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# Self-assembly of biosurfactant–inorganic hybrid nanoflowers as efficient catalysts for degradation of cationic dyes†

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Three-dimensional (3D) hierarchical nanostructures have generated a large amount of interest because of their unique, unusual properties and potential applications. In this article, copper(II) ions as the inorganic component and various biosurfactants as the organic component were used to successfully form 3D nanoflowers via a facile and effective self-assembly template synthesis strategy. It can be confirmed that the biosurfactant molecules can first form complexes with the copper ions, and these complexes then become nucleation sites for primary crystals of copper phosphate, indicating that the interaction between biosurfactant and copper ions leads to the formation of 3D nanoflowers. Several reaction parameters such as aging time and the concentration of the biosurfactant, which play a critical role in the formation process and morphologies of the nanoflowers, were investigated. Under the optimum synthetic conditions, a spherical flowerlike structure with hundreds of nanopetals was obtained. Moreover, the biosurfactant– $\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$  nanoflowers also showed high stability and catalytic activity for degradation of cationic dyes. Our results demonstrate that the biosurfactant–inorganic 3D nanoflowers, which combined the advantages of the biosurfactant and inorganic material, have potential applications in industrial biocatalysis, biosensors, and environmental chemistry.

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## Introduction

Nano-structured materials have attracted increasing attention in recent years and great contributions have been made in the morphology-controlled synthesis of micro- and nano-scale structures, such as nanodendrites, core/shell nanoparticles, nanowires, and nanoflowers.<sup>1–5</sup> Among them, “nanoflower” is a fantastic name for some of the nanomaterials whose microscopic images resemble flowers. A variety of materials such as carbon,<sup>6–8</sup> metals and other elemental materials,<sup>9–11</sup> alloys,<sup>12,13</sup> and metaloxides/hydroxides<sup>14</sup> have been widely reported to form flower-like structure.<sup>15,16</sup> Due to the large surface-to-volume ratio compared with that of bulk materials, these nanoflowers have many applications in catalysis, magnetism, nanodevices, sensing and biosensing and medicine.<sup>17–24</sup> But

nanoflowers are traditionally synthesized under harsh conditions such as high temperature, pressure and the use of toxic organic solvents. Thus, it is still a challenge to explore a low cost and facile synthetic method for the preparation of hierarchical nanoflowers.

Gratifyingly, self-assembly can spontaneously combine different components together to form different kinds of hybrid materials,<sup>25</sup> while the template synthesis is an effective approach to synthesize nanomaterials with various morphologies.<sup>26</sup> Thus, a self-assembled template synthesis provides a facile and effective low temperature synthetic strategy for the fabrication of well-defined nanoflowers. Especially, the bio-inspired materials with micro- and nano-scale have been proposed as a big breakthrough on the design of functional materials due to the huge advantage of the bio-molecules in directing and assembling the nanoflowers.<sup>27–30</sup> Various bio-molecules, such as enzyme,<sup>31–36</sup> protein,<sup>37</sup> amino acids<sup>38</sup> have been applied to synthesis nanoflower. For example, Zare's group reported the novel synthesis of hybrid nanoflowers comprising of  $\text{Cu}_3(\text{PO}_4)_2$  and proteins for the first time and they also synthesized immobilized enzymes with greatly enhanced activities.<sup>39</sup> Subsequently, using the same synthetic route, Wang *et al.* prepared  $\text{CaHPO}_4$ - $\alpha$ -amylase nanoflowers and they also further elaborated the mechanism for enhanced catalytic activity of immobilized enzyme.<sup>40</sup> Although biodegradable amphiphilic molecules have been widely used in the fabrication of

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nanomaterials<sup>41,42</sup> and self-assembly process assisted by amphiphilic molecules can provide a powerful low temperature tool for the synthesis of hierarchical structures,<sup>43</sup> the usage of bio-surfactants in the fabrication of nanoflower has not been reported so frequently.

In this paper, a facile and effective self-assembled template synthesis strategy for shape controlled synthesis of three-dimensional (3D) flower-like  $\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$  microstructures were provided using copper(II) ions as the inorganic component and various biosurfactants as the organic component. The hybrid nanoflowers were fully characterized by transmission electron microscopy (TEM), field emission scanning electron microscopy (FE-SEM), Fourier transform infrared (FT-IR) spectroscopy and X-ray diffraction (XRD). Different growth stages and concentration of biosurfactants on the effect of the morphologies of hybrid nanoflowers were intensively identified and studied. The synthesized biosurfactant- $\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$  hybrid nanoflowers exhibited high stability and catalytic activity for degradation of cationic dyes. Moreover, the catalyst for MB can be recycled and reused at least six cycles with only a slight dropping of catalytic efficiency, suggesting their promising applications in the treatment of waste water.

