Tunable Metallogels Based on Bifunctional Ligands: Precursor Metallogels, Spinel Oxides, Dye and CO₂ Adsorption

Noohul Alam and Debajit Sarma*

ABSTRACT: A semisolid gel material is a gift of serendipity via various chemical interactions, and metal incorporation (metallogels) imparts diverse functional properties. In this work, we have synthesized four metallogels from tetrapodal and hexapodal carboxylic acid/amide-based low-molecular-weight gelators with Ni(II) and Cu(II) salts. These metallogels can be tuned to be a low-temperature precursor of porous spinel oxides. These xerogels exhibit impressive water soluble dye and carbon dioxide adsorption, which coupled with the tunability and facile synthesis of porous spinel oxides underscores their potential in environmental remediation and energy applications.

INTRODUCTION

In recent years, soft materials attracted plenty of attention due to their astonishing capabilities in the copious facets of life. The semisolid gel materials are a gift of serendipity via various chemical interactions.¹ These materials are loaded with immobilized solvents like dimethyl sulfoxide,² N,N-dimethyl formamide,³,⁴ dichloromethane,⁵ tetrahydrofuran,⁶ water,⁷ methanol, and ethanol⁸ into their inorganic or organic gel matrices.⁹ The self-assembled semisolid gel materials derived from the low-molecular-weight gelator are called metallogels in the presence of a metal ion, otherwise termed as organogels.¹⁰ Particularly, the design of metal-incorporated gel materials is challenging and appealing because metal imparts several functional properties into the material, like conductivity,¹¹,¹² absorption/ion-exchange,¹³–¹⁵ catalytic applications,¹⁶,¹⁷ redox activity,¹⁸ and other energy-related applications.¹⁹,²⁰ Non-covalent interactions like π–π interactions, hydrophobic interactions,²²,²³ hydrogen bonding, and electrostatic forces imparted the three-dimensional metallogel network with immobilized solvent in the gel network. In metallogels, the cross-linked network structure is stable and formed via the metal–ligand interaction that can be tuned by replacing the metal ions.²⁷ Metallogels find applications in fields such as light-emitting diodes,²⁸ sensors,²⁹ biomaterials,³⁰,³¹ and photonics.³² The desolvated metallogels, viz., xerogels, are functionalized materials that can play an essential role as single-source precursors of metal oxides for energy applications and in environmental remediation.¹³–¹⁵,³³–³⁵

The search to diversify the energy dependency on nonrenewable fossil fuels to a renewable and sustainable source of energy is one of the most challenging issues currently because the combustion of fossil fuels results in the emission of carbon dioxide and other anthropogenic greenhouse gases. CO₂ is considered as the main cause of the fluctuation of global climate.³⁶ Therefore, the reduction of carbon dioxide from the atmosphere is one of the the main concerns currently. The porous metal–organic materials are found as good sorbents for the CO₂ at mild pressure and temperature. Also, the climate concerns demand usage of other green alternative ways of energy production. In this regard, the electrochemical energy storage devices can be a good alternate option. Graphite has been used as the anode substance in the Li-ion batteries because of its long cyclic stability, low cost, and excellent kinetics.⁴³ Ferrite spinels have been considered as alternatives of the graphite anode.⁴⁶–⁴⁸ The reaction mechanism of charging and discharging that occurs in the ferrite spinels is entirely different from typical Li-ion insertion/extraction.⁴⁷,⁴⁹,⁵⁰ Moreover, we can potentially control the electrochemical performance of ferrite spinels, and also, it can be improved by tuning the morphology.⁵¹ Among spinel ferrites, NiFe₂O₄ (NFO) and CuFe₂O₄ (CFO) have been developed and garnered great interest in the lithium-ion batteries due to very high theoretical capacities of NFO (915 mA h/g) and CFO (893 mA h/g), compared to that of graphite (372 mA h/g).⁵¹ Also,

Received: April 14, 2020
Accepted: June 23, 2020
Published: July 8, 2020

© 2020 American Chemical Society
17356
natural abundance and low cost make NFO and CFO spinels as promising alternate anode materials in lithium-ion batteries. The surface area and pore size of the NFO and CFO spinels highly influence the electrochemical activity by offering a large area for the electrochemical reactions, better cycling performance, and superior discharge capacities.51

Similarly, water pollution is also a primary global concern, and synthetic organic dyes (~7 × 10^9 tons of global annual production) is one of the chief contributors to it because they are carcinogenic,52 mutagenic, and toxic.56,57 Water-soluble dyes are used in the paper printing, leather, and textile industries.58 The presence of dyes even at an extremely low level (less than 1 mg/L) is clearly visible, and the color is an indicator of the water quality for the general community. Therefore, removal of the color from wastewater is usually more significant than the elimination of organic substances.59,60 Hence, there is scope to find out new adsorbents, which can be easily prepared and also do not required nonrenewable raw materials. In this account, the adsorption of dyes by the metallogel have gained interest.61

Herein, we have taken tetrapodal (LMWG1) and hexapodal (LMWG2) carboxylic acid/amide-based ligands. Both the tetrapodal and hexapodal ligands contain an amide functional group in their core and a carboxylic group at the terminal. Coordination of these ligands via their terminal carboxylic acid binding sites and intermediate amide binding sites with Ni/ Cu(II) ions results in metallogels Ni@MG1, Ni@MG2, Cu@MG3, and Cu@MG4. We have made metal oxides (NiO and CuO) by controlled thermal decomposition of precursor metallogels. More importantly, after getting the metal oxides successfully, we have tuned our synthesized metallogels to get NiFe2O4 and CuFe2O4 spinels. To the best of our knowledge, this is the first example of spinel ferrite synthesis from precursor metallogels. The synthesized spinel ferrites exhibit higher surface area as compared to previously reported spinels,51−64 which are made by various synthetic methods.65

We have also illustrated the application of Ni@MG1, Ni@MG2, Cu@MG3, and Cu@MG4 xerogels (the dried form of the gel) in the disposal of water containing dyes with high adsorption capacity. The adsorption kinetics, isotherm, and the plausible mechanism of adsorption by xerogels have been proposed.

RESULTS AND DISCUSSION

The synthesized bifunctional carboxylic/amide based ligands were used for ligation with the metal ions. The presence of the carboxylic group makes it an excellent ligand for the metal ions, and the presence of the amide functionality and aromatic rings increase the possibility of having hydrogen bonding and π−π stacking interactions. These are the ideal condition for the formation of the metallogel. We have employed the bifunctional ligands, LMWG1 and LMWG2 (Figures S1−S3, see the Supporting Information), with Ni2+ and Cu2+ for the synthesis of four metallogel compositions Ni@MG1, Ni@MG2, Cu@MG3, and Cu@MG4 (Figure 1).

