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ARTICLE

## Redox Reaction Mediated Direct Synthesis of Hierarchical Flower-Like CuO Spheres Anchored on Electrospun Poly(vinylidene difluoride) Fiber Surfaces at Low Temperatures

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Hierarchical poly(vinylidene difluoride) (PVDF) electrospun fiber mats anchored with flower-like CuO spheres (F-CuO@PVDF) have been prepared in an one-step redox reaction mediated process using copper foil as the copper source at a low-temperature of 80 °C. Structural and morphological studies have been carried out with X-ray diffraction, scanning electron microscopy, and high resolution transmission electron microscopy. The optimized reaction condition has been studied and discussed in detail. The amount of the flower-like CuO on F-CuO@PVDF has been gravimetrically determined to be 10.4 μg/cm<sup>2</sup>. The obtained F-CuO@PVDF could be utilized as a catalytic separation membrane and has shown effective catalytic ability and photostability for the photodegradation of rhodamine B (10<sup>-5</sup> M in aqueous solution) in cycled tests. Catalyst separation, recovery, and regeneration are not necessary for F-CuO@PVDF in the cycled tests.

### Introduction

Cupric oxide (CuO) has received massive studies based on their attractive properties and potential of applications in many fields.<sup>1</sup> Nanoscale CuO in different sizes and shapes have been prepared with proper reaction compositions and conditions.<sup>1-6</sup> Based on the abundant surface-to-volume ratio, flower-like CuO nanostructures have received researchers' attention. Vaseem et al.<sup>7</sup> reported a low-temperature (100 °C) synthesis route of flower-shape CuO nanostructures by using copper nitrate, NaOH, and hexamethylenetetramine (HMTA) as the raw materials. The OH<sup>-</sup> ions from NaOH or HMTA react with copper nitrate to form Cu(OH)<sub>2</sub>, which consequently converts into CuO crystals. The CuO crystals then form petal-like structures which aggregate together to result in flower-like CuO nanostructures. Yang and He<sup>8</sup> used poly(ethylene glycol) as a surfactant in the reaction composition for preparation of flower-like CuO nanostructures. Xu et al.<sup>9</sup> proposed that the self-assembly mechanism of primary CuO into 2D and 3D CuO crystal architectures are based on the electrical priority of the CuO primary crystals as they are oppositely charged on the opposite surfaces.

In addition to uses of Cu<sup>2+</sup> salts as the precursor, copper metal has been utilized as the raw material for preparation of CuO nanostructures.<sup>10-15</sup> Oxidation of copper foil could generate CuO nanostructures, including flower-like CuO spheres, on the copper substrate surfaces.<sup>11-14</sup> Similar results have been reported using copper powders as the raw materials.<sup>15</sup> In the

process of using Cu powders for preparation of flower-like CuO microspheres, the growth process of CuO structures is from outside to inside of the copper powders through an "alkali-oxidizing solution etching assisted crystallization" process.<sup>15</sup> Nevertheless, the CuO nanostructures only grew on the surfaces of the copper substrates in the above-mentioned cases. The uses of copper metal as the raw material for the preparation of free nanostructured CuO crystals in solutions have not been reported. Based on the attraction of using copper metal as the raw material, such as easy operation, less waste water production, and easy recycling raw copper agents, in this work, we have explored a new preparation method of flower-like CuO nanoparticles using copper foil as the raw material, based on the redox reaction between copper and Cu<sup>2+</sup>. The mechanism is to be discussed in the text.

On the other hand, electrospinning process is a convenient approach to prepare nanoscaled polymer fibers. The polymer fiber mats have high surface area-to-volume ratio and porosity<sup>16,17</sup> and have shown great potential of application in the fields of sensors, biomedicine, separation, cosmetics, and fuel cells.<sup>16-20</sup> Moreover, surface chemical modification<sup>21-23</sup> and incorporation of functional nanomaterials to the polymer nanofibers<sup>24</sup> have been carried out to introduce interested functionalities to the electrospun polymer fibers. One of the approach is to modify the polymeric fibers with nanostructured metals and metal oxides.<sup>25-30</sup> The applications of nanoparticles-modified electrospun polymer fibers include supercapacitors, lithium-ion battery, solar cells, catalysis, and sensors.<sup>24</sup> The application of the polymer-fiber supported nanoparticles in catalysis is especially noteworthy. This kind of catalysts usually show relatively high catalytic efficiency due to their high specific surface area.<sup>31,32</sup> The polymer-fiber/nanoparticles composite catalysts also have some other advantages, such as ease of recycling catalysts and good operation durability.

