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## Zeolitic Imidazole Framework (ZIF)-Sponge Composite prepared via a Surfactant-assisted Dip-Coating Method

Kun-Yi Andrew Lin<sup>a,\*</sup> and Hsuan-Ang Chang<sup>a</sup>

A rapid, simple and inexpensive dip-coating method is developed to prepare a three-dimensional hierarchical zeolitic imidazole framework (ZIF) composite using the commercially available melamine sponge as a support. With surfactant modification of sponge, self-assembling of ZIF nanocrystals to sponge skeletons is significantly facilitated and ZIF nanocrystals form a nearly uniform layer on sponge surfaces via electrostatic attraction and possibly  $\pi$ - $\pi$  stacking interaction. The effect of surfactant type used to modify sponge is also investigated. The resultant ZIF-sponges exhibit strengthened mechanical strength (i.e., hardness) and improved hydrophilicity. ZIF-sponge also shows a remarkably high adsorption capacity for Malachite Green dye, a toxic pollutant, of 4093 mg g<sup>-1</sup> based on the Langmuir isotherm modelling analysis. ZIF-sponges can be designed and easily fabricated to be filters, membranes, and adsorbents. The approach demonstrated here may be also extended to prepare other types of ZIF or metal organic framework (MOF) sponges.

Zeolitic imidazole frameworks (ZIFs) represent one of the most intriguing materials nowadays. Their hierarchical structure, functionalities of ligands, and metal sites make ZIFs versatile and promising materials for various applications including adsorption/separation<sup>1-4</sup>, gas storage<sup>5</sup>, catalysis<sup>6</sup>, and drug delivery agents<sup>7</sup>. Like most of the nanoscale materials, ZIFs typically are obtained as fine powders. For practical large-scale operations (e.g., adsorption and catalysis), fine powders must be processed into pellets or other large particles<sup>8</sup>. Some are fabricated to form monoliths<sup>9, 10</sup>. Pelletizing, extruding or preparing monoliths, however, requires long processing times and sometimes also involves specialized instrumentation, limiting large-scale productions. Recently, Sue *et al.* attempted to grow ZIF-8 on a silica spherical porous structure via the hydrothermal method<sup>11</sup>. Although ZIF-8 was grown on the silica porous structure, the resultant product was still very fine (< 100  $\mu$ m), which would require further processing to form large and easy-to-use products. A few studies proposed to use porous structures (e.g., ceramic foam<sup>12</sup>, alumina foam<sup>13</sup>, polyurethane foam<sup>8</sup>, silica foams<sup>14</sup>, acrylonitrile butadiene styrene foam<sup>15</sup>, polysulfone<sup>16</sup>, laser-perforated brass supports<sup>17</sup>) as supports to prepare large-size composites which can exhibit macroporous structures from the supports and micro/nano-porous properties from nanoscale

materials. However, like the composite of ZIF-8/silica porous structure mentioned above, most of these large-size composites are prepared via hydrothermal methods, which also require long incubation times (up to a few days) at elevated temperatures<sup>8, 11</sup>, multiple soaking and washing cycles<sup>15</sup>, and toxic solvents (e.g., Dimethylformamide)<sup>8</sup>. Thus, it remains challenging to employ these techniques to rapidly and simply fabricate 3-D macroporous composites coated by nanoscale ZIFs. Here, we propose to develop a rapid, inexpensive, and ready-to-use method to prepare a composite consisting of nanoscale ZIFs and macroporous 3-D hierarchical structures. Rather than using hydrothermal methods under high pressure, a simple dip-coating technique is employed in this study to prepare the composites of ZIF/3D structures. To demonstrate this approach, a commercially available sponge (i.e., melamine-formaldehyde sponges) was selected as a low-cost and widely available 3-D structure to support ZIFs. ZIF-67 was chosen as the representative ZIF owing to its quick synthesis in water at ambient temperature<sup>18, 19</sup>. Considering the surface properties of ZIF-67, we attempted to modify sponges with commercially available surfactants in order to facilitate ZIF-loading on sponges. Four surfactants were selected including sodium dodecyl benzene sulfonate (SDBS), representing an anionic surfactant, cetyl trimethylammonium bromide (CTAB),

