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Lamellar supramolecular materials based on a chelated metal complex for organic dye adsorption†

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Poisonous industrial wastes have become the major threat to people's health. Recycling these components and making them into useful materials is needed urgently. We report that with the assistance of dodecylamine (DA), the chelating metal pollutant Cu-EDTA can be made into the lamellar Cu-EDTA@2DA supramolecular material. Since Cu-EDTA is notorious for its highly solubility and stability in water, this work for the first time showed that it can be made into supramolecular material which precipitated out from water. Furthermore, this Cu-EDTA@2DA supramolecular material shows excellent efficiency in adsorbing organic dyes, and can be recycled upon desorption of dyes in *N,N*-dimethylformamide (DMF). As far as we know, this is the first case of using industrial waste to build well-defined useful supramolecular materials. We expect that the strategy of 'fight poison with poison' can be an effective and economic approach to treat environmental pollution.

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Introduction

Molecular self-assembly has become a very efficient approach to construct various functional materials,^{1–5} among which novel building blocks^{6–10} play crucial roles in the formation of diverse self-assembled structures, and considerable attention has been paid to synthetic chemistry or supramolecular chemistry to create desired self-assembled materials.^{1,4,11,12} However, so far little effort has been made to employ industrial waste in the fabrication of molecular self-assemblies. It is well-known that there are many chemicals in industrial waste water and most of them jeopardize and threaten the safety of ecological systems and the health of human beings due to serious environmental pollution.^{13–16} Therefore, building self-assembled materials using industrial wastes is highly desired both from the view of environmental protection and recycle of chemicals.

Among various industrial wastes and pollutants, heavy metals jeopardize serious damage to people's health. Usually, precipitation method can effectively remove free metal ions from water,^{14,17} but those in chelating states, are hardly be precipitated^{14,18} and are not biodegradable so that can accumulate in living organisms to exert permanent harm to human

beings.^{19,20} It is so difficult to remove chelating metals from water that many countries and areas have to forbidden the use of metal plating technique, where solution containing ethylenediaminetetraacetate (EDTA), or other chelating agents were used to wash the final product to remove the excess metal ions by the formation of metal-EDTA chelating complexes.^{18,21} Therefore, building self-assembled materials using chelating metal complexes not only can help to solve environmental pollution, but also an issue to save the metal plating industry.

Herein we report that upon employment the strategy of molecular self-assembly, the Cu-EDTA chelating complexes can be made into lamellar supramolecular materials which precipitate out of water. In our strategy, dodecylamine (DA) was employed to bind with Cu-EDTA to form the Cu-EDTA@2DA supramolecules, which further self-assemble into giant lamellar structure and precipitate out of water. It is striking that this Cu-EDTA@2DA supramolecular material displays very high efficiency to adsorb organic dyes. Since organic dyes are a family of robust environmental pollutant which display toxicity and carcinogenic effect for aquatic organisms,²² a lot of efforts were made specifically to remove them from water. To this end, various supramolecular systems have been designed.^{23–26} In contrast to literature results, our work for the first time demonstrates the success of building dye adsorbents with the self-assembled materials based on chelating metal complexes, which on their own are notorious pollutants. Most significantly, the dyes can be desorbed from the Cu-EDTA@2DA supramolecular material simply by immersion into *N,N*-dimethylformamide (DMF), which manifests that both the Cu-EDTA@2DA supramolecular material and the dyes can be