The hydrothermal process has been utilized for incorporation of nanoparticles to some substrate surfaces to result in hierarchical heterostructures.<sup>29,30</sup> Nevertheless, it is still attractive to explore a convenient and scalable approach to prepare hierarchical

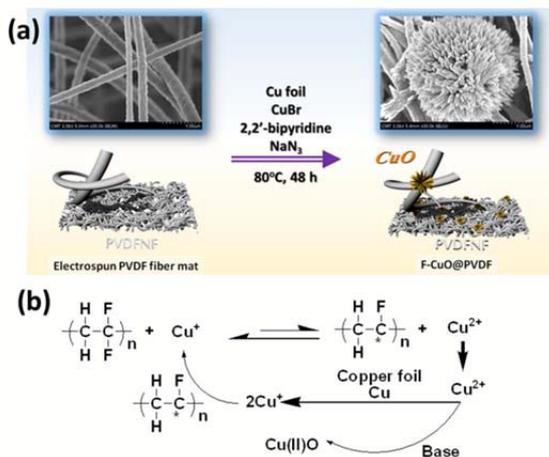
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heterostructures of flower-like nanoparticles anchored on electrospun polymer fibers. In this work, we report a facile low-temperature solution method to directly grow flower-like CuO nanostructures on electrospun poly(vinylidene difluoride) (PVDF) nanofibers. In the process (Figure 1), copper foil, rather than Cu<sup>2+</sup> salts, has been used as the copper source for preparation of the flower-like CuO spheres-anchored PVDF nanofibers (F-CuO@PVDF). Moreover, the application of the hierarchical F-CuO/PVDF as an immobilized catalyst for photodegradation of rhodamine B (RhB) has been examined.<sup>33</sup>



**Figure 1.** In situ preparation of flower-like CuO crystals and anchoring the crystals on the surface of electrospun PVDF fiber mat for formation of F-CuO@PVDF sample.

## Experimental

### Materials

PVDF pellets (Kynar 741), having a weight-averaged molecular weight of about 250,000 Da, were obtained from Arkema Inc., Philadelphia, PA, USA. Electrospun PVDF fiber mats have been obtained with an electrospinning process according to the method reported previously.<sup>22</sup> 2,2'-Dipyridine (>99%), copper(I) bromide (CuBr) (98%), and sodium hydroxide (NaOH) were purchased from Acros Organics Co. Sodium azide (≥99.5%, NaN<sub>3</sub>) and RhB were received from Aldrich Chemical Co. Hydrogen peroxide was from Echo Chemical Co. Analytical grade chemicals were used without further purification. Copper foil in a thickness of 12 μm was received from Chang Chun Petrochemical Co. F-CuO@PVDF was immersed in DMF to dissolve PVDF fibers in DMF. The residual F-CuO was collected with centrifugation, washed with DMF, and dried under vacuum at 80 °C for XRD and TEM measurements.

### Instrumental methods

Field emission SEM micrographs were recorded with a Hitachi S-4800 FESEM instrument at an acceleration voltage of 3 kV. Element mapping on sample surface was conducted with a Hitachi S-3000N SEM equipped with a Horiba ES-320 energy-dispersive X-ray micro analyzer. TGA measurements were performed with a Thermal Analysis TA-Q500 TGA instrument at a heating rate of 10 °C min<sup>-1</sup> under an air flow (100 mL min<sup>-1</sup>).

XRD pattern was identified with a wide-angle X-ray diffractometer from MAC Science Co. (model: MVP 18 AH) with Cu Kα line (λ=1.542 Å) as a radiation source. TEM and HRTEM images were recorded with an JEOL JEM-2000FX HRTEM instrument. The F-CuO sample collected from F-CuO@PVDF was dispersed in DMF and then the dispersion solution was dropped onto a copper grid and dried in vacuum at 50 °C for 24 h. UV-vis spectra were obtained with a Perkin Elmer Lambda 25 UV/vis/NIR spectrometer.