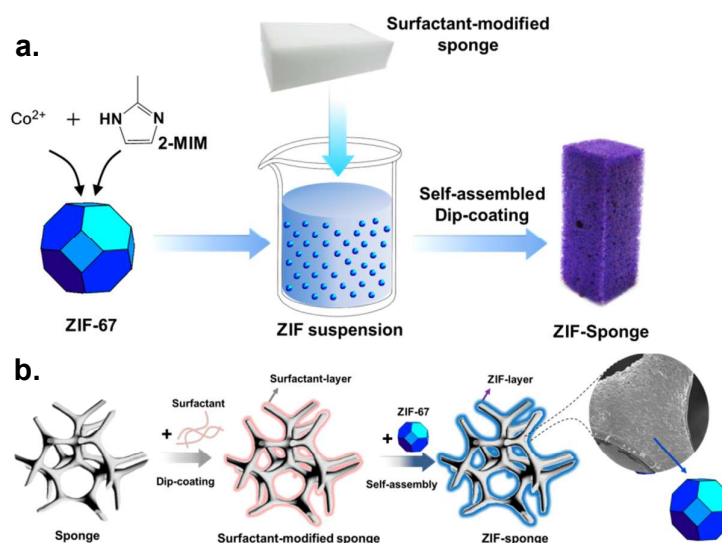


Fig. 1. Schematic illustrations showing the preparation of ZIF-sponge: (a) surfactant-assisted dip-coating self-assembling process and (b) surface-modification of the sponge skeleton first with surfactant and then ZIF-67.

<sup>a</sup> Department of Environmental Engineering, National Chung Hsing University, 250 Kuo-Kuang Road, Taichung, Taiwan, R.O.C.

† Footnotes relating to the title and/or authors should appear here. Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

a cationic surfactant, Span-80 (i.e., sorbitane monooleate, denoted as SPAN), a non-ionic and relatively hydrophobic surfactant and Triton X-100 (T-100), a non-ionic and relatively hydrophilic surfactant. Even though the present study focuses on the preparation and investigation of ZIF-67/sponge, the approach in fact may be extended to preparation of other ZIFs/sponge or metal organic frameworks (MOFs)/sponge composites.

The preparation of the ZIF-sponge is illustrated in Fig. 1a. ZIF-67 nanocrystal was first synthesized based on the reported procedure<sup>19</sup> and its X-ray diffraction (XRD) pattern is shown in Fig. S1, which can be readily indexed according to the literature<sup>18</sup>, validating that ZIF-67 nanocrystals were well-developed. A piece of sponge (e.g., 1 cm × 1 cm × 2 cm) was washed with ethanol and water, and dried in a conventional oven at 60 °C. The sponge was then compressed manually and immersed in a glass vial containing 20 ml of surfactant solution with a pre-set concentration (i.e., 500–4000 mg L<sup>-1</sup>). As illustrated in Fig. 1b, the dip-coating of the sponge in the surfactant solution allowed the deposition of surfactant molecules on the surface of sponge skeletons. To facilitate deposition of surfactant on the sponge, the vial was placed on an orbital shaker at 300 rpm for 30 min. The sponge was then washed thoroughly with DI water and ethanol, and dried at 60 °C to obtain the surfactant-modified sponge. Next, a ZIF-67 suspension was prepared by adding 50 mg of ZIF-67 to 20 ml of DI water and the mixture was sonicated for 30 min to disperse ZIF-67 nanocrystals in DI water. The surfactant-modified sponge was then added to the ZIF-67 suspension and stirred on the orbital shaker at 300 rpm for 3 hr to allow the self-assembling process of ZIF-67 and the surfactant-modified sponge to proceed. A layer of ZIF-67 formed on the sponge surface as illustrated in Fig. 1b.