## Experimental

### Reagents and materials

Sodium cholate (SC), sodium deoxycholate (SDC), sodium dihydrogen phosphate ( $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ ) and disodium phosphate dodecahydrate ( $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ ) were obtained from Sinopharm Chemical Reagent, Co., Ltd (Shanghai, China). Copper sulfate pentahydrate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) was purchased from Fuchen Chemical Reagent Factory (Tianjin, China). Polypeptide GG-4 were the products of GL Biochem, Co., Ltd (Shanghai, China) and Meilunbio, Co., Ltd (Dalian, China), respectively. Rhodamine B (RhB), rhodamine 6G (R6G) and methylene blue (MB) were purchased from Kermel Chemical Reagent, Co., Ltd (Tianjin, China). The structures of SC, SDC, GG-4 and RhB, R6G, MB were shown in Fig. S1†. All other chemicals were of analytical grade or better. Ultrapure water with a resistivity of 18.25 MΩ cm was obtained using a UPH-IV ultrapure water purifier (China).

### Synthesis of biosurfactant-inorganic nanoflowers

Biosurfactant- $\text{Cu}_3(\text{PO}_4)_2$  nanoflowers were synthesized similar to the previous literature.<sup>25</sup> Briefly, 20 μL of aqueous  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  solution (120 mM) was added into 3 mL of phosphate buffered saline (PBS) solution (2 mM, pH 7.4) with different concentrations of biosurfactants. The solution was incubation at room temperature for 72 h and the obtained blue products were washed with water for three times, centrifuged at 7000 rpm for 5 min and then dried at room temperature.

### Characterization of biosurfactant-inorganic nanoflowers

Transmission electron microscopy (TEM) observations were carried out on a JEM-100 CXII (JEOL) at an accelerating voltage of 80 kV. For sample preparation, the obtained powder was

placed on a ultrathin carbon-coated copper grid and the excess powder was wicked away with filter paper, which was then dried by using a near infrared reflection (NIR) lamp before observations. Field-emission scanning electron microscopy (FE-SEM) observations were carried out on SU8010 (HATACHI), a drop of wet powder was placed on a silica wafer to form a thin film then dried by using NIR lamp. Energy-Dispersive X-ray Spectroscopy (EDS) analysis and elemental mapping were also performed on the same FE-SEM microscope. FT-IR spectra were recorded 4000 to 400  $\text{cm}^{-1}$  on a VERTEX-70/70v spectrometer (Bruker Optics, Germany). The samples for FT-IR spectra were prepared by using KBr pellets mixed with the powder we obtained. XRD patterns of the samples were obtained between 10 and 90 in the  $2\theta$  scan mode ( $2.5 \text{ min}^{-1}$ ) using a Rigaku D/Max 2200 PC diffractometer with Cu Kα radiation ( $\lambda = 0.15418 \text{ nm}$ ) and a graphite monochromator at room temperature. UV-vis measurements were carried out on a computer manipulated spectrometer (UV-vis 4100, Hitachi, Japan).

### Degradation of cationic dyes

Three cationic dyes RhB, R6G and MB were chosen as samples to investigate the catalytic activity of our nanoflowers for degradation of cationic dyes by  $\text{H}_2\text{O}_2$ . The initial concentration of dye solutions were  $12.5 \mu\text{g mL}^{-1}$ , concentration of dye solutions during degradation were detected by UV-vis measurements. The degradation rates were calculated using the following equation:

$$\text{DR} = \frac{C_0 - C_t}{C_0} \times 100\%$$

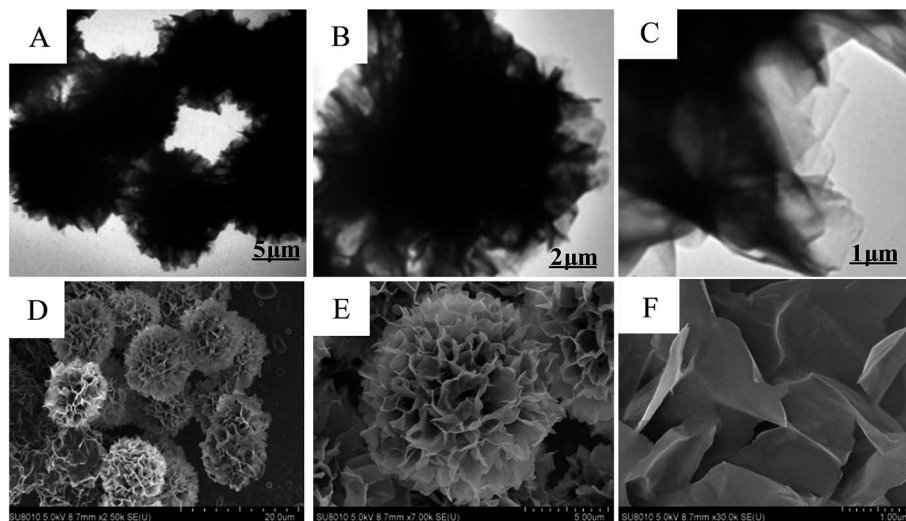
where  $C_0$  and  $C_t$  are initial concentration and concentration at time  $t$ .