### Preparation of hierarchical flower-like CuO anchored on electrospun PVDF fiber (F-CuO@PVDF)

Electrospun PVDF fiber mats (7 \* 7 cm<sup>2</sup>) covered with copper foil (1 cm width) on all sides were immersed in a water solution containing NaN<sub>3</sub> (0.05 M), CuBr (0.005 M), and 2,2'-bipyridyl (0.005M). The reaction was performed at 80 °C for 48 h. After the reaction, the PVDF fiber mats were drawn out, washed with distilled water under ultrasonication, and dried under vacuum at 80 °C to result in the sample of F-CuO@PVDF.

### F-CuO@PVDF catalyzed photodegradation of RhB aqueous solution

The ability of F-CuO@PVDF to catalyze the photodegradation of RhB was taken at ambient temperature with the assistance of visible light irradiation and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). 32 mL of H<sub>2</sub>O<sub>2</sub> (30 wt%) was added to 318 mL of RhB solution (10<sup>-5</sup> M) to form the pre-testing solution. This solution was stirred at ambient temperature for 15 min under dark. Afterwards, F-CuO@PVDF (96 cm<sup>2</sup>, containing 3.1 mg of F-CuO) was set in the testing solution. The reaction system was irradiated by a fluorescent light (λ ≥ 420nm). At scheduled time interval, the testing solution was sampled and the corresponding RhB concentration was recorded with a UV-vis absorption spectroscopy.

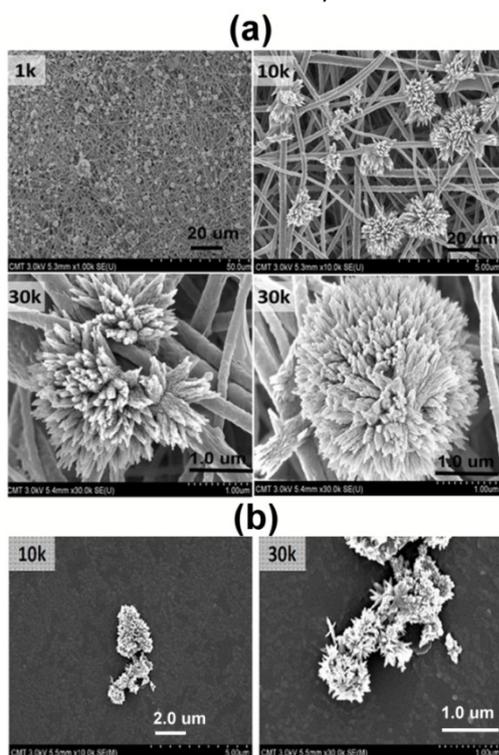
## Results and discussion

### A direct and low-temperature process for preparation of hierarchical flower-like CuO anchored on electrospun PVDF fiber

Hierarchical flower-like CuO nanostructures anchored on electrospun polymer fibers are attractive to enhance the performance of CuO nanocrystals in many fields of application. Although flower-like CuO nanostructures have been obtained in solutions using Cu<sup>2+</sup> salts as the precursors<sup>7-9</sup> and on the copper foil substrate surfaces with the process of direct oxidation of copper metals,<sup>11-14</sup> a convenient and scalable approach to prepare hierarchical heterostructures of flower-like CuO nanoparticles anchored on electrospun polymer fibers has not been reported and is explored in this work. As shown in Figure 1, the explored process uses copper foil as the Cu source and has been carried out at a low-temperature. Electrospun PVDF fiber mats, which were partially covered with copper foil, were immersed with an aqueous solution containing sodium azide (0.05 M), CuBr (0.005 M) and 2,2'-bipyridyl (0.005 M). The system was reacted at 80 °C to give