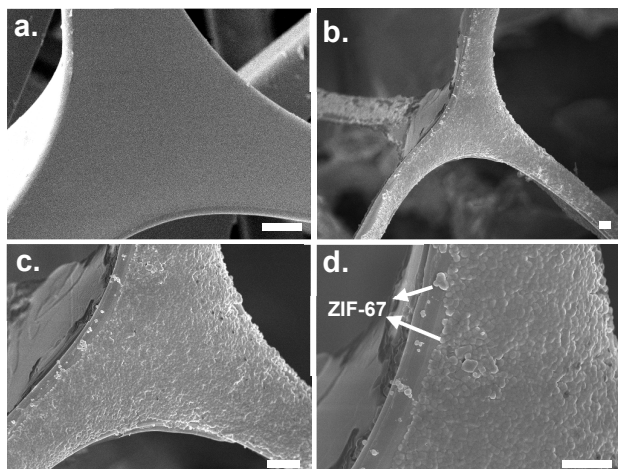
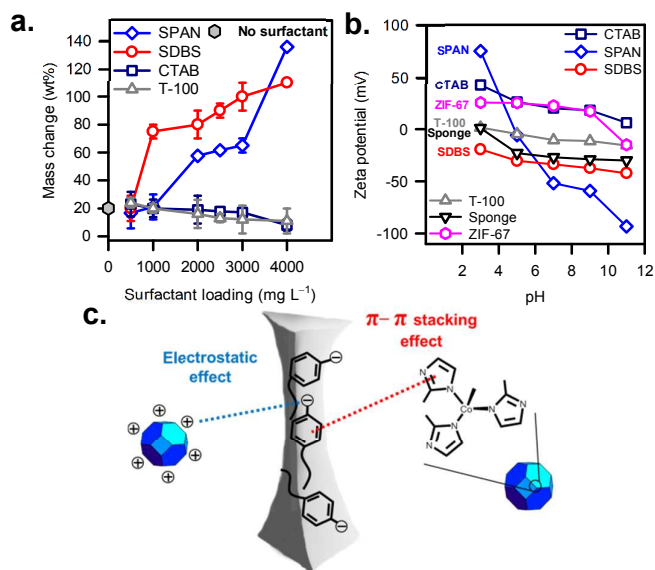


Fig. 2. SEM images of (a) pristine sponge, (b)-(d) ZIF-sponge prepared with the assistance of SDBS under different magnifications (the scale bar is 2  $\mu\text{m}$ ).

Next, the sponge was withdrawn from the suspension and washed repeatedly with DI water and ethanol, and dried at 90 °C under reduced pressure for 12 hr to obtain the self-assembled ZIF-coated sponge, abbreviated as ZIF-sponge-X, where X denotes the surfactant used to modify sponges. Fig. 2a displays a SEM image of the pristine sponge, showing the clean and smooth surface of a joint of the sponge skeleton. Once the surface was modified with surfactants and loaded with ZIF-67, the surface of the skeleton became roughened as seen in Fig. 2b, in which three axes of the