The multifunctional (carboxylic acid/amide) LMWGs were designed in such a way that they possess selective ligation properties toward metal ions. We expected that this variation could be employed to synthesize the precursor metallogel for the synthesis of spinel oxide. We have tuned the synthesis of the metallogel by introducing a 1:2 (Cu/Ni:Fe) metal ratio for the precursor metallogel (Figure 2).

Under a field-emission scanning electron microscope (FESEM), we have examined the molecular aggregations of the metallogels. The FESEM images of the Ni@MG1 and Ni@MG2 reveals that they form a porous, spongy structure, and the transmission electron microscopy (TEM) studies indicate aggregation of the nanofiber-like structure (Figure 3a,c and Figure S4a, see the Supporting Information). The FESEM images of the Cu xerogels (Cu@MG3 and Cu@MG4) show a more compact structure compared to the Ni xerogels (Ni@MG1 and Ni@MG2), and the TEM studies reveal that the gel network is formed by aggregation of nanoparticles rather than nanofibers as observed in Ni xerogels. (Figure 3b,d and Figure S4b, see the Supporting Information). The average particle size of Cu@MG3 was found to be around 45 nm, from the TEM image (Figure S4c). The selected-area electron diffraction (SAED) images revealed that the xerogels are amorphous (Figure 3e,f). The amorphous nature of the synthesized metallogels are also confirmed from the powder X-ray diffraction analysis (Figure S5).

Rheological studies were conducted to estimate the viscoelastic nature of the metallogel. The storage (G') and the loss (G'') moduli were plotted against frequency for the metallogel samples (Figure 4a and Figure S6, see the Supporting Information). It was observed that in all the metallogel samples, G' was found to be higher than G'' over the entire test frequency range; e.g., the G' − G'' difference for

![Figure 1. Schematics of the synthesis of metallogels based on the tetra/hexapodal ligands.](image)

![Figure 2. Pictorial representation of the formation of precursor metallogels and the subsequent thermal decomposition to spinels.](image)
the Ni@MG1 and Ni@MG2 were found to be 27254 and 38233 Pa at 0.1 Hz frequency. These results indicate that all the obtained metallogels are elastic, but in the case of copper-incorporated metallogels, the values of the $G' - G''$ difference were 59731 and 111327 Pa for Cu@MG3 and Cu@MG4, respectively, at 0.1 Hz frequency.

The morphology indicates that the xerogels might exhibit porosity. Therefore, N$_2$ gas adsorption–desorption studies were performed on the xerogels. The permanent porosities of the Ni@MG1, Ni@MG2, Cu@MG3, and Cu@MG4 xerogels were affirmed through the reversible adsorption–desorption experiment at 77 K, which indicates a type-III adsorption isotherm with the mesoporous nature of the xerogels (Figure S7, see the Supporting Information). Furthermore, the BET surface areas and pore size distributions with pore volumes of the Ni@MG1, Ni@MG2, Cu@MG3, and Cu@MG4 xerogels were also calculated. The BET specific surface areas of xerogels were 13–38 m$^2$/g with total pore volumes of 0.055–0.01 cm$^3$/g (Table S1, see the Supporting Information). Based on our results, Ni@MG1 and Ni@MG2 have larger surface area than Cu@MG3 and Cu@MG4, which is in agreement with the microscopic studies and the dye adsorption properties of Ni@MG1 and Ni@MG2.

To examine the thermal stability of the xerogels, thermogravimetric analyses (TGA) were performed. The thermal behaviors of Ni@MG1, Ni@MG2, Cu@MG3, and Cu@MG4 were examined from room temperature to 800 °C. The TGA results show that all of the xerogels have weight loss before 150 °C, which is due to the removal of physisorbed moisture and coordinated solvent molecules. In the nickel-based metallogel, approximately 55 to 60% weight loss was observed in between 360 and 490 °C, but in the case of copper-based metallogels, there is two-step weight loss observed; initially, a loss of ∼36–37% in the range of ∼250–340 °C and then second weight loss of ∼18–20% around 400–520 °C may be due to the decomposition of xerogels (Figure 4b).

To identify the calcined product, Ni@MG2 and Cu@MG4 samples were heated at 500 °C for 3 h in a tube furnace. The PXRD patterns of calcined samples were found to match with the reported NiO and CuO ICSD reference numbers 92132 and 69758, respectively (Figure 5 and Figure S8, see the Supporting Information).

The thermogravimetric studies indicate that these metallogels could be employed to synthesize the precursor metallogel for the synthesis of spinel oxide at relatively low temperature with a high surface area. We have used a 1:2 (Cu/ Ni:Fe) metal ratio for the synthesis of the precursor metallogel (Figure 2). Also, the formation of the precursor metallogel and its elastic nature were confirmed by rheological studies where $G’$ was found to be higher than $G''$ over the entire test region (Figure S9, see the Supporting Information). Thermal decomposition of these precursor xerogels at 500 °C for 3 h resulted in the formation of the NiFe$_2$O$_4$ (NFO) and CuFe$_2$O$_4$
We believe that this was possible due to the selective ligation of the carboxylic group (possibly the octahedral coordination) and the amide (possibly the tetrahedral coordination), which resulted in the spinel oxide instead of a mixture of binary oxides.

To confirm the structures of both NFO and CFO spinels, we have performed PXRD studies (Figure 5 and Figure S8, see the Supporting Information). The NFO spinel synthesized from the metallogel crystallizes in the cubic space group \( Fd-3m \) with \( a = 8.337 \, \text{Å} \) and \( V = 579.47 \, \text{Å}^3 \) (ICSD reference number 40040), and the PXRD pattern of NFO shows the existence of the pure nickel ferrite spinel phase only. The CFO spinel synthesized from the metallogel crystallizes in the cubic space group \( Fd-3m \) with \( a = 8.416 \, \text{Å} \) and \( V = 596.15 \, \text{Å}^3 \) (ICSD reference number 188854), but there are some iron oxide (ICSD reference number 26410) peaks (Figure S8).

The SEM micrographs of NiO, CuO, NiFe₂O₄ (NFO) and CuFe₂O₄ (CFO) synthesized from metalloids, and precursor metalloids are shown in (Figures S10 and S11, see the Supporting Information). The morphologies of the metal oxide and mixed metal oxide are uniform, and all are spherical-shaped nanoparticles. Additionally, from the images, it is clearly seen that these nanoparticles are nearly closed packed; this would help in the electron transport at the time of photoelectrochemical and electrochemical applications.65 We also carried out the energy-dispersive X-ray (EDX) study to get details about the elements present in the metal oxide and mixed metal oxide. In the case of nickel ferrite spinel, the ratio of atomic weight percent of nickel and iron metal was Ni:2.2 Fe, and for copper ferrite spinel, it was Cu:1.7Fe (Figure S11, see the Supporting Information).