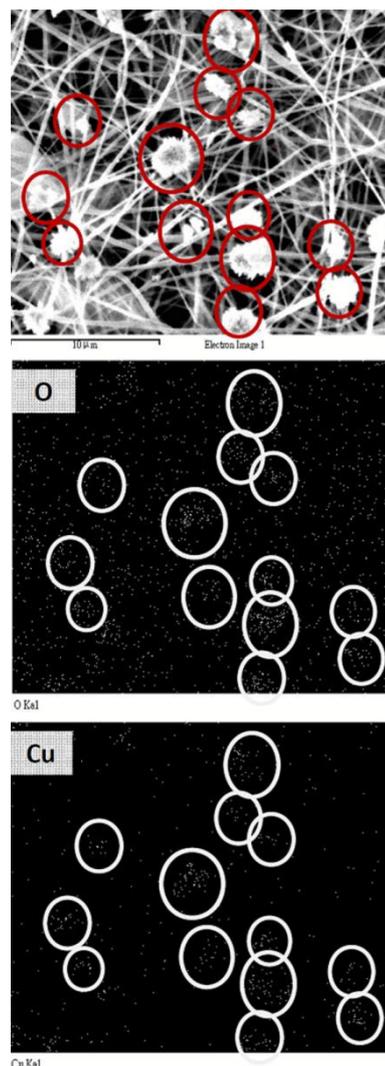
the F-CuO@PVDF sample possesses flower-like CuO nanostructures anchored on the PVDF nanofiber.

The reaction mechanism is illustrated in Figure 1. Oxidation of copper in zero valent into  $\text{Cu}^{2+}$  (CuO) in the reaction process could be attributed to a mechanism similar to the atom transfer radical addition (ATRA).<sup>33</sup> As the C-F groups of PVDF are active initiating sites for atom transfer radical polymerization,<sup>34,35</sup> they could react with Cu(I)Br so as to oxidize Cu(I)Br to be Cu(II)BrF. It has been well demonstrated that under a basic condition,<sup>1-6</sup> salts of  $\text{Cu}^{2+}$  form CuO crystals under heat. The presence of weak base  $\text{NaN}_3$  helps to promote the conversion reaction. On the other hand, partial  $\text{Cu}^{2+}$  could react with copper metal through a redox reaction to generate more  $\text{Cu}^+$  in the reaction system. The oxidation reaction of Cu to  $\text{Cu}^+$  makes the copper foil as a reactant and copper source for generation of CuO in the reaction system.



**Figure 2.** SEM micrographs of (a) the prepared F-CuO@PVDF sample in different amplification rates and (b) CuO particles collected from the redaction solution.

As shown in the scanning electron microscopy (SEM) pictures, the CuO flowers on the PVDF fibers are composed of triangle CuO petals. Most of the CuO flowers are in the size of about 2.5  $\mu\text{m}$ . Nevertheless, some small and not-as-beautiful CuO flowers could be seen in the SEM micrographs. The sizes of the CuO flowers are not very uniform. Most of the flower-like CuO crystals seed at the crossing points of the PVDF fibers. It is noteworthy that not all CuO crystals show beautiful and whole flower-like structures. Some small and particle-like CuO crystals could be seen on the PVDF fibers. As a result, the formation of CuO flowers might be proposed to be an in situ nucleation and growth process.<sup>12</sup> Based on the nucleation and growth process, the intersecting points and the aggregation sections of the PVDF fibers could be the favour positions for



**Figure 3.** Low-resolution SEM micrograph of the prepared F-CuO@PVDF sample and the corresponding EDX element-mapping images. The distribution of Cu and O elements are in agreement with the positions of the flower-like CuO crystals of the sample. The scale bar is 10  $\mu\text{m}$ .

CuO crystal formation on the fiber mats. Hence, as shown in Figure 2 most of the CuO crystals appear at the above-mentioned positions. On the other hand, CuO crystals might still form in the solution. The CuO crystals formed in the reaction solution have been collected with centrifugation. Their structures look like an aggregation of randomly-gathering petals (Figure 2). The structures are similar to that of the samples prepared with the conventional solution procedure in the cases of the reaction conditions were not well controlled and optimized.<sup>7</sup> The result indicates that the electrospun polymeric fibers might be of assistant for the formation of flower-like CuO crystals. Figure 3 collects the EDX element-mapping images of the F-CuO@PVDF sample. The carbon and fluoride elements, corresponding to the distribution of PVDF fibers, appear randomly in the element-mapping images (see supporting materials). On the other hand, the element-mapping images of copper and oxygen, which correspond to the distribution of the CuO crystals, are in agreement with the