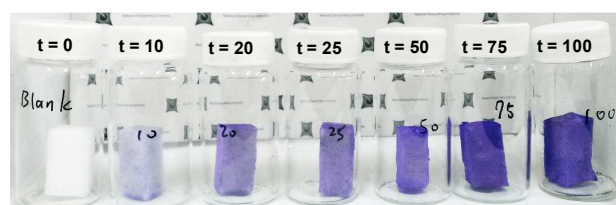
joint were covered by the layer of ZIF-67. Fig. 2c reveals that the layer of ZIF-67 appears to be a uniform layer and no obvious aggregation was observed. This suggests that ZIF-67 nanocrystals were well-dispersed in the suspension and attached to the sponge surface via certain attractions between the surface and ZIF-67. Under a higher magnification (Fig. 2d), ZIF-67 nanocrystals can be also observed; they range in size from 100 to 600 nm. The macroscopic images of ZIF-sponges (Fig. S2) show ZIF-sponges prepared without and with assistances of surfactants. It can be found that the white-colored pristine sponge became purplish in color, indicating that the sponge was coated with ZIF-67. Regardless of surfactant type, ZIF-sponges appear to be visually similar. The XRD patterns of the pristine sponge and the various ZIF-sponges are shown in Fig. S3. While the pristine sponge is amorphous, the XRD features of ZIF-67 can be still clearly observed in the XRD patterns of ZIF-sponges, validating that ZIF-67 was loaded on sponges and the crystallinity of ZIF-67 was well-preserved after self-assembling with sponge.

Considering that the surfactant type might lead to different amounts of ZIF-loading on the sponge surface, we varied the concentration of surfactant during the modification of sponge. ZIF-loading (in terms of wt%) on the surfactant-modified sponges was also measured to further investigate whether the surfactant type affected the formation of the layer of ZIF on the sponge. The result can be seen in Fig. S4a, which shows the total weight change as a function of surfactant concentration. The total weight change was defined as weight increase (wt%) caused by the surfactant modification and the ZIF-loading compared to the weight of a pristine sponge. As the surfactant concentration increased, the total weight change also increased. However, significant differences in the total weight change occurred between different types of surfactants. In the case of CTAB (4000 mg L<sup>-1</sup>), the weight increased by 55 wt%, whereas the weight increased by 64 wt% using T-100 (4000 mg L<sup>-1</sup>) to modify the sponge. On the other hand, with the SDBS modification (4000 mg L<sup>-1</sup>), the weight increased by 155 wt% and with SPAN, the weight change was raised up to 255 wt%. Considering that the total weight change occurred due to both surfactant modification and ZIF-loading, the respective weight change caused by each factor was also measured and is shown in Fig. S4b and Fig. 3a. The weight increases caused by surfactants were comparable between SDBS, CTAB and T-100, whereas the weight increase was relatively high using SPAN to modify the sponge. This could be because SPAN is a relatively hydrophobic surfactant which could exhibit a higher affinity to the hydrophobic melamine sponge compared to the other three relatively hydrophilic surfactants. Fig. 3a reveals the weight increase owing to ZIF-loading on surfactant-modified sponges. One can see that with CTAB and T-100, the weight change by ZIF-loading did not increase when the sponge was modified by a higher surfactant concentration. As revealed in Fig. S4b, when sponge was modified with a higher surfactant concentration, a higher amount of surfactant was indeed deposited on the sponge. However, such a higher amount of surfactant did not improve ZIF-loading in the cases of CTAB and T-100. This suggests that no strong affinities existed between ZIF-67 and CTAB as well as T-100, leading to the limited loading of ZIF-67 on the surfactant-modified sponge. On the other hand, the weight changes were greater when sponges were modified with higher concentrations of SDBS and SPAN.



**Fig. 3.** (a) Effects of surfactant type and concentration on ZIF-loading on sponge; (b) zeta potentials of surfactants, sponge and ZIF-67 in water at pH = 3–11; and (c) illustration showing the possible mechanisms leading to ZIF-loading on surfactant-modified sponge.