The BET specific surface areas of NFO and CFO ferrite spinels were 276.31 and 201.13 m²/g, respectively, with average pore sizes of 1.459 and 0.638 nm, respectively. The total pore volumes of NFO and CFO were 0.57 and 0.406 cm³/g, respectively (Figure S12, see the Supporting Information). These synthesized ferrite spinels from the precursor metallogel exhibit high surface area as compared to many reported procedures (Table S2, see the Supporting Information).

The presence of the polar functional groups (amide linkage) prompted us to examine the adsorption behavior toward water-soluble organic dyes. The materials show fast and efficient absorption of methylene blue (MB) and congo red (CR) (Figures 6a–g, Figures S13 and S14, see the Supporting Information).

**Adsorption Kinetics Studies.** To understand the adsorption behavior of Ni@MG1, Ni@MG2, Cu@MG3, and Cu@MG4 xerogels, we have performed the adsorption kinetics experiments (Figures S13 and S14, see the Supporting Information).
Information). For better understanding, the linear forms of the two kinetic models pseudo-first-order and pseudo-second-order were employed to examine the adsorption kinetic behavior. The pseudo-first-order kinetic equation is represented as

\[
\ln(q_t - q_e) = \ln q_e - k_1t
\]

where \(q_t\) (mg/g) and \(q_e\) (mg/g) stand for the amounts of dyes adsorbed at a given time interval \(t\) (min) and dyes adsorbed at equilibrium, respectively, and \(k_1\) (min\(^{-1}\)) is the pseudo-first-order rate constant.

The pseudo-second-order adsorption rate equation is represented as

\[
\frac{t}{q_t} = \frac{1}{k_2(q_e^{\text{max}})^2} + \frac{t}{q_e^{\text{max}}}
\]

where \(k_2\) (g/mg·min) is the pseudo-second-order rate constant.

The kinetic parameters calculated with the help of pseudo-first-order kinetic models and pseudo-second-order kinetic models are presented in Table 1 (Figures S15-S18, see the Supporting Information). The obtained results from both models clearly indicate that the pseudo-second-order model seems to be best fitted because, for both CR and MB dyes, \(R^2\) values acquired from the pseudo-second-order model are far closer to 1. Furthermore, the \(q_e^{\text{cal}}\) (calculated) values are much closer to \(q_e^{\text{exp}}\) (experimental) values by applying the pseudo-second-order model in comparison to the pseudo-first-order model (Table 1). From these results, we can say that the adsorption processes of CR and MB on Ni@MG1, Ni@MG2, Cu@MG3, and Cu@MG4 xerogels follow the pseudo-second-order model.

**Adsorption Isotherms.** The equilibrium adsorption isotherm model has an equal importance because it helps to understand how the adsorbates interact with adsorbents. Langmuir adsorption isotherm and Freundlich adsorption isotherm models were taken into account to evaluate the adsorption behavior. The Langmuir isotherm model is based on the hypotheses that (a) all the adsorption sites are identical and each adsorption site can take only one molecule, (b) the adsorption energy is independent of the surface coverage, and (c) after adsorption, the adsorbate molecules cannot change their position.\(^{66,67}\) The following equation represents the Langmuir isotherm model

\[
\frac{C_e}{q_e} = \frac{C_e}{q_{\text{max}}} + \frac{1}{(q_{\text{max}})k_L}
\]

where.
The values of constant, equilibrium adsorption capacity, and the maximum stand for the equilibrium concentration, Langmuir adsorption $C_{\text{max}}$ can be calculated from the intercept and slope of the linear plot of $q$ versus $C_e$.

The Freundlich adsorption isotherm model talks about the multilayer adsorption on the energetically heterogeneous surface. The following equation represents the Freundlich isotherm model

$$\ln q_e = \ln k_F + \frac{1}{n} \ln C_e$$

where $1/n$ stands for the heterogeneity factor and $k_F$ is the Freundlich constant. The Freundlich constant ($k_F$) can be obtained by plotting $\ln q_e$ versus $\ln C_e$. The isotherm and the data fitted by the Langmuir adsorption model for CR and MB on Ni@MG1, Ni@MG2, Cu@MG3, and Cu@MG4 xerogels are presented in Figure 7 (Figure S19–S22, see the Supporting Information). All the parameters obtained from the adsorption isotherm models are listed in Table 2. $R^2$ values (the correlation coefficient) demonstrated that the Langmuir model is best fitted in comparison to the Freundlich model.

Therefore, the adsorption mechanism of congo red and methylene blue dyes on Ni@MG1, Ni@MG2, Cu@MG3, and Cu@MG4 xerogels is well explained by the Langmuir rather than Freundlich isotherm model. Furthermore, the low values of $1/n$ (heterogeneity factor) also favored Langmuir-like adsorption in comparison to the Freundlich adsorption isotherm. Our adsorption capacity results are well compared with different kinds of adsorbents reported in the literature.

**Dye Adsorption Mechanism.** Several types of materials were utilized as adsorbents in the removal of toxic organic dyes from polluted waste. Usually, (i) the surface area of the material, (ii) different charge interactions involved in between the adsorbate and adsorbent, and (iii) the pore structures of the materials were reported as an essential cause for the dye adsorption. Both the organic dyes (CR and MB) contain aromatic rings and surface charge in their structures. Therefore, there are possibilities that xerogels can adsorb the dye through electrostatic interactions and hydrogen bonding. Among all, there is a chance to establish $\pi-\pi$ interactions in between the $\pi$ cloud of benzene rings of dyes and the adsorbent. Particularly, our synthesized materials are derived from amide functional group containing ligands; amide is a fascinating group because the $-\text{C}=\text{O}$ moiety of the amide functional group can behave as an electron donor and the $-\text{NH}$ moiety can behave as an electron acceptor. Therefore, we expected that the amide group also plays an essential role in the adsorption of both cationic and anionic dyes. The proposed mechanisms for adsorption of CR and MB dyes are presented in Figure 8. The nickel-based xerogel shows good adsorption capacity than copper-based xerogels, and this may be due to the larger surface area of the nickel-containing xerogel than copper-containing xerogels (Table S1 and Table S4, see the Supporting Information). Also, the porosity of the materials for the tetrapodal ligands is higher than that of the hexapodal ligands. It is to be noted that for the tetrapodal-ligand-based metallogels, the metal-to-ligand ratio was 2:1, whereas for the hexapodal ligand, the metal-to-ligand ratio was 3:1. In general, the adsorption capacities are higher for the material with higher surface area.