position and distribution of the flower-like CuO crystals appearing in the corresponding SEM image. The amount of CuO crystals of the F-CuO@PVDF sample has been determined with a thermogravimetric method. In the thermogravimetric analysis (TGA), PVDF fiber mat degrades totally and both PVDF fibers and F-CuO@PVDF exhibit similar thermal degradation patterns. As a result, the CuO crystals might not alter the thermal degradation behaviour of PVDF fibers and not involve in their thermal degradation reactions. The char yield of F-CuO@PVDF corresponds to the weight fraction of the CuO crystals of the F-CuO@PVDF sample. The CuO weight fraction of F-CuO@PVDF has been determined to be about 1.64 wt%, which corresponds to  $32.8 (\mu\text{g CuO})/(\text{cm}^2 \text{ F-CuO@PVDF})$ . As some CuO crystals have been collected from the reaction solution, the yield of CuO generated on the fiber has been calculated to be about 84 wt%. Nevertheless, the yield of CuO could not be obtained by the weight loss of Cu foil, due to weight gain of the Cu foil from surface oxidation.

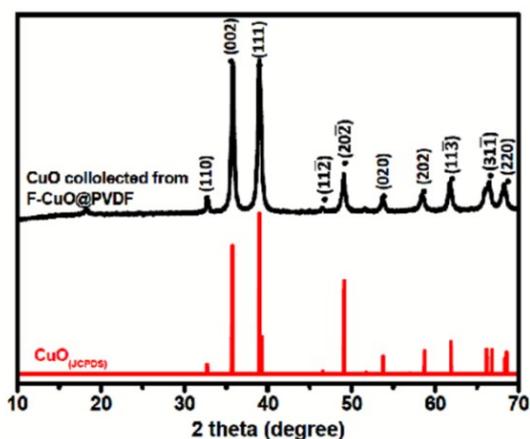


Figure 4. XRD pattern of CuO crystals collected from the prepared F-CuO@PVDF sample through a PVDF-washed-out process.

The CuO crystals of the F-CuO@PVDF sample were collected with a solution process in which PVDF fibers were washed out with *N,N*-dimethylformamide (DMF). The collected CuO samples have been applied to X-ray diffraction (XRD) analysis. As shown in Figure 4, the diffraction peaks are indexed to show agreement with the XRD pattern of the standard monoclinic structure of CuO from the JCPDS file No. 48-1548.<sup>36</sup> It is noteworthy that almost no other peaks, rather than the CuO-corresponding peaks, appear in the XRD pattern, indicating that the obtained sample is CuO in high purity. Figure 5 shows the transmission electron microscopy (TEM) images of the collected CuO crystals. The petals in the low-magnification TEM images are similar to those observed in the SEM micrographs. Some of the petals have sharp tips and some do not, as some tips of the petals might be broken in the collection process of CuO from the surface of F-CuO@PVDF. The width of the petals is about 40-50 nm. The lattice fringe is marked with in the high resolution TEM image (HRTEM, Figure 5b) to show a lattice spacing of about 0.232 nm, which corresponds to the *d* value of [111] facet of the CuO crystals.<sup>36,37</sup>

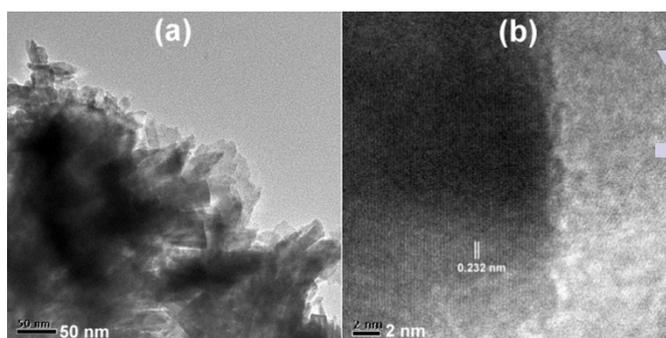


Figure 5. TEM images of CuO crystals collected from the prepared F-CuO@PVDF sample through a PVDF-washed-out process.