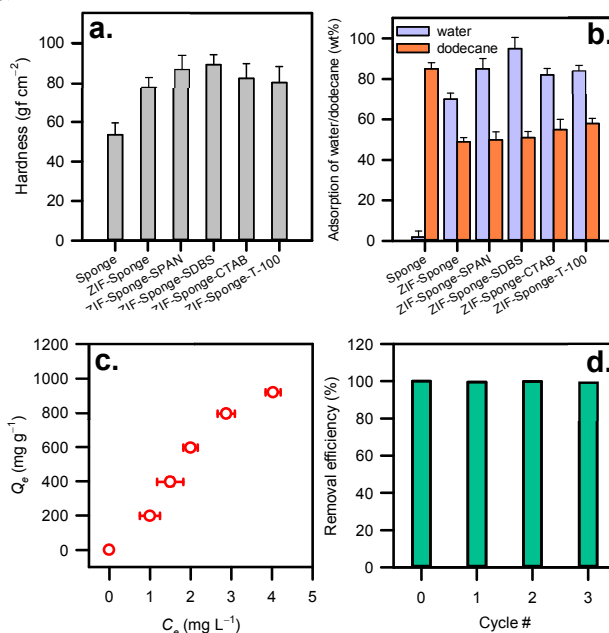
To probe into possibilities leading to such a noticeable difference, zeta potentials of various surfactants were measured and are shown in Fig. 3b. It can be seen that CTAB, as expected, exhibits positive surface charges at pH = 3–11, whereas T-100, a non-ionic surfactant, remained quite neutral at the testing pH range. In contrast, the zeta potential of SPAN was found to change significantly when pH was increased from 3 to 11 and exhibited a negative surface charge at pH > 5. SDBS was also found to be negatively surface-charged at each tested pH. The surface charge of ZIF-67 was found to be positive at a wide range of pH (Fig. 3b). The positive charge of ZIF-67 could be attracted to SDBS and SPAN via the electrostatic effect and therefore led to the noticeably higher ZIF-67 loadings in ZIF-sponge-SDBS and ZIF-sponge-SPAN. In addition to the electrostatic effect, it has been suggested that MOFs can interact with organics through several other mechanisms, including Lewis acid-base interactions, hydrogen bonding, and  $\pi$ - $\pi$  stacking interactions<sup>20–22</sup>. Considering that 2-methylimidazole of ZIF-67 contains an imidazole ring which is considered aromatic, ZIF-67 might be also attracted to the SDBS-modified surface via the  $\pi$ - $\pi$  interaction with a benzene ring of SDBS. These potential interactions between ZIF-67 and the SDBS-modified sponge are illustrated schematically in Fig. 3c. ZIF-67 was adsorbed to the sponge primarily via the electrostatic attraction and possibly through the  $\pi$ - $\pi$  interaction. Interestingly, we also found that the sponge itself could exhibit slight negative-charge on its surface. Thus, a ZIF-sponge without assistance of surfactant was also prepared as shown in Fig. S2. This indicates that ZIF-67 can be also attracted to sponge surface, possibly via the electrostatic effect. However, the weight change owing to ZIF-loading was only 20 wt%. This was comparable to the weight changes owing to ZIF-loading in the ZIF-sponges which were modified by four surfactants with concentrations of 500 and 1000 mg L<sup>-1</sup>. This suggests that when sponges were modified by relatively low concentrations of surfactants, the surfactant modification did not significantly affect ZIF-loading on each sponge. The surfactant concentration has to reach 2000 mg L<sup>-1</sup> or higher to result in noticeable effects on the ZIF-loading to sponges. Although the sponge surface itself exhibited slight negative surface-charge and consisted of triazine rings which



**Fig. 4.** Pictures showing ZIF-sponge-SDBS prepared at different dip-coating times in minute using 3000 mg L<sup>-1</sup> of SDBS at ambient temperature.

allow the  $\pi$ - $\pi$  interaction between the sponge and ZIF-67, the layer of surfactant (i.e., SPAN and SDBS) appeared to be more effective in facilitating ZIF-loading. This suggests that the layer of surfactants might offer more accessible adsorption sites to interact with ZIF-67 nanocrystals perhaps due to the configurational flexibility of long-chain SPAN and SDBS surfactants.