Furthermore, to confirm the interaction of the adsorbed dyes with the xerogel, FTIR analyses were performed (Figure S23, see the Supporting Information). In the case of CR, a 3470 cm$^{-1}$ adsorption peak stands for the stretching of primary amine $-\text{N}=\text{H}$, which was slightly shifted and reduced after

**Table 2. Adsorption Isotherm Parameters for CR and MB Dyes on Ni@MG1, Ni@MG2, Cu@MG3, and Cu@MG4 Xerogels**

| sample code | dye    | $q_{\text{max}}$ (mg/g) | $q_{\text{max}}$ ± error | $k_L$ | $R^2$ | $1/n$ | $k_F$ | $R^2$ |
|-------------|--------|-------------------------|--------------------------|-------|-------|-------|-------|-------|
| Ni@MG1      | CR     | 1428.57                 | 1428.57 ± 43.0           | 0.0094 | 0.9931 | 0.5394 | 45.0737 | 0.9691 |
| Ni@MG1      | MB     | 980.39                  | 980.39 ± 10.0            | 0.0454 | 0.9983 | 0.3693 | 116.85  | 0.9483 |
| Ni@MG2      | CR     | 1191.8                  | 1191.8 ± 66.0            | 0.0390 | 0.9807 | 0.5054 | 38.6327 | 0.9759 |
| Ni@MG2      | MB     | 704.22                  | 704.22 ± 10.0            | 0.0208 | 0.9981 | 0.4111 | 53.3887 | 0.8748 |
| Cu@MG3      | CR     | 497.51                  | 497.51 ± 13.0            | 0.0088 | 0.9957 | 0.4575 | 21.9046 | 0.9023 |
| Cu@MG3      | MB     | 529.10                  | 529.10 ± 8.0             | 0.0498 | 0.9975 | 0.2834 | 87.5053 | 0.9034 |
| Cu@MG4      | CR     | 526.315                 | 526.315 ± 11.0           | 0.0093 | 0.9971 | 0.4203 | 29.2272 | 0.9284 |
| Cu@MG4      | MB     | 458.7                   | 458.7 ± 4.20             | 0.0652 | 0.9993 | 0.2570 | 90.3237 | 0.8344 |

Note: $q_{\text{max}}$ stands for maximum adsorption capacity evaluated with the help of the Langmuir adsorption isotherm model.
adsorption. The absorption band at 1611 cm\(^{-1}\) indicates the \(\text{N}=\text{N}\) stretching and was also slightly shifted toward lower energy, whereas the peaks observed at 1226, 1124, and 1065 cm\(^{-1}\) correspond to the \(\text{S}=\text{O}\) stretching and were shifted and also reduced after the adsorption. Moreover, the absorption peaks at 831, 750, and 696 cm\(^{-1}\) for the aromatic groups\(^7\) in congo red were completely reduced after the adsorption. These results demonstrated that there are noncovalent interactions in between the congo red and Ni@MG1 that may be due to the participation of electrostatic interaction, \(\pi-\pi\) interaction, and hydrogen bonding.

\(\text{CO}_2\) Uptake Analysis. The presence of the immobilized amide functional group and surface area of synthesized xerogels encourage us to study the \(\text{CO}_2\) adsorption. Before \(\text{CO}_2\) adsorption, we have activated the xerogel samples in the oven at 100 °C for 24 h, and then adsorption analysis were performed within the pressure range of 0 to 1 atm at 298 K. The study reveals that the synthesized materials exhibit excellent \(\text{CO}_2\) adsorption capacity in the family of metallogels (Figure 9, Table S5, see the Supporting Information). The adsorption and desorption paths of \(\text{CO}_2\) were the same in the case of nickel metallogels, and the capacities were lower than those of copper analogues. This may be attributed to the lower polarizing power of Ni(II) than Cu(II), which results from the Jahn–Teller distortion of the Cu(II) ions. The Cu@MG3 xerogel shows higher \(\text{CO}_2\) adsorption capacity than Cu@MG4 due to the higher surface area. However, in the copper-incorporated metallogel, the desorption path of \(\text{CO}_2\) does not follow the adsorption path; i.e., it shows hysteresis (Figure S24, see the Supporting Information). The results affirmed that on decreasing the external pressure, the adsorbed \(\text{CO}_2\) was not immediately released. The \(\text{CO}_2\) adsorption study indicates that the amide functionality, the choice of metal ion, and surface area have an effect on the overall capacity of the material.

**CONCLUSIONS**

Multifunctional metallogel synthesis from designed tetrapodal and hexapodal carboxylic-acid-amide ligands, its water-soluble dye adsorption, and thermal decomposition to metal oxide have been accomplished. The synthesis can be tuned to prepare precursor metallogels for spinel oxides. The designed bifunctional carboxylic acid-amide based ligands have selective ligating properties toward metal ions. These variations in the ligation of the amide and the carboxylic acid are the cause of the formation of the spinel oxide instead of binary oxide. We have successfully synthesized ferrite (\(\text{NiFe}_2\text{O}_4\) and \(\text{CuFe}_2\text{O}_4\)) spinels with high surface area (\(\sim 200–275\) m\(^2\)/g).

The equilibrium adsorption data of congo red and methylene blue on the xerogel-based adsorbents were estimated by Langmuir isotherm and Freundlich isotherm models. The Langmuir model shows a better fit, and the adsorption process conforms to the pseudo-second-order kinetic model. From our obtained results, we can say that the synthesized xerogels are promising candidates as adsorbents for congo red (497–1428 mg/g), methylene blue (458–980 mg/g), and carbon dioxide (22–40 mg/g, at 298 K and 1 atm).

Our work shows that these multifunctional metallogels can act as single-source precursors for spinel oxides and also as adsorbents for carbon dioxide and water-soluble synthetic organic dyes. Further work is necessary to see the versatility of the metallogel for the formation of spinel oxide and its potential application for the remediation and renewable energy application.

**EXPERIMENTAL SECTION**

**Materials Used.** 1,3,5-Benzentricarboxyl trichloride, 5-aminoisophthalic acid, and terephthaloyl chloride were bought from Sigma-Aldrich. 4-Dimethylaminopyridine and methylene blue were bought from Sisco Research Laboratories (SRL). Congo red was bought from Alfa Aesar, and all the metal salts and solvents were bought from Central Drug House (CDH) and utilized without further purification. The solvents N,N-dimethylformamide and N,N-dimethylacetamide (DMA) were used without further distillation.