#### Optimization of reaction condition for preparation of F-CuO@PVDF samples

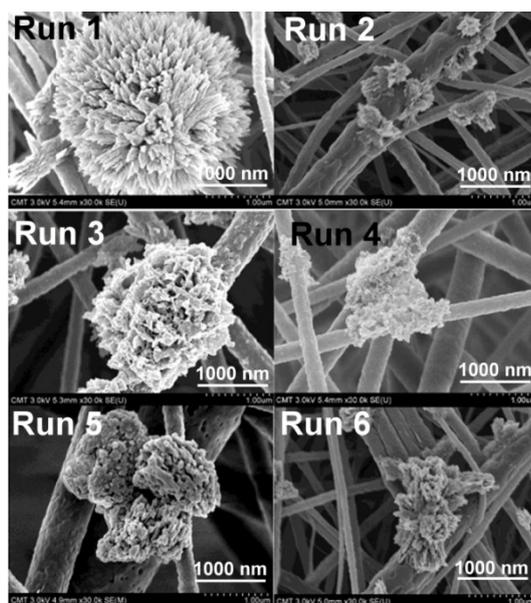
The preparation process of F-CuO@PVDF has been performed with different reaction conditions and reactant composition. The results are collected in Table 1 and the corresponding SEM micrographs of the products are shown in Figure 6. The reactions were carried out for 48 h to provide sufficient time for the tests, so as to minimize the effect of reaction time on the results and to make all the observed changes in the experiments results be reasonably attributed to the altered factor in the tests. First, as the added amount of CuBr is very small, the copper of the formed CuO should majorly come from the copper foil rather than CuBr. The reaction mechanism is discussed in the previous session and illustrated in Figure 1. Here the result from Run 2 (in Table 1) further supports to the utilization of copper foil as the copper source in the reaction. As the copper foil was not applied to the PVDF nanofibers mat in Run 2, only very few CuO crystals in random structures form on PVDF fibers. The amount of copper-containing raw material (CuBr) is not as much enough for formation of many and beautiful flower-like CuO crystals. Based on the reaction mechanism shown in Figure 1b, CuBr plays a key role in the initial reaction of chains reactions for formation of F-CuO. In Run 4 CuBr was not added to the reaction system. Alternatively the  $\text{Cu}^+$  ions in Run 4 come from the reaction between copper foil and  $\text{NaN}_3$  (based condition). As result, only a few CuO crystals still formed in the test of Run 4. On the other hand, Vaseem et al.<sup>7</sup> prepared flower-like CuO nanostructures with a solution containing NaOH and reported that NaOH played an important role in aggregation of the individual CuO petals into flower-like structures. As a result, a test which used NaOH to replace sodium azide as a base source has been performed (Run 3 in Table 1). Some CuO crystals still formed on the PVDF fibers. Nevertheless, their flower-like morphology is not as beautiful as that shown with the sample of Run 1 which employed sodium azide as the reactant. In the solution process,<sup>7,38</sup> addition of NaOH generates a high concentration of  $\text{OH}^-$  which promotes the aggregation of CuO petals into flower-like structures. Nevertheless, in our case a slow growth and assembly process tends to form flower-like CuO on PVDF fibers. As a result, addition of NaOH (or high concentration of  $\text{OH}^-$ ) is negative for

the formation of flower-like CuO on PVDF fibers. The effect of reaction temperature has been examined with Run 5 in which the reaction has been performed at 30 °C. No flower-like CuO crystals appear. Proper heating the reaction system would convert the Cu(II) salts into CuO crystallites which serve as the building blocks for assembly of CuO nanostructures.<sup>7,36</sup> As a result, 30 °C is not a temperature high enough for the formation reaction of CuO from Cu(II) salts.

The above discussion suggests that the reaction condition and reactants of Run 1 is necessary for preparation of hierarchical flower-like CuO nanostructures on electrospun polymer fibers. As the reaction condition for Run 1 gives the optimum result, in Run 6 the test has been carried out under the condition of Run 1 but shortening the reaction time to 24 h. Flower-like CuO crystals in relatively small sizes are obtained. On the other

**Table 1.** Experiments for preparation of F-CuO@PVDF under various reaction compositions conditions.

Run no.	Temperature (°C)	Time (h)	Reactants				
			Copper foil	2,2'-bipyridine (0.005 M)	CuBr (0.005 M)	NaN <sub>3</sub> (0.05 M)	NaOH (0.05 M)
1	80	48	✓	✓	✓	✓	
2	80	48		✓	✓	✓	
3	80	48	✓	✓	✓		✓
4	80	48	✓	✓		✓	
5	30	48	✓	✓	✓	✓	
6	80	24	✓	✓	✓	✓	