## Results and discussion

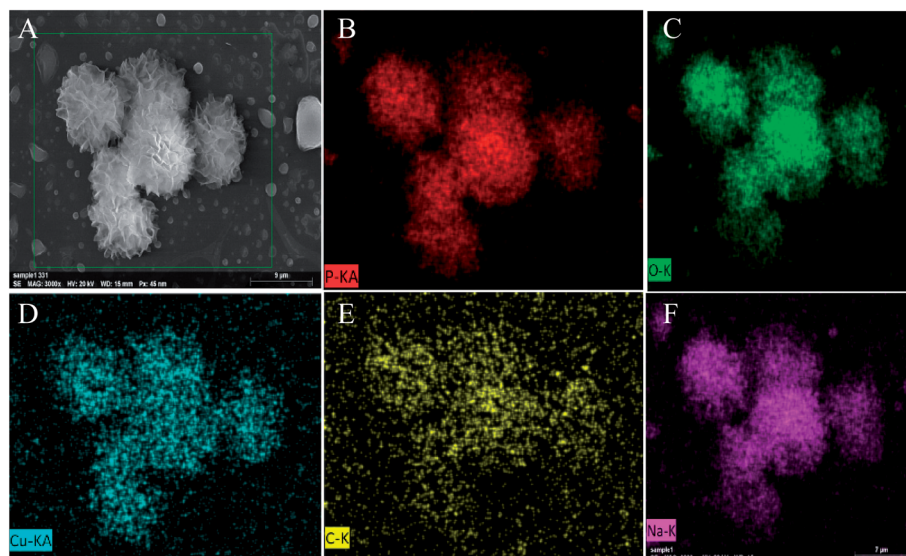
### Microstructures of biosurfactant-inorganic nanoflowers

Xie's group have reported the biomolecule-assisted synthesis of  $\text{Bi}_2\text{S}_3$  flowerlike patterns which need a relatively high reaction temperature ( $150^\circ\text{C}$ ).<sup>44</sup> However, in our experiment, the biosurfactant-inorganic nanoflowers were prepared by a facile and efficient low temperature (at room temperature) process by using  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  as the precursor, and biosurfactants as the assistant of the formation of 3D flower-like microstructures. To validate our design, SC- $\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$  nanoflowers were firstly prepared. Blue precipitates were formed after 3 days incubation and TEM images shows that the nanoflower morphologies were formed (Fig. 1A–C). SEM images further confirmed the flower-like morphology (Fig. 1D–F) and it can be observed that the samples consist of large quantities of flower-like nanostructures with diameters in the range of 15–30 μm which possess high surface-to-volume ratios and have good monodispersity. Subsequently, the elemental mapping (Fig. 2) and EDS pattern (Fig. S2†) further confirm that C, Na, Cu, P and O elements are homogeneously distributed inside the nanoflowers which gave a proof that the nanoflowers obtained were complex of SC and  $\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ . When SC was replaced by





**Fig. 1** The detailed characterizations of SC- $\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$  nanoflowers ( $0.1 \text{ mg mL}^{-1}$  SC). TEM image of (A) hybrid nanoflowers, (B) a local partial enlarged image of (A), and (C) nanopetals (a local partial enlarged image of (B)). SEM images of (D) hybrid nanoflowers, (E) single nanoflower (a local partial enlarged image of (D)) and (F) nanopetals (a local partial enlarged image of (E)).



**Fig. 2** (A) SEM image of SC- $\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$  nanoflowers. SEM element mapping analyses of nanoflowers: (B) P, (C) O, (D) Cu, (E) C, (F) Na.

other two biosurfactants SDC and GG-4, flower-like microstructures were also been found as shown in Fig. S3 (ESI<sup>†</sup>). We have calculated the surface area and as  $3.20 \text{ m}^2 \text{ g}^{-1}$  and an average pore size of  $3.23 \text{ nm}$  through BET measurement (Fig. S4<sup>†</sup>).

### FT-IR and XRD analysis

FT-IR spectroscopy directly confirms the formation of 3D nanoflowers. In the spectrum of  $\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$  and SC- $\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$  nanoflowers (Fig. 3A), the peaks at  $1054$  and  $1150 \text{ cm}^{-1}$  were attributed to P–O and P=O vibrations,<sup>36</sup> while the bands at  $566$  and  $603 \text{ cm}^{-1}$  were attributed to the bending vibrations of bridging phosphorous such as O=P–O which

indicated the existence of phosphate groups.<sup>35</sup> The weak peak at  $1620 \text{ cm}^{-1}$  came from the crystal water in  $\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ . Compared to the spectrum of  $\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ , the typical bands of SC at  $2800$ – $3000 \text{ cm}^{-1}$  for  $-\text{CH}_2$  and  $-\text{CH}_3$  were also observed in the spectrum of SC- $\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$  nanoflowers, indicating the presence of SC component in the hybrid material. Moreover, the spectrum of hybrid nanoflowers didn't show significant shift of the peaks or any new adsorption peaks, indicating the hybrid nanoflowers formed *via* self-assembly instead of covalent bonding.