**Synthesis of LMWG1 and LMWG2 Ligands.** The LMWG1 ligand was made with the help of the reported literature with minor modification.\(^7\) In 15 mL of anhydrous N,N-dimethylacetamide, 5-aminoisophthalic acid (9.2 mmol, 1.66 g) and 4-dimethylaminopyridine (0.12 mmol, 0.014 g) were dissolved under a \(\text{N}_2\) atmosphere. Then terephthaloyl chloride (4.5 mmol, 0.913 g) was solubilized in 10 mL of anhydrous DMA and added drop wise to it. Under a \(\text{N}_2\) gas atmosphere, the mixture was stirred for 48 h. To get the precipitate of the product and to solubilize the excess 4-dimethylaminopyridine and 5-aminoisophthalic acid, 50 mL of 5% HCl was added. The LMWG2 ligand was synthesized with some modification of the reported literature.\(^7\) We have used 1,3,5-benzenetricarboxyl trichloride (3 mmol, 0.79 g) in place of terephthaloyl chloride, and all the remaining things were the same. The obtained product was purified by washing with 50 mL of 5% HCl followed by 20 mL of water, 20 mL of methanol, and finally with ether. For LMWG1, \(^1\)H NMR (DMSO-\(d_6\), ppm): 13.32 (broad peak, 4H, COOH), 10.76

---

**Figure 9.** \(\text{CO}_2\) adsorption capacity (mg/g) of (a) Ni@MG1 and Ni@MG2 and (b) Cu@MG3 and Cu@MG4.
(2H, s, CONH), 8.70 (4H, s, ArH), 8.24 (2H, s, ArH), 8.17 (4H, s, ArH), yield = 1.89 g (85.32%), and for LMWG2, \(^{1}H\) NMR (DMSO-\(d_{6}\)): \(\delta\) 13.38 (broad peak, 6H, s, COOH), 10.95 (3H, s, CONH), 8.84 (3H, s, ArH), 8.73 (6H, s, ArH, 2), 8.26 (3H, s, ArH, 3), yield = 1.93 g (92.34%). The spectra of LMWG1 and LMWG2 ligands are shown in Figures S1–S3 (see the Supporting Information).

**Metallogel Synthesis.** In this work, we have adopted the reported synthetic technique for metallogel preparation. In a typical synthesis, we have prepared the 0.1 mmol/mL solution by dissolving LMWG1 in DMA solvent. 0.5 mL (0.1 mmol/mL) of LMWG1 was placed separately in different vials, and 0.05–2.0 equiv. of nickel and copper acetate concerning the ligand LMWG1 concentration was also solubilized in dimethylformamide and put separately in different vials. In the final step, the dimethylformamide solution of nickel and copper acetate was added to the solution of ligand LMWG1 so that the final volume was 1 mL in each glass vial. Then, after 10 min, by the glass vial inversion method, the formation of the metallogel was confirmed at room temperature. The same procedure was followed for the metallogels derived from ligand LMWG2 except that 0.05–3.0 equiv. of nickel and copper acetate was taken in different glass vials with respect to the ligand LMWG2 (0.1 mmol/mL) concentration (Figure 1). The minimum gelation concentration for the LMWG1 ligand and metal was found to be in a 1:2 ratio, but for LMWG2, it was in a 1:3 ratio.

**Spinel Precursor Metallogel Synthesis.** To make a spinel precursor metallogel, 0.5 mL of 0.1 M LMWG2 was taken in glass vials, and 0.25 mL from each of the dimethylformamide solution of 0.2 M Ni(CH\(_3\)COO)\(_2\)·4H\(_2\)O and 0.4 M Fe(NO\(_3\))\(_3\)·9H\(_2\)O were added into the 0.1 M LMWG2-containing glass vial. Then, after 30 min, formation of spinel precursor metallogels was confirmed through the glass vial inversion method. All the remaining things were the same to make the copper-containing spinel precursor metallogel except that 0.2 M Ni(CH\(_3\)COO)\(_2\)·4H\(_2\)O was replaced with the 0.2 M Cu(CH\(_3\)COO)\(_2\)·H\(_2\)O metal salt solution (Figure 2).

**Spinel Oxide Synthesis from the Precursor Metallogel.** We have taken the dried spinel precursor metallogels Ni:2Fe@LMWG2 and Cu:2Fe@LMWG2 and heated them in a tube furnace at 500 °C for 3 h (Figure 2).

**Field-Emission Scanning Electron Microscope (FESEM).** The morphology of xerogels was analyzed using a field emission scanning electron microscope (ZEISS GEMINISEM 500 with an energy-dispersive X-ray spectroscopy detector).

**Transmission Electron Microscopy (TEM).** Metallogel samples were also analyzed using a transmission electron microscope (JEOL-JEM 2100) instrument operating at 120 kV.

**Rheological Measurements.** The rheological studies for all the metallogels were carried out using an AntonPaar (MCR 302) modulated compact rheometer. Samples were scanned at room temperature from 0.1 to 20 Hz on a parallel plate (9 mm diameter) at 1% strain to obtain the gain modulus (\(G^'\)) and loss modulus (\(G^\prime\)).

**BET Surface Area Analysis.** The \(N_2\) gas sorption studies were carried out to get the Brunauer–Emmett–Teller (BET) surface area using a Quantachrome Autosorb iQ2 analyzer. Generally, around 100 mg of xerogels was taken in the sample holder 9 mm in width. Before performing the experiment, xerogels were kept in a vacuum oven at 110 °C for 24 h; after that, samples were degassed at 120 °C for 6 to 7 h.

**Thermogravimetric Analysis (TGA).** Thermogravimetric analysis was performed using an SDT Q600 (TA Instruments). The scan rate was 10 °C/min under nitrogen, with a flow rate of 100 mL/min.

**Powder X-ray Diffraction Analysis (PXRD).** PXRD analysis was conducted using a Rigaku MiniFlex 600 diffractometer with Cu Kα radiation (\(\lambda = 1.5418\) Å).

**Fourier Transform Infrared (FTIR) Spectra.** FTIR spectra of xerogel samples were measured in the range of 4000 to 400 cm\(^{-1}\) using a PerkinElmer Spectrum 400 in KBr mode.

**UV–vis Spectra.** A spectrophotometer (Shimadzu UV2500) recorded the UV–vis spectra using 1 cm path-length quartz cuvettes.