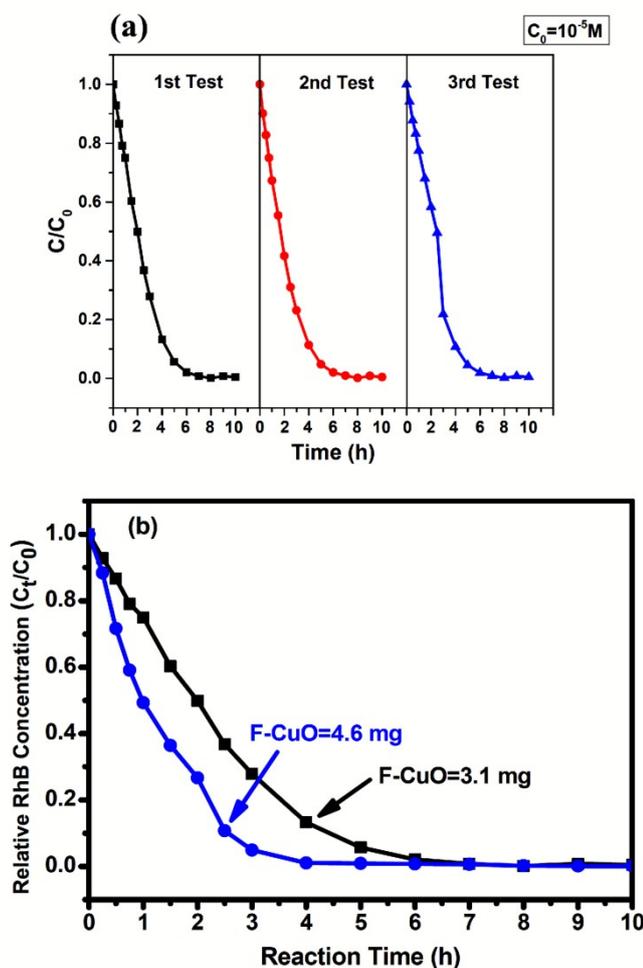
**Figure 6.** SEM micrographs of the CuO crystals on PVDF fiber mat prepared with different reaction conditions listed in Table 1.

hand, the rate of formation of CuO crystals in the developed system could be significantly increased with increasing the concentrations of the agents based on the reactions proposed in Figure 1b. While the concentrations of the agents are increased from 0.005 M to 0.075 M, a short 4-h reaction time is enough to produce CuO crystals. A lot of CuO crystals form and almost fully cover the PVDF fiber mats in a 24-h reaction (see the supporting materials). Nevertheless, the obtained CuO crystals are not in beautiful flower-like structure. As a result, in the developed system CuO crystals could be obtained in high reaction rate but a slow reaction rate is needed for the assembly of CuO into the flower-like structure.

#### Application of F-CuO@PVDF for photochemical degradation of RhB

The application of CuO in many fields have been widely reported.<sup>1</sup> Being a semiconductor, CuO has a narrow band gap<sup>39</sup> and is a suitable photocatalyst used under visible light irradiation. The uses of CuO crystals as a photocatalyst for the photodegradation of RhB has been studied.<sup>36,40</sup> Hence, the prepared F-CuO@PVDF samples have been used for the photocatalytic degradation of RhB. Compared to the free CuO structures, F-CuO@PVDF could be considered as an immobilized catalyst and obviously has the corresponding advantages such as easy operation and convenience in catalyst separation, recovery, regeneration, and utilization.<sup>41</sup> Moreover, as the electrospun PVDF fiber mat could serve as a separative membrane, the F-CuO@PVDF is a catalytic membrane which combines both of the functions of membrane separation and catalytic degradation. The amount of the flower-like CuO crystals in the F-CuO@PVDF mats used for the photodegradation of RhB aqueous solution (around 10<sup>-5</sup> M, 0.35 L) is about 3.1 mg (96 cm<sup>2</sup> of F-CuO@PVDF). The time-dependent relative concentration of the RhB solution has been recorded with an ultraviolet-visible (UV-vis) spectroscopy with the absorption peak of RhB at 553 nm. As shown in Figure 7, the concentration of RhB decreases gradually. In a blank test in which the F-CuO@PVDF mats were immersed in the RhB solution in dark for 7 h, no obvious decreases in the