Furthermore, the kinetics of ZIF-loading on sponges modified by various surfactants was measured to provide important information on ZIF-sponge design and preparation. As shown in Fig. 4, the color of the sponge modified with 3000 mg L<sup>-1</sup> of SDBS changed from white to deep-purple as the dip-coating time increased from 0 to 100 min. This reveals that a longer dip-coating time considerably increased ZIF-loading on sponges. To investigate the effect of dip-coating time, the weight change owing to ZIF-loading as a function of dip-coating time is shown in Fig. S5. ZIF-loading increased with dip-coating time and approached to saturation after 2-hr dip-coating. The kinetic data were then analyzed using two common adsorption rate laws: the pseudo first order and the second order rate laws as described in Text S1 (see ESI†). The fitting results using the pseudo first and second rate laws are represented as the dashed and the solid lines in Fig. S5. The corresponding rate constants and correlation coefficients are summarized in Table S1. One can see that while the kinetics of ZIF-loading can be well-described by the two rate laws, the pseudo second rate law seemed to be more appropriate. Estimated ZIF-loadings at equilibrium were also obtained and SDBS appeared to be the most effective S1



**Fig. 5.** Physical properties of ZIF-sponges: (a) hardness and (b) adsorptions of water and dodecane at 25 °C.; (c) adsorption isotherm of MG to ZIF-sponge-SDBS at 25 °C. and (d) recyclability of ZIF-sponge-SDBS for MG at 25 °C.

In addition, considering that sponge is a flexible and soft material, hardness is one of the critical parameters of sponge and foam materials. Thus, we also investigated the change in hardness of sponges after ZIF-loading. Fig. 5a shows hardness of the pristine sponge and various ZIF-sponges measured by a durometer specialized for measurement of sponge hardness (Fig. S6 and Text S2). Prior to ZIF-loading, the sponge exhibited a hardness of 58 gf cm<sup>-2</sup>, whereas ZIF-sponge, without surfactant modification, showed a hardness of 78 gf cm<sup>-2</sup>, indicating that ZIF-loading solidified sponge and improved hardness. When sponges were loaded with additional ZIF-67 with the assistance of surfactants, especially by SDBS and SPAN, the hardness was significantly enhanced to 89 and 87 gf cm<sup>-2</sup>, respectively, an increase of more than 50%. ZIF-sponge-CTAB and ZIF-sponge-T-100 both also exhibited enhanced hardness compared to the pristine sponge. This reveals that ZIF-sponges have much higher mechanical strength, making them a more durable material.

Surface areas of sponges after the loading of ZIF-67 were also measured and are listed in Table S2. Surface areas of the pristine ZIF-67 and the melamine sponge are also listed for comparison. As reported, the pristine ZIF-67 exhibited a high surface area of 1710 m<sup>2</sup> g<sup>-1</sup>, whereas surface area of the melamine sponge was extremely low (i.e., < 1 m<sup>2</sup> g<sup>-1</sup>). After loading ZIF-67 on sponges, the resultant ZIF-sponges all exhibited noticeably higher surface areas than the melamine sponge. The increase of surface area in ZIF-sponge-SPAN was found to be the highest, followed by ZIF-sponge-SDBS, ZIF-sponge-T-100 and then ZIF-sponge-CTAB in the same order of the weight change as seen in Fig. 3a. This suggests that the higher loading of ZIF-67 assisted by a favourable surfactant (e.g., SPAN) can result in a higher extent of ZIF-67 surface coverage, thereby increasing the surface area of sponge.

