1780.91 mg/g        | [13]       |
| Amyloid/ZIF-8 hybrid aerogel| Hg$^{2+}$        | 1376 mg/g           |            |
|                             | Au$^{3+}$        | 503 mg/g            | This work  |
|                             | Pb$^{2+}$        | 318 mg/g            |            |
Supporting information References

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