**Adsorption Experiments.** All adsorption experiments of the aqueous solutions of Congo red and methylene blue were carried out at room temperature. 4 mg of adsorbent was dispersed in solutions (4 mL) of various concentrations under stirring until equilibrium was reached. 1 mL of the aliquot was taken out and then centrifuged for 3 min to measure the concentration of the supernatant with the help of a UV–vis spectrophotometer. To calculate adsorption capacity at equilibrium \(q_e\) (mg/g), the following equation was used

\[
q_e = \frac{(C_0 - C_e)V}{m}
\]

where \(C_0\) (mg/L) stands for initial concentration, \(C_e\) (mg/L) stands for equilibrium concentration, \(V\) (L) represents the total volume of dye solution, and \(m\) (g) represents the adsorbent weight. To perform adsorption kinetics studies, 20 mg of each Ni@MG1, Ni@MG2, Cu@MG3, and Cu@MG4 materials were added to 20 mL of an aqueous solution of 10 mg/L MB and CR dyes, and then 1 mL of aliquots was taken out at certain time intervals to measure the concentration of the supernatant. To calculate the amount of dye adsorbed at a particular time \(t\) (\(q_t\)), the following equation was used

\[
q_t = \frac{(C_0 - C_t)V}{m}
\]

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c01710.

\(^{1}H\) and \(^{13}C\) NMR spectra, scanning electron microgram, powder X-ray diffraction, rheological studies, surface area studies, UV–vis spectrum, IR spectrum, adsorption kinetics, isotherms, and comparison tables (PDF)

**AUTHOR INFORMATION**

**Corresponding Author**

Debajit Sarma — Department of Chemistry, Indian Institute of Technology Patna, Bihta, Bihar 801106, India; orcid.org/0000-0002-9830-4808; Email: debajit@iitp.ac.in

**Author**

Noohul Alam — Department of Chemistry, Indian Institute of Technology Patna, Bihta, Bihar 801106, India

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c01710
Author Contributions
N.A. and D.S. designed and conducted the research. The manuscript was co-written by N.A. and D.S. Both the authors have approved the final version of the manuscript.

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
Authors acknowledge IIT Patna for generous financial and infrastructural support. N.A. acknowledges IIT Patna for a research fellowship. D.S. thanks the Science and Engineering Research Board DST, Govt. of India, for the research grant under sanction ECR/2018/001306. The authors also acknowledge the anonymous reviewers for their effort in reviewing and enhancing the quality of the work.