XRD analysis (Fig. 3B and the inset) were performed to further confirm the crystallinity of the nanoflowers. It can be seen that the positions and intensities of the diffraction peaks of  $\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$  are consistent with those obtained from the





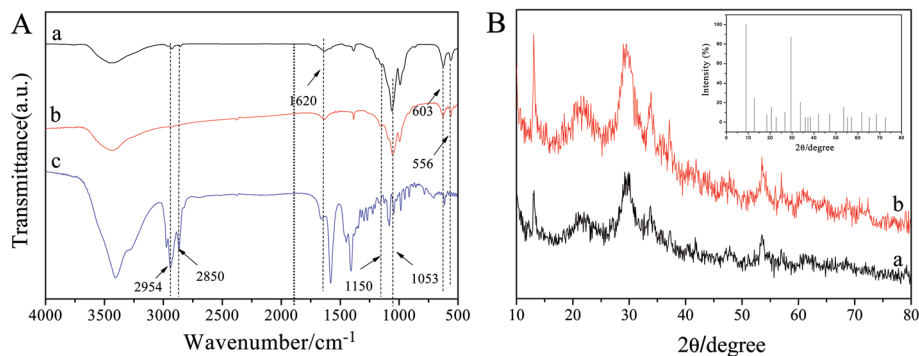


Fig. 3 (A) FT-IR spectra of (a) SC-Cu<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·3H<sub>2</sub>O nanoflowers; (b) Cu<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>; (c) SC; (B) XRD patterns of (a) Cu<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> and (b) SC-Cu<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·3H<sub>2</sub>O nanoflowers, inset is the standard card of Cu<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·3H<sub>2</sub>O (JPSCD00-022-0548).

JCPDS card (00-022-0548). Thus, it can be concluded that even after incorporating SC, the SC-Cu<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·3H<sub>2</sub>O nanoflowers were still well crystallized.<sup>33</sup>

#### Effects of the dosage of SC on the morphologies of SC-Cu<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·3H<sub>2</sub>O nanoflowers

In order to explore the effect of the dosage of biosurfactants on the morphologies of SC-Cu<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·3H<sub>2</sub>O nanoflowers, the concentrations of SC which ranged from 0 to 0.5 mg mL<sup>-1</sup> were first investigated as a sample. As shown in Fig. 4, in the absence of SC, large amorphous crystals of Cu<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·3H<sub>2</sub>O, but no nanoflowers were formed (Fig. 4A<sub>1</sub> and A<sub>2</sub>). However, when SC was added, the flower-like nanostructures emerged. When the concentration of SC was 0.05 mg mL<sup>-1</sup>, there were many slices that resembled the petals of flowers with rough fringes (Fig. 4B<sub>1</sub>). Besides, some nanoflowers with an average size of ~20 μm were also formed in this concentration (Fig. 4B<sub>2</sub>). With the increase of SC concentration from 0.05 to 0.1 mg mL<sup>-1</sup>, the petal-like structure gradually formed flowerlike structure

(Fig. 4C<sub>1</sub> and C<sub>2</sub>), while the average size of the nanoflowers decrease from ~20 μm to ~15 μm when SC concentration increased to 0.5 mg mL<sup>-1</sup> (Fig. 4D<sub>1</sub> and D<sub>2</sub>). The decrease of the average size of the nanoflowers may be attribute to the steric hindrance's enhancement with increase the SC molecules attached to Cu<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·3H<sub>2</sub>O crystal nucleus. The results demonstrated that SC worked as the size- and shape-controlling agent in the synthesis process and the sizes of the nanoflowers were strongly dependent on SC concentration.<sup>33,36</sup>

#### Effects of the growth time on the morphologies of SC-Cu<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·3H<sub>2</sub>O nanoflowers

In order to get more information about the growth mechanism of SC-Cu<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·3H<sub>2</sub>O nanoflowers, the morphologies of the hybrid materials were recorded by SEM images as a function of the growth time of the nanoflowers. The experiments were carried out in identical concentrations but for different incubation time (1, 3, 6, 12 and 15 h) and the SEM images shown in Fig. 4 suggest a progressive process of nanoflower assembly. It