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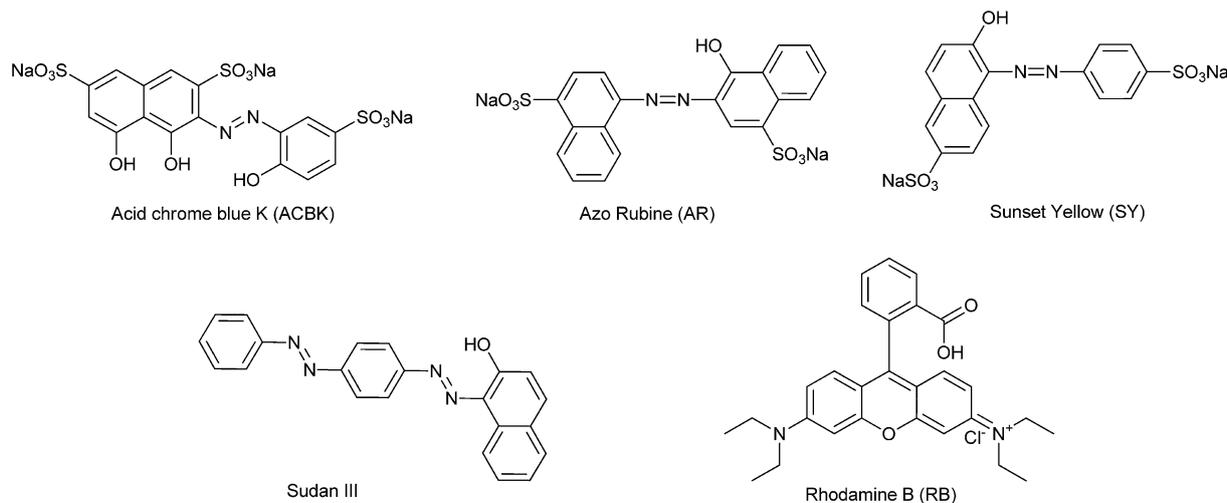


Fig. 1 Chemical structure of different dyes.

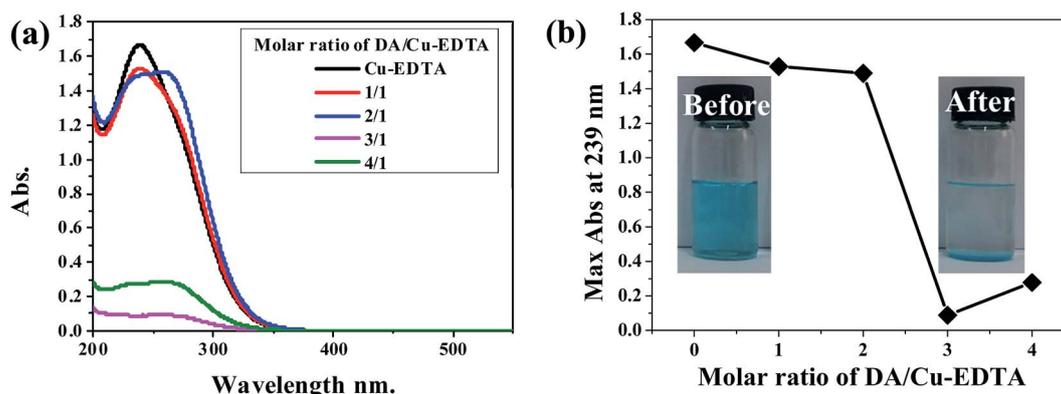


Fig. 2 (a) Change of the absorption spectra with increasing the molar ratio of DA/Cu-EDTA; (b) variation of the maximum absorbance at 239 nm with the molar ratio of DA/Cu-EDTA. The inset is the photo for the samples before and after addition of DA.

recycled. We expect that this work may open a new vista for the practical application of molecular self-assembly technique.

Materials and methods

Materials

Dodecylamine (DA) was from SCRC, ethylenediaminetetraacetate acid disodium salt (EDTA-2Na) and copper(II) chloride hydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) were from Beijing Chemical Company. Acid chrome blue K (ACBK) was purchased from SCRC. Azo Rubine (AR) and Sunset Yellow (SY) were from TCI. Sudan III and Rhodamine B (RB) were from Beijing Chemical Company. The chemical structures of the dyes are shown in Fig. 1. All chemicals were of A.R. grade and were used as received.

Preparation of layered materials

The supramolecular materials of Cu-EDTA@2DA were prepared as follow: 0.3724 g of $\text{Na}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$, 0.1704 g of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and 0.5550 g of dodecylamine were dissolved in 67 g of water.