REFERENCES

(1) Chan, S. Y.; Goh, S. S.; Dou, Q.; Chan, B. Q. Y.; Choo, W. S.; Young, C. J.; Loh, X. J. Unprecedented Acid-Promoted Polymerization and Gelation of Acrylamide: A Serendipitous Discovery. Chem. – Asian J. 2018, 13, 1797–1804.
(2) Ma, X.; Liu, S.; Zhang, Z.; Niu, Y.; Wu, J. A novel thermo-responsive supramolecular organogel based on dual acylhydrazone: fluorescent detection for Al³⁺ ions. Soft Matter 2017, 13, 8882–8885.
(3) Zhang, Y.; Zhou, Q.-F.; Huo, G.-F.; Yin, G.-Q.; Zhao, X.-L.; Jiang, B.; Tan, H.; Li, X.; Yang, H.-B. Hierarchical self-assembly of a thiol-ene click amphiphilic mixture: An efficient strategy for metalorganic supramolecular materials and versatile applications. Chem. Commun. 2016, 52, 8055–8074.
(4) Díaz, D. D.; Kuhs, T.; Fering, M.; Saha, S.; Esquena, J.; Banerjee, R.; Díaz, D. D. Supramolecular metalgel that imparts self-healing properties to other gel networks. Chem. Mater. 2016, 28, 3210–3217.
(5) Li, Y.; Yang, G.; Jiang, Z.; Xiao, H.; Chen, L.; Liu, Y.; Wei, T.-B.; Zhang, Y.-M. Competitive coordination control of the AEI and micro states of supramolecular gel: an efficient approach for reversible dual-channel stimuli-response materials. Soft Matter 2014, 10, 8427–8432.
(6) Dastidar, P. Supramolecular gelling agents: can they be designed? Chem. Soc. Rev. 2008, 37, 2699–2715.
(7) Dey, B.; Mondal, R. K.; Mukherjee, S.; Sapatni, B.; Mukherjee, N.; Mandal, A.; Senapati, D.; Babu, S. P. S. A supramolecular hydrogel of a benign DNA-hydrogel. RSC Adv. 2015, 5, 105961–105968.
(8) Lin, Q.; Yang, Q.-P.; Sun, B.; Fu, Y.-P.; Zhu, X.; Wei, T.-B.; Zhang, Y.-M. Competitive coordination control of the AEI and micro states of supramolecular gel: an efficient approach for reversible dual-channel stimuli-response materials. Soft Matter 2014, 10, 8427–8432.
(9) Dastidar, P. Supramolecular gelling agents: can they be designed? Chem. Soc. Rev. 2008, 37, 2699–2715.
(10) Zhu, G.; Dordick, J. S. Solvent effect on organogel formation by low molecular weight molecules. Chem. Mater. 2006, 18, 5988–5995.
(11) Aiyappa, H. B.; Saha, S.; Wadge, P.; Banerjee, R.; Kurungot, S. Fe (III) phytate metalgel as a prototype anhydroys, intermediate temperature proton conductor. Chem. Sci. 2015, 6, 603–607.
(12) Saha, S.; Schön, E.-M.; Cativieja, C.; Díaz, D. D.; Banerjee, R. Proton-Conducting Supramolecular Metalgels from the Lowest Molecular Weight Assembler Ligand: A Quote for Simplicity. Chem. – Eur. J. 2013, 19, 9562–9568.
(13) Lim, Y. J. C.; Goh, S. S.; Liow, S. S.; Xue, K.; Loh, X. J. Molecular gel sorbent materials for environmental remediation and wastewater treatment. J. Mater. Chem. A 2019, 7, 18759–18791.
(14) Hong, Y.; Gao, Z.; Chen, M.; Hooi, D. S. Metal–Organic Gels of Catechol-Based Ligands with Ni (II) Acetate for Dye Adsorption. Langmuir 2018, 34, 9435–9441.
(15) Dietrich, D.; Licht, C.; Nuhnens, A.; Höffert, S.-P.; De Laporte, L.; Janiak, C. Metal–Organic Gels Based on a Bisamide Tetracarbosilane Ligand for Carbon Dioxide, Sulfur Dioxide, and Selective Dye Uptake. ACS Appl. Mater. Interfaces 2019, 11, 19654–19667.
(16) Díaz, D. D.; Kübbeck, D.; Koopmans, R. J. Stimuli-responsive gels as reaction vessels and reusable catalysts. Chem. Soc. Rev. 2011, 40, 427–448.
(17) Huang, J.; He, L.; Zhang, J.; Chen, L.; Su, C.-Y. Dynamic functionalised metalogel: An approach to immobilised catalysis with improved activity. J. Mol. Catal. A: Chem. 2010, 317, 97–103.
(18) Mitsumoto, K.; Cameron, J. M.; Wei, R. J.; Nishikawa, H.; Shiga, T.; Nihei, M.; Newton, G. N.; Oshio, H. A Multi-Redox Responsive Cyanometalate-Based Metallogel. Chem. – Eur. J. 2017, 23, 1502–1506.
(19) Doan-Nguyen, V. V. T.; Subrahmanyan, K. S.; Buta, M. M.; Gerbec, J. A.; Islam, S. M.; Kanie, K. N.; Wilson, C. E.; Balasubramanian, M.; Wiaderek, K. M.; Borkiewicz, O. J.; Chapman, K. W.; Chupas, P. J.; Moskovits, M.; Dunn, B. S.; Kanatzidis, M. G.; Seshadri, R. Molybdenum polysulphide chalcogels as high-capacity, anion-redox-driven electrode materials for Li-ion batteries. Chem. Mater. 2016, 28, 8357–8365.
(20) Shan, X.; Liu, J.; Mu, H.; Xiao, Y.; Mei, B.; Liu, W.; Lin, G.; Jiang, Z.; Wen, L.; Jiang, L. An Engineered Superhydrophilic/ Superaerophobic Electro catalyst Composed of the Supported CoMoS₃ Chalcogel for Overall Water Splitting. Angew. Chem. Int. Ed. 2020, 59, 1659–1666.
(21) Lehn, J.-M. From supramolecular chemistry towards constitutive dynamic chemistry and adaptive chemistry. Chem. Soc. Rev. 2007, 36, 151–160.
(22) Tuncaboylu, D. C.; Sari, M.; Oppermann, W.; Okay, O. Tough and self-healing hydrogels formed via hydrophobic interactions. Macromolecules 2011, 44, 4997–5005.
(23) Sutar, P.; Maji, T. Coordination polymer gels: soft metal–organic supramolecular materials and versatile applications. Chem. Commun. 2016, 52, 8055–8074.
(24) Das, U. K.; Puranik, V. G.; Dastidar, P. Supramolecular Synthon Transferability and Gelation by Dipimryl Ammonium Monocarboxylate Salts. Cryst. Growth Des. 2012, 12, 5864–5868.
(25) Tan, A. Y.-Y.; Yam, V. W.-W. Recent advances in metalgels. Chem. Soc. Rev. 2013, 42, 1540–1567.
(26) Abdallah, D. J.; Weiss, R. G. Organogels and Low Molecular Mass Organic Gelators. Adv. Mater. 2000, 12, 1237–1247.
(27) Rajamalli, P.; Malakar, P.; Atta, S.; Prasad, E. Metal-induced gelation from pyridine cored poly(aryl ether) dendrons with in situ synthesis and stabilization of hybrid hydrogel composites. Chem. Commun. 2014, 50, 11023–11025.
(28) Gather, M. C.; Köhnen, A.; Meierholz, K. White organic light-emitting diodes. Adv. Mater. 2011, 23, 233–248.
(29) Murata, M.; Aoki, M.; Nishi, T.; Ikeda, A.; Shinkai, S. New cholesterol-based gelators with light- and metal-responsive functions. J. Chem. Soc., Chem. Commun. 1991, 1715–1718.
(30) Zhang, S. Fabrication of novel biomaterials through molecular self-assembly. Nat. Biotechnol. 2003, 21, 1171.
(31) Xu, F.; Padhy, H.; Al-Dossary, M.; Zhang, G.; Behzad, A. R.; Stingl, U. L.; Rothenberger, A. Synthesis and properties of the metallo-supramolecular polymer hydrogel poly[methyl vinyl ether-alt-mono-sodium maleate]: AgNO₃: Ag/Cu⁺ ion exchange and effective antibacterial activity. J. Mater. Chem. B 2014, 2, 6406–6411.
(32) Ajayagosh, A.; Praveen, V. K.; Vijayakumar, C.; George, S. J. Molecular Wire Encapsulated into π Organelges: Efficient Supra-molecular Light-Harvesting Antennae with Color-Tunable Emission. Angew. Chem. 2007, 119, 6376–6381.
(33) Al-Dossary, M.; Padhy, H.; Xu, F.; Behzad, A. R.; El Tall, O.; Rothenberger, A. Copper-based hydrogels with dicarboxylate spacer ligands for selective carbon dioxide separation applications. New J. Chem. 2018, 42, 18242–18251.
(34) Cheng, N.; Hu, Q.; Guo, Y.; Wang, Y.; Yu, L. Efficient and selective removal of dyes using imidazolium-based supramolecular gels. ACS Appl. Mater. Interfaces 2015, 7, 10258–10265.
(35) Subrahmanyan, K. S.; Mallakas, C. D.; Sarma, D.; Armatas, G. S.; Wu, J.; Kanatzidis, M. G. Ion-exchangeable molybdenum sulfide
porous chalcogel: Gas adsorption and capture of iodine and mercury. *J. Am. Chem. Soc.* **2015**, *137*, 13943–13948.

(36) Wang, J.; Jia, C.-S.; Li, C.-J.; Peng, X.-L.; Zhang, L.-H.; Liu, J.-Y. Thermodynamic properties for carbon dioxide. *ACS Omega* **2019**, *4*, 19193–19198.

(37) Ananthumakkool, B.; Soni, R.; Bhanage, S. N.; Kurungot, S. Novel scalable synthesis of highly conducting and robust PEDOT paper for a high performance flexible solid supercapacitor. *Energy Environ. Sci.* **2015**, *8*, 1339–1347.

(38) Salunkhe, R. R.; Kamachi, Y.; Torad, N. L.; Hwang, S. M.; Sun, Z.; Dou, S. X.; Kim, J. H.; Yamauchi, Y. Fabrication of symmetric TiO2 nanoparticle@carbon mesoporous microfiber composite as a safe and high-performance lithium-ion battery. *ACS Nano* **2014**, *8*, 2977–2985.