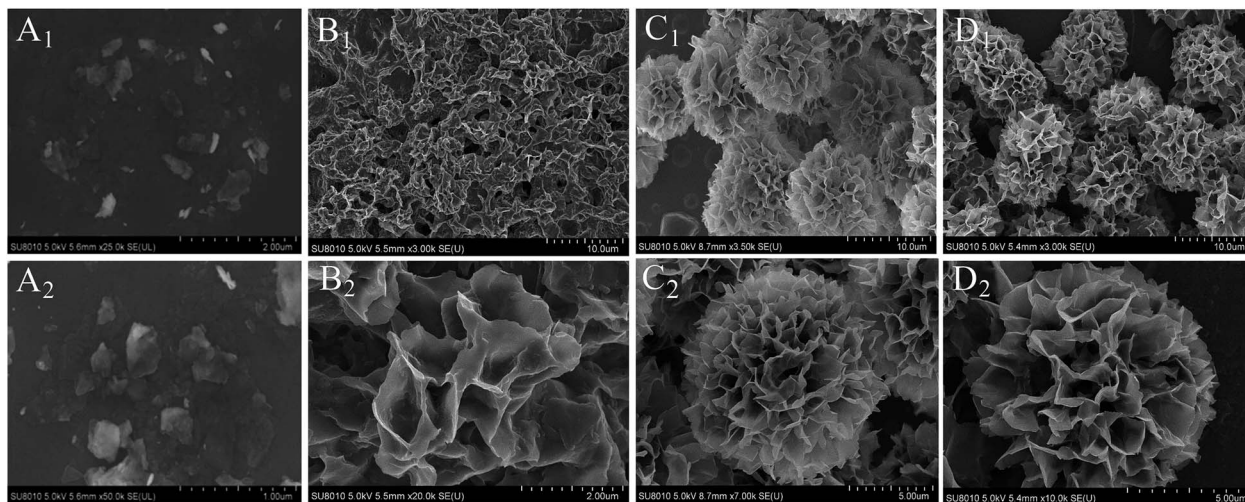


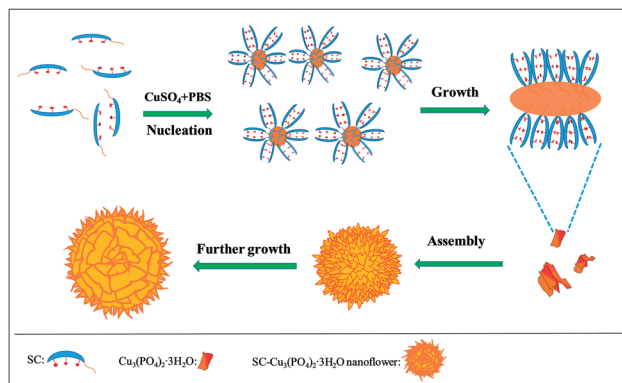
Fig. 4 Effect of different concentrations of SC on the morphologies of SC-Cu<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·3H<sub>2</sub>O nanoflowers hybrid nanoflowers. (A<sub>1</sub>, A<sub>2</sub>) 0 mg mL<sup>-1</sup>; (B<sub>1</sub>, B<sub>2</sub>) 0.05 mg mL<sup>-1</sup>; (C<sub>1</sub>, C<sub>2</sub>) 0.1 mg mL<sup>-1</sup>; (D<sub>1</sub>, D<sub>2</sub>) 0.5 mg mL<sup>-1</sup>. (A<sub>2</sub>, B<sub>2</sub>, C<sub>2</sub> and D<sub>2</sub>) are the local partial enlarged images of (A<sub>1</sub>, B<sub>1</sub>, C<sub>1</sub> and D<sub>1</sub>), respectively. Other conditions: 120 mmol L<sup>-1</sup> Cu<sup>2+</sup>, 0.1 mol L<sup>-1</sup> PBS at pH = 7.4, and reaction for 72 h at 25 °C.



can be observed that the blue precipitates can be obtained as soon as the addition of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  solution to PBS solution which contains SC. At an early growth stage (1 h), both primary crystals of  $\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$  and copper-cholate complexes which formed mainly through coordination between carboxyl groups in the SC backbone and  $\text{Cu}^{2+}$  were appeared.<sup>41–43</sup> Moreover, these complexes can provide a location for nucleation of the primary crystals of  $\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$  (Fig. 5A<sub>1</sub> and A<sub>2</sub>). When the reaction time reached to 3 h (Fig. 5B<sub>1</sub> and B<sub>2</sub>), the copper-cholate complexes combined into large agglomerates. Subsequently, the kinetically controlled growth of  $\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$  crystals occurred on the surface of these agglomerates. As time sequentially increased to 6–12 h, anisotropic growth of these crystals led to the formation of flower-like structure (Fig. 5C<sub>1</sub>, C<sub>2</sub>, D<sub>1</sub> and D<sub>2</sub>). When the reaction time reached 15 h, a branched flower-like structure completely formed (Fig. 5E<sub>1</sub> and E<sub>2</sub>). That is to say, in this growth process, SC induced the nucleation of the  $\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$  crystals to form the scaffold for the petals, and also served as a “glue” to bind the petals together.<sup>33</sup> Based on the experimental results, the formation mechanism of SC- $\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$  flowerlike structures as a function of the growth time was shown in Scheme 1.

### Catalytic behaviors for the degradation of cationic dyes

It's known that copper compound possess intrinsic peroxidase-like activity in the presence of  $\text{H}_2\text{O}_2$ .<sup>44–46</sup> Therefore, the peroxidase-like activities of the copper-cholate complexes in biosurfactant-incorporated nanoflowers were investigated. Three cationic dyes RhB, R6G and MB (structures of the three dyes were shown in Fig. S1†) were chosen to investigate the peroxidase-like activity of SC- $\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$  nanoflowers. Firstly, the concentration of each dye detected by UV-vis absorption at different time points during the degradation process were measured and the results were shown in Fig. 5. It can be seen that a visual color change of cationic dyes solution ( $12.5 \mu\text{g mL}^{-1}$ ) occurred only when  $\text{H}_2\text{O}_2$  and nanoflowers were co-existence which indicated that the SC- $\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$



Scheme 1 The formation mechanism of SC- $\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$  flowerlike structures as a function of the growth time.

nanoflower had degraded all the three dyes dramatically and exhibited excellent catalytic activities for cationic dyes degradation reaction in the presence of  $\text{H}_2\text{O}_2$  (Fig. 6A–C and S5†). The morphology of nanoflower after degradation had also been investigated, as is shown in Fig. S6,† it can be seen that after the degradation of dyes, partial nanoflowers had disaggregated into nanoplates.