The resulting mixture was stirred at 45 °C for 2 h and finally left at room temperature. After 48 h, blue precipitates were found at the bottom of the Erlenmeyer flask. The precipitates were separated, washed with distilled water for several times, and dried in the vacuum oven at room temperature for 24 h for further analysis.

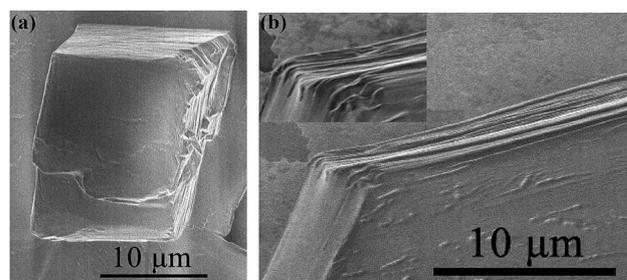


Fig. 3 SEM image of the precipitates formed with Cu-EDTA and DA. (a) shows the image of the precipitates observed on a horizontal silicon wafer, while (b) is the image obtained by tilting the silicon wafer to 45°.

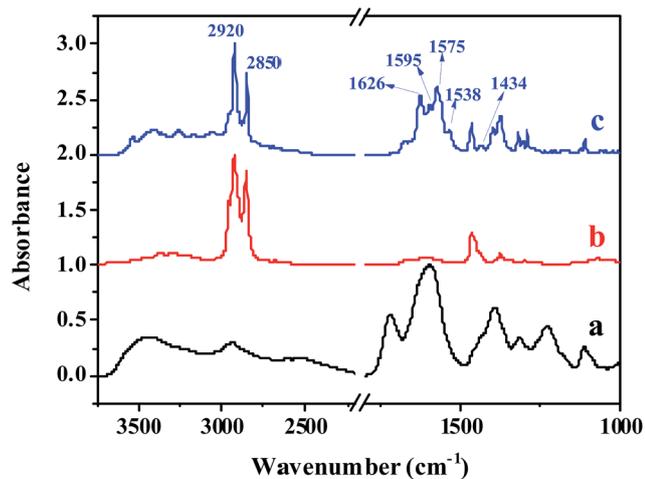


Fig. 4 FT-IR spectra of (a) Cu-EDTA, (b) DA and (c) Cu-EDTA@2DA supramolecular materials.

Characterization

Scanning electron microscopy (SEM) measurements were made on Hitachi S4800 operated at 10 kV. Elemental analysis was carried out with the Elementar Vario MICRO CUBE (Germany). Powder X-ray diffraction (XRD) patterns were measured using a Rigaku Dmax-2400 diffractometer with Cu K α radiation. Ultraviolet-visible (UV-vis) spectral measurements were performed on a Shimadzu UV-1800 spectrophotometer. The concentration of Cu²⁺ in liquid phase was determined by Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES) (PROFILE SPEC, Leeman). Fourier transform infrared (FT-IR) spectra were recorded with a Bruker Vector-22 spectrophotometer. For FT-IR measurements, the dry powders of the Cu-EDTA@2DA samples were pressed onto the KBr pellet. X-ray photoelectron spectroscopy (XPS) spectra were recorded on an AXIS-Ultra Imaging Photoelectron Spectrometer from Kratos Analytical Ltd, using monochromatic Al-K α radiation in a vacuum of 2×10^{-8} Pa. Zeta potentials were obtained with a temperature-controlled ZetaPALS Zeta Potential Analyzer.