(39) Jeong, G.; Kim, J.-G.; Park, M.-S.; Seo, M.; Hwang, S. M.; Kim, Y.-U.; Kim, J.-H.; Dou, S. X. Core–shell structured silicon nanoparticles@TiO2—carbon mesoporous microfiber composite as anode material. *Adv. Mater.* **2014**, *26*, 1943–1949.

(40) Jeong, G.; Kim, J.-G.; Park, M.-S.; Seo, M.; Hwang, S. M.; Kim, Y.-U.; Kim, J.-H.; Dou, S. X. Core–shell structured silicon nanoparticles@TiO2—carbon mesoporous microfiber composite as a safe and high-performance lithium-ion battery anode. *ACS Nano* **2014**, *8*, 2977–2985.

(41) Jeong, G.; Kim, J.-G.; Park, M.-S.; Seo, M.; Hwang, S. M.; Kim, Y.-U.; Kim, J.-H.; Dou, S. X. Core–shell structured silicon nanoparticles@TiO2—carbon mesoporous microfiber composite as anode material. *Adv. Mater.* **2014**, *26*, 1943–1949.

(42) Hardin, W. G.; Slanac, D. A.; Wang, X.; Dai, S.; Johnston, K. P.; Stevenson, K. J. Highly active, nonprecious metal perovskite electrocatalysts for bifunctional metal–air battery electrodes. *J. Phys. Chem. Lett.* **2013**, *4*, 1254–1259.

(43) Xu, T.; Lin, N.; Cai, W.; Yi, Z.; Zhou, J.; Han, Y.; Zhu, Y.; Qian, Y. Stabilizing Si/graphite composites with Cu and in situ synthesized carbon nanotubes for high-performance Li-ion battery anodes. *Inorg. Chem. Front.* **2018**, *5*, 1463–1469.

(44) Wang, P.; Li, X.; Wu, G. Petal-like Li4Ti5O12−TiO2 nanosheets as high-performance anode materials for Li-ion batteries. *Nanoscale* **2013**, *5*, 6936–6943.

(45) Yang, S.; Feng, X.; Zhi, L.; Cao, Q.; Maier, J.; Müllen, K. Nanographene-constructed hollow carbon spheres and their favorable electroactivity with respect to lithium storage. *Adv. Mater.* **2010**, *22*, 838–842.

(46) Guo, H.; Zhang, Y.; Marschilok, A. C.; Takeuchi, K. J.; Takeuchi, E. S.; Liu, P. A first principles study of spinel ZnFe2O4 for electrode materials in lithium-ion batteries. *Phys. Chem. Chem. Phys.* **2017**, *19*, 26322–26329.

(47) Cama, C. A.; Pelliccione, C. J.; Brady, A. B.; Li, J.; Stach, E. A.; Ljung, K.; Menna, J. Photocatalytic conversion of Cu 2+/Cu0 and Fe 3+/Fe0 interconversions observed upon electrochemical insertion of Li into NiFe2O4 ferrite and zinc aluminate. *ACS Appl. Mater. Interfaces* **2018**, *10*, 39832–39839.

(48) Reddy, G. K.; Boolchand, P.; Smržnits, P. G. Unexpected behavior of Copper in Modified Ferrites during High Temperature WGS Reaction-Apects of Fe3+-Fe2+ Redox Chemistry from Mössbauer and XPS Studies. *J. Phys. Chem. C* **2012**, *116*, 11019–11031.

(49) Nyutu, E. K.; Conner, W. C.; Auerbach, S. M.; Chen, C.-H.; Su, B. L. Ultrasonic nozzle spray in situ mixing and microwave-assisted preparation of nanocrystalline spinel metal oxides: nickel ferrite and zinc aluminate. *J. Phys. Chem. C* **2008**, *112*, 1407–1414.

(50) Arunachalam, P.; Nagarani, S.; Prasad, S.; AlSáhi, M. S.; Al-Mayouf, A. M.; Moyoode, M.; Ganapathy, S. Facile coprecipitation synthesis of nickel doped copper oxide nanocomposites as electrocatalyst for methanol electrooxidation in alkaline solution. *Mater. Res. Express* **2018**, *5*, No. 015152.

(51) Langmuir, I. The adsorption of gases on plane surfaces of glass, mica and platinum. *J. Am. Chem. Soc.* **1919**, *40*, 1361–1403.

(52) Khan, N. A.; Hasan, Z.; Jhung, S. H. Adsorptive removal of hazardous materials using metal-organic frameworks (MOFs): a review. *J. Hazard. Mater.* **2013**, *234-235*, 444–456.

(53) Ren, S.; Sun, P.; Wu, A.; Sun, N.; Sun, L.; Dong, B.; Zheng, L. Ultra-fast self-healing PVA organogels based on dynamic covalent chemistry for dye selective adsorption. *New J. Chem.* **2019**, *43*, 7701–7707.
(71) Huo, S.-H.; Yan, X.-P. Metal–organic framework MIL-100 (Fe) for the adsorption of malachite green from aqueous solution. J. Mater. Chem. 2012, 22, 7449–7455.

(72) Tanhaei, M.; Mahjoub, A. R.; Safarifard, V. Sonochemical synthesis of amide-functionalized metal-organic framework/graphene oxide nanocomposite for the adsorption of methylene blue from aqueous solution. Ultrason. Sonochem. 2018, 41, 189–195.

(73) Khan, A. A.; Kumari, S.; Chowdhury, A.; Hussain, S. Phase tuned originated dual properties of cobalt sulfide nanostructures as photocatalyst and adsorbent for removal of dye pollutants. ACS Appl. Nano Mater. 2018, 1, 3474–3485.

(74) Tran, H. N.; Wang, Y.-F.; You, S.-J.; Chao, H.-P. Insights into the mechanism of cationic dye adsorption on activated charcoal: the importance of $\pi-\pi$ interactions. Process Saf. Environ. Prot. 2017, 107, 168–180.

(75) Wang, G.-Y.; Song, C.; Kong, D.-M.; Ruan, W.-J.; Chang, Z.; Li, Y. Two luminescent metal–organic frameworks for the sensing of nitroaromatic explosives and DNA strands. J. Mater. Chem. A 2014, 2, 2213–2220.

(76) Zheng, B.; Bai, J.; Duan, J.; Wojtas, L.; Zaworotko, M. J. Enhanced CO$_2$ binding affinity of a high-uptake rht-type metal–organic framework decorated with acylamide groups. J. Am. Chem. Soc. 2011, 133, 748–751.

(77) Karan, C. K.; Bhattacharjee, M. Self-Healing and Moldable Metallogels as the Recyclable Materials for Selective Dye Adsorption and Separation. ACS Appl. Mater. Interfaces 2016, 8, 5526–5535.