Meanwhile, in order to trace the degradation process, the changing concentrations of cationic dyes solutions over time were detected by UV-vis (Fig. S5A–C†). The comparison of degradation rates for different dyes shown in Fig. S5D† revealed that at the first stage (1 h), the degradation rates were MB > RhB > R6G. Subsequently the degradation rate of RhB increased, while MB and R6G were both degraded with a lower speed. In general, R6G had the lowest degradation rate, MB performed the highest degradation speed. The linear fit of the  $\ln(C_t/C_0)$  data reveals that the catalytic reaction exhibits pseudo-first-order kinetics for the degradation of the three dyes (Fig. S7†). The rate constant  $k$  of the oxidation reaction was determined to be 0.89, 0.25 and  $0.22 \text{ h}^{-1}$ , corresponding to MB, RhB and R6G respectively, based on eqn (1) and (2). The degradation rate for the three dyes are MB > RhB > R6G.

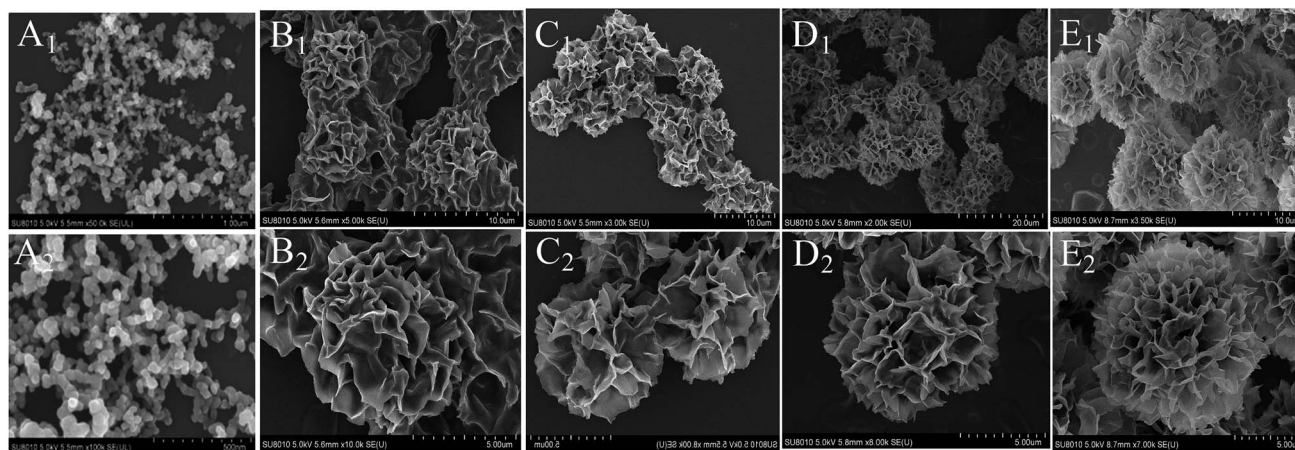


Fig. 5 Effect of different growth time on the morphologies of SC- $\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$  nanoflowers. (A<sub>1</sub>, A<sub>2</sub>) 1 h; (B<sub>1</sub>, B<sub>2</sub>) 3 h; (C<sub>1</sub>, C<sub>2</sub>) 6 h; (D<sub>1</sub>, D<sub>2</sub>) 12 h; (E<sub>1</sub>, E<sub>2</sub>) 15 h. (A<sub>2</sub>, B<sub>2</sub>, C<sub>2</sub>, D<sub>2</sub> and E<sub>2</sub>) are the local partial enlarged images of (A<sub>1</sub>, B<sub>1</sub>, C<sub>1</sub>, D<sub>1</sub> and E<sub>1</sub>), respectively. These series of experiments were carried out in identical concentrations:  $120 \text{ mmol L}^{-1} \text{ Cu}^{2+}$ ,  $0.1 \text{ mol L}^{-1} \text{ PBS}$  at pH 7.4,  $0.1 \text{ mg mL}^{-1} \text{ SC}$ , and reaction at  $25^\circ\text{C}$ .