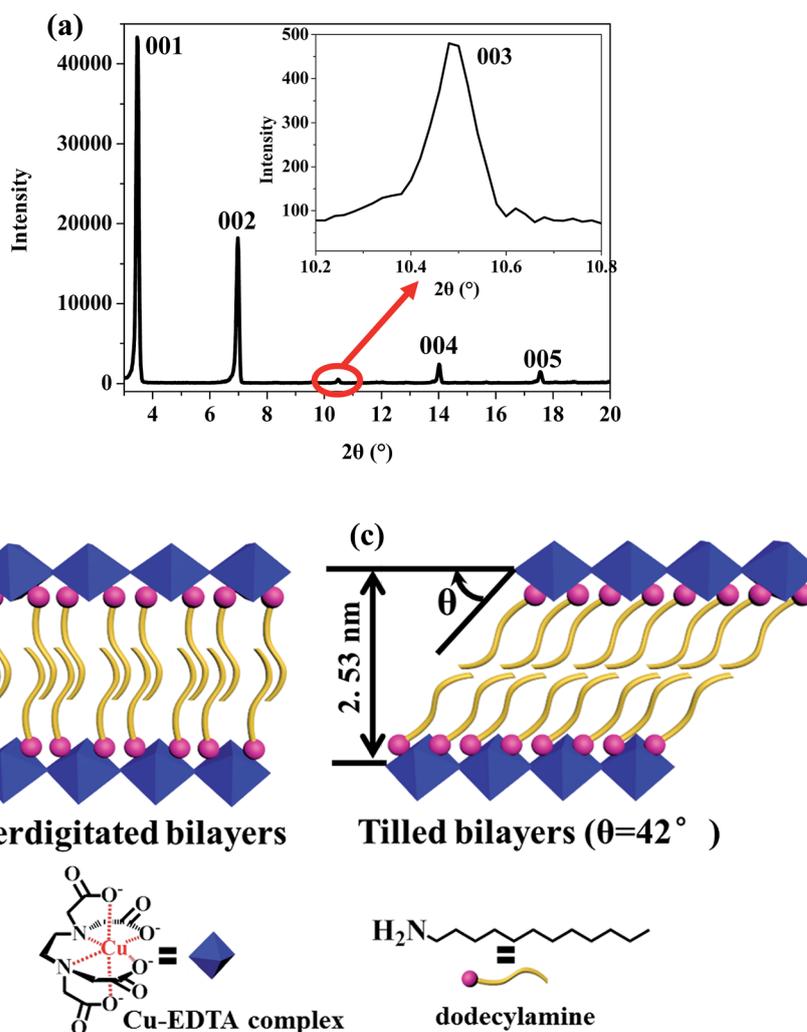


Fig. 5 (a) XRD patterns of the supramolecular material of Cu-EDTA@2DA. (b) and (c) are the schematic illustration of the possible molecular packing in the lamellar material of Cu-EDTA@2DA.

Adsorption experiments

Adsorption of dye from aqueous solutions was examined with UV-vis spectrophotometer. A standard work curve of dyes was obtained firstly, and the removal efficiency of dyes can be calculated according to the following equation:

$$RE = \frac{C_0 - C_e}{C_0} \times 100\%$$

where C_0 and C_e are the initial and equilibrium dye concentrations (mg L^{-1}), respectively.

Results and discussion

Cu-EDTA is one of the notorious industrial wastes produced in copper-splating industry, since it is very stable in water and can hardly be precipitated. However, we found that upon addition of DA into the aqueous solution of Cu-EDTA, blue precipitates occur immediately. Fig. 2 shows the drop of the UV-vis absorption of the solution with varying the ratio between Cu-EDTA and DA. The absorption decreases to the minimum at the DA/Cu-EDTA molar ratio of 3/1. ICP measurements suggested that around 64% Cu-EDTA have been precipitated.

Amazingly, SEM observation (Fig. 3) revealed that the blue precipitates are perfect lamellar materials. FT-IR measurements (Fig. 4) suggested the coexisting of EDTA and DA in the precipitates. It is clear in Fig. 4 that the characteristic vibration features for both EDTA and DA are observed in the precipitates. Detailed analysis of the FT-IR spectra can be found in the