We also investigated interfacial properties of the resultant ZIF-sponges. Contact angle measurement was attempted; however sponge samples had to be compressed to thin films to prevent the capillary effect during the measurement. Because the thin films do not reflect exact interfacial properties of sponge, water and dodecane adsorptions to ZIF-sponges were performed to evaluate hydrophilicity and hydrophobicity of sponges, respectively (Fig. 5b). Prior to ZIF-loading, water adsorption to the pristine sponge was very low within the testing time (1 min). Once the sponge was loaded with ZIF-67, the water adsorption was tremendously increased. ZIF-sponge exhibited a much higher water adsorption, even though it lacked surfactants. With the assistance of surfactants, the water adsorption was further improved. In particular, ZIF-sponge-SDBS shows a water adsorption of 95 wt%, almost equal to the pristine sponge, revealing that hydrophilicity of sponge was greatly improved because of the layer of ZIF-67. In the case of dodecane adsorption, the pristine sponge was found to exhibit a high dodecane adsorption (~85 wt%), demonstrating a high hydrophobicity as expected for a melamine sponge. Once sponges were loaded with ZIF-67, their dodecane adsorption was reduced to less than 50 wt% even in ZIF-sponge, the one without surfactants. Other ZIF-sponges were also found to adsorb much less dodecane compared to the pristine sponge. These results validate that ZIF-sponges exhibited quite distinct interfacial properties compared to the pristine sponge. This also suggests that hydrophobicity and hydrophilicity can be manipulated by changing ZIF-loading.

Considering the layer of ZIF-67 and sponge-structure of ZIF-sponge, it can be designed as porous filters, membranes and adsorbents. Therefore, we used ZIF-sponge to remove Malachite Green (MG), an extensively-employed dye, disinfectant and antifungal therapeutic reagent in aquacultural water. MG has been proven to cause carcinogenesis, mutagenesis, teratogenesis and respiratory diseases<sup>23, 24</sup>; its removal from water is therefore of much importance. Fig. 5c displays the adsorption isotherm of MG to ZIF-sponge-SDBS, which was further analyzed using the Langmuir adsorption isotherm model (Text S3, see ESI<sup>†</sup>). The maximum adsorption capacity of ZIF-sponge-SDBS for MG estimated by the Langmuir isotherm was 4093 mg g<sup>-1</sup> with a correlation coefficient of 0.972, which, to our best knowledge, is the highest adsorption capacity for MG to date<sup>25, 26</sup>. Even in Fig. 5c, ZIF-sponge-SDBS had exhibited a capacity of ~1000 mg g<sup>-1</sup>, showing its ultra-high capacity for MG possibly owing to the  $\pi$ - $\pi$  interaction between MG and ZIF-67 of ZIF-sponge<sup>26</sup>. ZIF-sponge-SDBS can be also regenerated easily by washing with ethanol at ambient temperature and re-used for removal of MG as seen in Fig. 5d, in which the regenerated ZIF-sponge-SDBS shows stable and recyclable adsorption capacity over multiple times. The mass changes of ZIF-sponge during the cyclic adsorption test have been also monitored and shown in Fig. S7 (ESI<sup>†</sup>), which indicates that the mass change of ZIF-sponge due to the adsorption process was less than 0.75 wt% of its initial weight in each cycle. This implies that ZIF-67 nanocrystals remained quite stably on the sponge without huge loss. In addition, the cobalt concentrations in the treated solution and the regenerating ethanol were below the detection limit of atomic absorption spectrometer, showing that cobalt ions were not leached out from ZIF-67 nanocrystals during the adsorption and regeneration processes.

### Conclusion

In this study, self-assembled ZIF-sponges were successfully prepared by the surfactant-assisted dip-coating method. The presence of surfactants (e.g., SDBS) could enhance the affinity of sponge toward ZIF-67 nanocrystals via the electrostatic and  $\pi$ - $\pi$  stacking effects, and were shown to facilitate the self-assembly of ZIF-67 with sponge skeletons. The resultant ZIF-sponges were found to exhibit higher hardness and hydrophilicity, which enable ZIF-sponges to be used in wider applications. ZIF-sponge also exhibited a ultra-high capacity to remove malachite green, a toxic pollutant, from water. Thus, ZIF-sponges can be designed to be filters, membrane, and adsorbents. This study offers a straightforward and effective route to prepare ZIF-coated sponges with any shapes; the technique may be extended to prepare other MOF-sponges via this self-assembled dip-coating method.

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