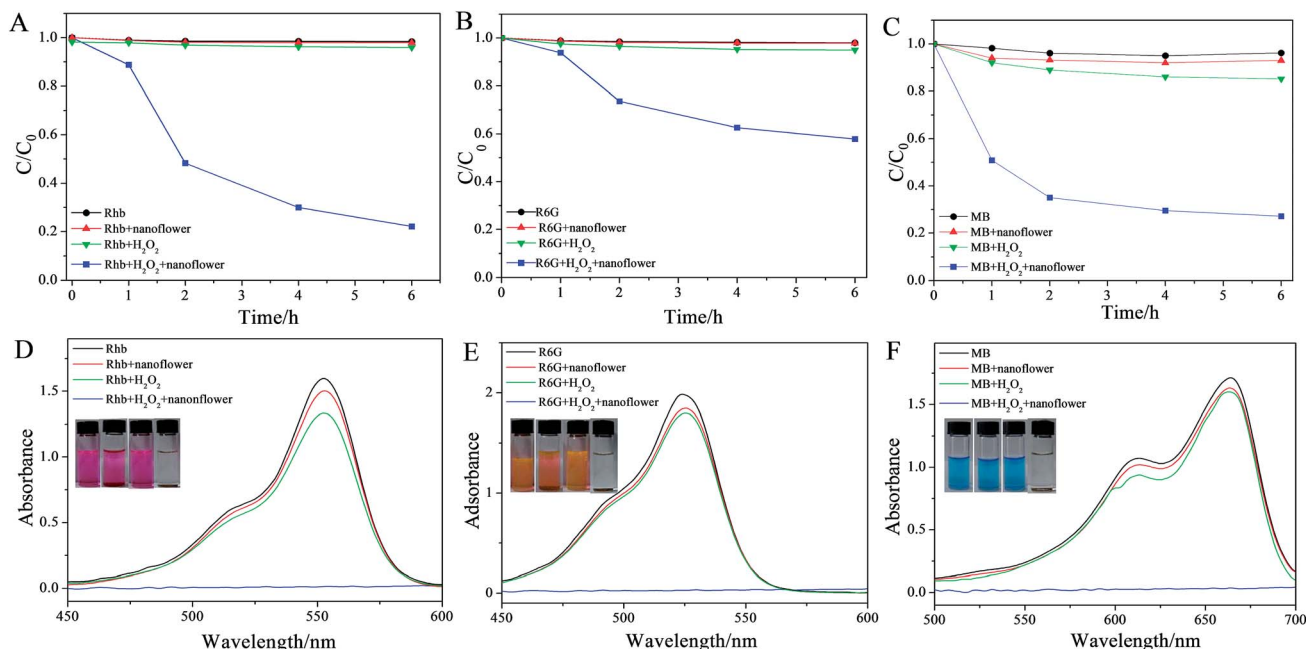


Fig. 6 Catalytic activity of  $\text{SC-Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$  nanoflower for degradation of (A) RhB; (B) R6G; (C) MB, and UV-vis spectrum of (D) RhB; (E) R6G; (F) MB. Inset photos were the color changes of cationic dyes solutions (from left to right): blank control ( $12.5 \mu\text{g mL}^{-1}$  dye solutions),  $125 \mu\text{g mL}^{-1}$   $\text{SC-Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$  nanoflower,  $125 \text{ mmol L}^{-1} \text{H}_2\text{O}_2$ ,  $125 \mu\text{g mL}^{-1}$   $\text{SC-Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$  nanoflower and  $125 \text{ mmol L}^{-1} \text{H}_2\text{O}_2$ . The reaction condition is under room temperature, reaction time is 15 h.

$$-dC_t/dt = kC_t \quad (1)$$

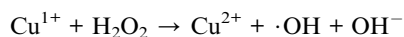
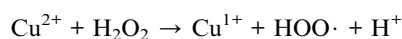
$$\ln(C_0/C_t) = kt \quad (2)$$

As we all know, oxidation is the most common method used to degrade dyes and other organic pollutants. In addition to a prompt removal of the colors,  $\text{OH}^\cdot$  radicals was simultaneously able to fully oxidize the dyes, with a complete mineralization of carbon into  $\text{CO}_2$ . Sulfur heteroatoms were converted into innocuous  $\text{SO}_4^{2-}$  ions. The mineralization of nitrogen was more complex. Nitrogen atoms in the  $-3$  oxidation state, such as in amino-groups remain at this reduction degree and produced  $\text{NH}_4^+$  cations, subsequently and very slowly converted into  $\text{NO}_3^-$  ion. The feasibility of such a degradation could be determined by varying the chemical structures.<sup>47</sup> The degradation mechanism of the RhB mainly involved the broken of benzene ring in RhB combined with de-ethylation and hydroxylation process,<sup>48</sup> while for MB, it mainly involved the broken of  $\text{C}=\text{N}$ ,  $\text{C}=\text{S}-\text{C}$  bond the MB central aromatic ring by  $\text{H}^\cdot$ /electron transfer followed with demethylation.<sup>49</sup> As we know, it was more effortless to break  $\text{C}=\text{N}$  and  $\text{C}=\text{S}-\text{C}$  bond than the benzene ring, leading to a higher degradation rate for MB than RhB. As for RhB and R6G which have similar structures, the difference between degradation rate may due to that RhB had more ethyls than R6G, which was beneficial to accelerate de-ethylation and hydroxylation process.

It is known that copper compound possess intrinsic peroxidase-like activity in the presence of  $\text{H}_2\text{O}_2$ , which has been reported by many groups.<sup>38,45</sup> To verify the peroxidase-like activity is actually occurring in their system, A. K. Dutta *et al.* tested the as-prepared CuS NPs through the catalytic oxidation

of a peroxidase substrate, TMB in the presence of  $\text{H}_2\text{O}_2$ . Similar to  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$ , this  $\text{Cu}^{2+}$  ion may acts as Fenton-like reagent and interact with the substrate in presence of hydrogen peroxide, resulting in a colored reaction product.<sup>45</sup>

The reason of the catalytic activity of  $\text{SC-Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$  nanoflowers was associated with  $\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$  framework while the biosurfactants were only induced the nucleation of  $\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$  crystals to form the nanoflowers. The reaction equations are displayed as follows:



In order to further investigate the influence factors of the catalytic activity, MB solution ( $12.5 \mu\text{g mL}^{-1}$ ) was taken as a sample to investigate the influence of concentrations of nanoflowers and  $\text{H}_2\text{O}_2$  on dye degradation. A visible color disparity of MB solution was observed whether change concentration of hybrid nanoflowers (Fig. 7A) or  $\text{H}_2\text{O}_2$  (Fig. 7B). The UV/vis absorption spectra also confirm a more thorough degradation of MB solutions with the higher concentration of hybrid nanoflowers or  $\text{H}_2\text{O}_2$ . What's more, the recycling experiment for the degradation of MB using  $\text{SC-Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$  nanoflower/ $\text{H}_2\text{O}_2$  system was also taken, the degradation process was shown in Scheme 2. After 6 cycles, the nanoflowers still performed excellent catalytic activity and the final degradation rate of MB solution remained above 95% in each cycle, which indicated a stable structure and outstanding catalytic activity of our nanoflowers. The degradation rates of MB





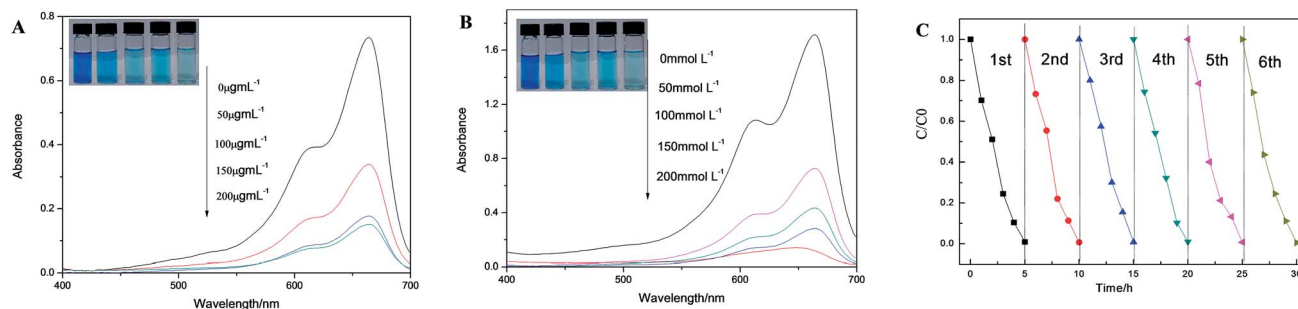
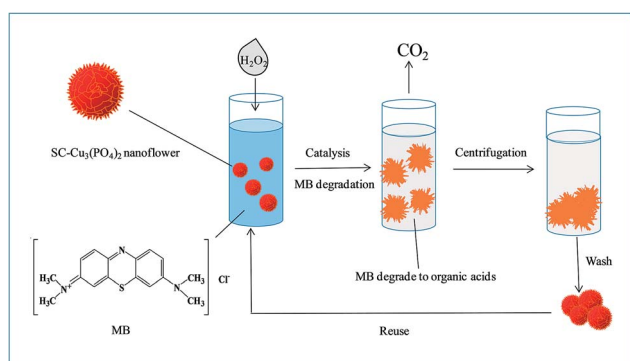


Fig. 7 (A) UV/vis absorption spectra of MB solutions containing  $\text{H}_2\text{O}_2$  upon the addition of different concentrations of hybrid nanoflowers ( $0\text{--}200\text{ }\mu\text{g mL}^{-1}$ ). (B) UV/vis absorption spectra of MB solutions containing hybrid nanoflowers upon the addition of different concentrations of  $\text{H}_2\text{O}_2$  ( $0\text{--}200\text{ mmol L}^{-1}$ ). Inset photos were the color change of the solutions. Other conditions:  $12.5\text{ }\mu\text{g mL}^{-1}$  MB solution,  $125\text{ }\mu\text{g mL}^{-1}$  hybrid nanoflowers and reaction 15 h at  $25\text{ }^\circ\text{C}$ . (C) The first six cycling runs for degradation of  $12.5\text{ }\mu\text{g mL}^{-1}$  MB solution which contains  $125\text{ }\mu\text{g mL}^{-1}$  nanoflowers and  $125\text{ mmol L}^{-1}$   $\text{H}_2\text{O}_2$ .



Scheme 2 The scheme of recycling of nanoflowers as an efficient catalyst for degradation of MB.

solution which contains nanoflowers and  $\text{H}_2\text{O}_2$  for the six cycles were displayed in Fig. 7C.

## Conclusion

In summary, a facile and effective self-assembled template method for low temperature synthesis of 3D flower-like  $\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$  microstructures through biosurfactants-assisted self-assembly with copper ions were designed. Based on the comprehensive test results and analysis, the following main conclusions are obtained. It can be concluded that the biosurfactants were particularly employed as nucleation and growth sites for deposition of copper phosphate and as structural guiding supporters to form the flower morphology. What's more, the concentration of biosurfactants and the growth time were critical to the sizes and morphologies of the hybrid nanoflowers and our  $\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$  nanoflowers can still performed high catalytic efficiency after reused 6 times, indicating its potential as an efficient and stable catalyst for degradation of organic pollutions in waste water.

## Conflicts of interest

There are no conflicts to declare.

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