following text. Meanwhile, the ratio of Cu-EDTA : DA was found to be 1 : 2 with elemental analysis. This means that every Cu-EDTA chelating complex bind with two DA molecules to form the Cu-ETDA@2DA supramolecule in the lamellar materials. XRD measurements in Fig. 5a display sharp peaks featuring the 001, 002, 003, 004, and 005 diffractions. The distance corresponding to the 001 diffraction is 2.53 nm, which is in between one and two folds of the extending length of DA (1.9 nm),²⁸ suggesting the presence of highly ordered interdigitated bilayers of DA (ref. 28–30) or tilted DA bilayers with the tilting angle of 42° ,^{31–34} as illustrated in Fig. 5b and c. The presence of DA bilayers can also be inferred from the FT-IR spectra in Fig. 4, supported by the two strong sharp bands at 2850 and 2920 cm^{-1} , which features the symmetric and asymmetric vibration of the highly ordered alkyl chains in DA.^{42,43} This means that the formation of the lamellar structure is driven by the hydrophobic effect of the Cu-ETDA@2DA supramolecule, which behaves just as conventional amphiphiles. It is possible that double tail structure of Cu-ETDA@2DA allows the packing parameter close to 1, so that they self-assemble into lamellar structures.²⁷

The formation of perfect supramolecular materials of Cu-EDTA@2DA which can precipitates from water is very amazing. On the one hand, so far it still remains challenging to precipitate Cu-EDTA from water, since they are very stable against strong base, acid, and oxidant. A lot of cost efforts were made to liberate copper from its complex with EDTA.^{35–38} However, our work shows that upon using the strategy of

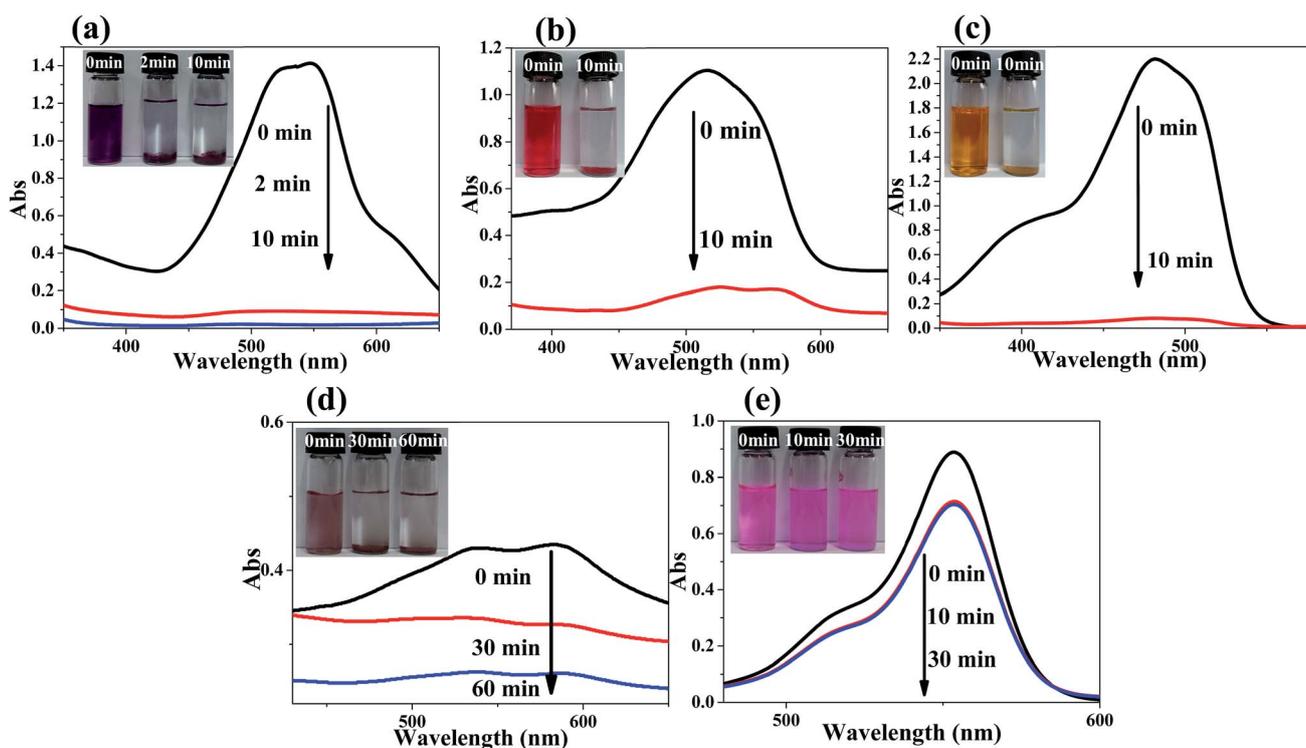


Fig. 6 Absorption spectra of (a) ACBK, (b) AR, (c) SY, (d) Sudan III, and (e) RB solutions in the presence of 5 mg supramolecular material of Cu-EDTA@2DA at different time intervals. The volume for the dye solutions are all 5 mL, and the concentration of the dyes are all 50 mg L^{-1} . pH for all the system are kept at 8.1 room temperature.

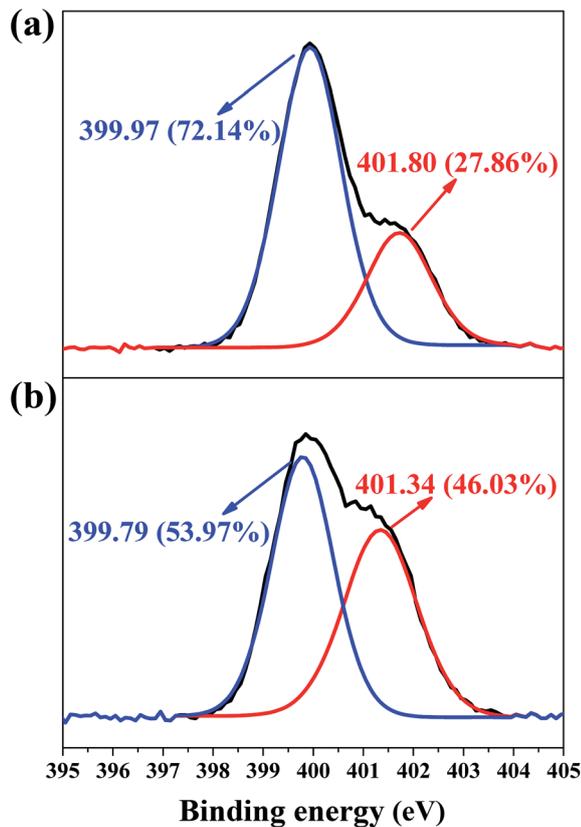


Fig. 7 XPS measurements for N1s electrons of (a) Cu-EDTA and (b) Cu-EDTA@2DA supramolecular materials.

supramolecular self-assembly, the Cu-EDTA complex can be precipitated as a whole from water, which greatly lowered the energy cost and made it possible to put into practical applications in water treatment. On the other hand, the presence of alternative hydrophilic and hydrophobic domains in the perfect lamellar precipitates of Cu-EDTA@2DA enabled them being adsorbents for a number of organic pollutants. Fig. 6a–c shows that the UV-vis absorption of three anionic dyes, Acid Chrome Blue K (ACBK), Azo Rubine (AR), and Sunset Yellow (SY), reduced drastically upon addition of the layered materials. Similarly, the UV-vis absorption of charge neutral dyes, such as Sudan III, was also found declined slowly with addition of the Cu-EDTA@2DA layered material (Fig. 6d), which indicated that the layered material was capable of removing oil-soluble dyes, too. However, the material shows negligible adsorption toward cationic dyes, such as Rhodamine B (RB), (Fig. 6e). This means that the absorption of these ionic dyes is mainly *via* electrostatic and hydrophobic interaction.

Indeed, zeta potential measurements revealed the surface electrical potential for the blue precipitates being 20.1 ± 2 mV. FT-IR measurements (Fig. 4) suggest that the positive charge is originated from the $-\text{NH}_3^+$ group, which can be verified by the asymmetric and symmetric deflection of $-\text{NH}_3^+$ groups at 1626 cm^{-1} and 1538 cm^{-1} in the FT-IR spectra.^{32,39} Meanwhile, there are also weak bands at 1597 cm^{-1} in the FT-IR spectra, which belongs to the bending motion of $-\text{NH}_2$ group.^{32,40} The

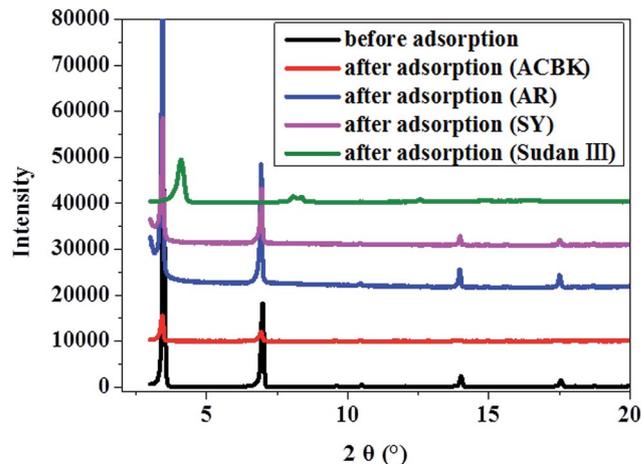


Fig. 8 XRD patterns for the supramolecular materials of Cu-EDTA@2DA before and after the adsorption of various dyes.

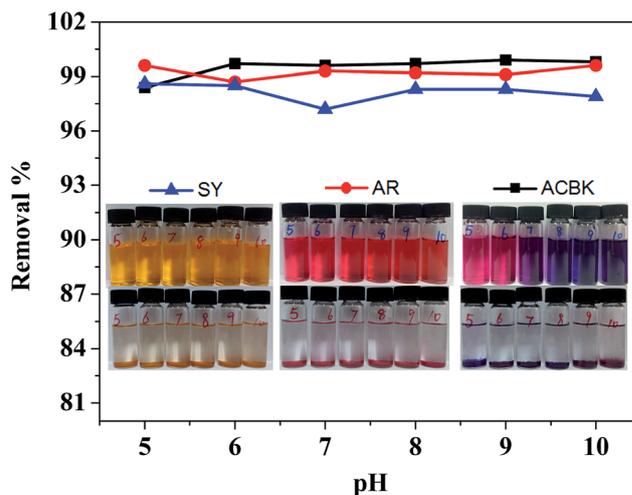


Fig. 9 Influence of pH on the dye removal efficiency. Inset are the photos of the solution with dyes before (upper) and after adsorption with Cu-EDTA@2DA. The numbers on the bottles are the pH of the system.

coexistence of $-\text{NH}_3^+$ and $-\text{NH}_2$ groups was further verified with the XPS measurement. As is shown in Fig. 7, both Cu-EDTA and Cu-EDTA@2DA displays two peaks around 399.7 and 401.4 eV, which are the N1s energy corresponding to $-\text{NH}_2$ and $-\text{NH}_3^+$,^{32,41} respectively. However, it is noticed that in the Cu-EDTA@2DA system, the fraction of $-\text{NH}_3^+$ is 46.03%, which is significantly higher than the fraction of 27% for the free Cu-EDTA. This means that the binding of DA to the Cu-EDTA coordinating complex have produced more cationic charges, which generates electrostatic attraction to remove anionic dyes from water. As to the removal of charge neutral dyes, it can be attributed to the solvation of the dyes in the hydrophobic domains formed by the long alkyl chains of DA.

The adsorption of dyes didn't change the layer spacing after adsorption of the anionic dyes ACBK, AR and SY (Fig. 8),

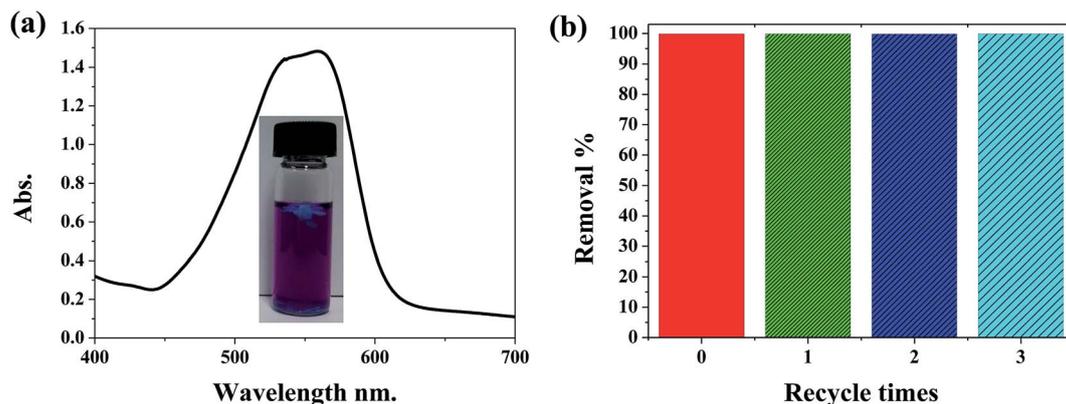


Fig. 10 (a) UV spectra of ACBK-Cu-EDTA@2DA supramolecular materials after adsorption in DMF. (b) The removal efficiency of ACBK after adsorption with the regenerated Cu-EDTA@2DA supramolecular materials. Adsorption condition: 50 mg regenerated Cu-EDTA@2DA supramolecular materials, 5 mL 50 mg L⁻¹ ACBK solution, room temperature.

suggesting the presence of large separations between the two adjacent bilayers which is probably required by the repulsive forces between them. Upon adsorption of negatively charged dyes, the dyes can just be hosted in between the bilayer spacing. However, as to the adsorption of neutral dye Sudan III, the dye molecules have to squeeze into the bilayers, so that the bilayer has to rearrange to form close stacking. As a result, the inter-layer spacing decreased from 2.53 nm to 2.29 nm after adsorption of Sudan III (Fig. 8).

Significantly, the Cu-EDTA@2DA supramolecular materials display broad pH windows for the dye removal. Fig. 9 shows that the removal efficiency for these dyes is hardly affected by changing pH in the pH range of 5–10, suggesting they are indeed potent adsorbing materials that can be used in wide range of industrial polluted water system.

Regeneration of the adsorbent is an important factor in practical application, especially in the ‘green’ protocol of pollution treatment. Desorption of the dyes can be achieved by addition of DMF to the dye-saturated precipitates. Fig. 10a shows that upon addition of DMF to the dark purple ACBK/Cu-EDT@2DA precipitates, the supernatant becomes purple and the precipitate recover its original blue color. Most interestingly, this blue precipitate display a high adsorption efficiency of over 99% even after three cycles (Fig. 10b), which indicates that the layered materials could be regenerated. Similarly, other dyes, such as AR, SY, and Sudan III were also find desorbed from the Cu-EDT@2DA in DMF. It is should be mentioned that there are also release of Cu-EDTA to the water as the dyes were adsorbed by the Cu-EDTA@2DA lamellar materials, and the releasing rate is about 36% determined with (ICP-AES). However, this released Cu-EDTA can be further precipitated cooperatively by addition of a cationic polyelectrolyte polyethyleneamine (PEI) and sodium dodecyl sulphate (SDS), and the final copper concentration can be lowered to 1.79 mg L⁻¹. Systematic analysis will be reported in a forthcoming work.

Conclusion

The water pollutant industrial waste Cu-EDTA can be employed to form supramolecular materials with the assistance of dodecylamine (DA) in the form of lamellar precipitates. This lamellar material has both positive charges and hydrophobic domains which are capable of adsorb both anionic and neutral organic dyes. The adsorbed dyes can be desorbed in DMF. In this way, both the dyes and the Cu-EDTA@2DA supramolecular materials can be recycled. This work for the first time realized the precipitation of Cu-EDTA as a supramolecular material, which demonstrated an economic strategy of ‘Fight poison with poison’ in the field of environmental science.

Acknowledgements

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