concentration of RhB has been observed. The result indicates that RhB molecules do not physically adsorb with the F-CuO@PVDF mats and the decreases in the RhB concentration is due to the occurrence of photodegradation of RhB. The photodegradation of RhB almost completes in about 7 h as at this period of time the absorption of RhB becomes almost not detectable. On the other hand, in the control test which does not employ any CuO photocatalyst, only about 4% of RhB concentration decreases in 1 h test. The RhB concentration decrease is attributed to the catalyst-free photodegradation of RhB, as a similar result has been reported.<sup>42</sup> Hence, as the PVDF electrospun fibers did not absorb RhB molecules in the experiments, the disappearance of RhB is attributed to the CuO-catalyzed photodegradation.



**Figure 7.** (a) Cycle tests of photodegradation of RhB aqueous solution ( $10^{-5}$  M, 0.35 L) catalyzed with F-CuO@PVDF (3.1 mg of F-CuO) and (b) the effect of F-CuO amounts on the photodegradation efficiency.

The RhB photodegradation efficiency (*PE*) of the CuO catalyst could be calculated with the equation of

$$PE \text{ (mmol RhB/(g CuO}\cdot\text{h))} = (V\cdot C)/W\cdot t \quad (\text{Eq. 1})$$

Where *V* is the volume of RhB solution in mL, *C* the concentration of RhB solution in mol L<sup>-1</sup>, *W* the weight of CuO catalyst in gram, and *t* the reaction time in hour. The *PE* of F-CuO anchored on PVDF fibers (3.1 mg F-CuO for 350 mL 10<sup>-5</sup> M RhB solution, 7 h) could be calculated to be about 0.16 mmol

g<sup>-1</sup> h<sup>-1</sup>. The value is about 10-fold of the efficiency (0.016 mmol g<sup>-1</sup> h<sup>-1</sup>) calculated from the data (20 mg CuO for 50 mL 10<sup>-5</sup> M RhB solution, 1.5 h) previously reported to spindle-like CuO crystals,<sup>36</sup> and could be attributed to the flower-like structure of the F-CuO crystals. Moreover, the long experimental time needed for complete degradation of RhB could be only due to the very small amount of F-CuO (3.1 mg, compared to the amount of 20 mg used in the literature<sup>36</sup>) used in the tests. Hence, the degradation time could be reasonably reduced with increasing the F-CuO amounts. A simple test shows (see the supporting materials) that an 50% increase in the F-CuO amount (from 3.10 to 4.6 mg with increasing the F-CuO@PVDF membrane area in the test) could effectively reduce the degradation time to about 4.0 h (Figure 7b). Further reduction of the photodegradation time might be achieved with employment of more F-CuO amounts.

Figure 7a also shows the recycled tests of the photodegradation of RhB solution for 3 cycles. For each cycle a fresh testing solution of RhB has been applied. The efficiency of the F-CuO@PVDF catalyst and the time-dependent degradation pattern of RhB are almost of the same in the 3 cycles of the test. It could be concluded that F-CuO@PVDF has both high catalytic efficiency and photostability in the photodegradation of RhB in aqueous solution. F-CuO crystals do not peel off from the F-CuO@PVDF mat and the flower-like CuO crystals are stable during the photodegradation operation. After the 3-cycle photocatalysis test, the F-CuO particles remain intact throughout the membranes, as the SEM micrographs shown in the supporting materials. Moreover, it is noteworthy that catalyst separation, recovery, and regeneration are not necessary for F-CuO@PVDF in the cycled tests.

## Conclusions

A convenient approach has been developed to in situ synthesize flower-like CuO crystals and anchor them on the surface of electrospun PVDF fiber mats so as to result in hierarchical F-CuO@PVDF samples. The process could be operated at a low temperature of 80 °C. Copper foil, rather than copper(II) salts, has been utilized as the copper source in the solution process for growth of nanostructured flower-like CuO crystals. Moreover, the obtained F-CuO@PVDF could be considered as a catalytic separation membrane immobilized with CuO catalysts. The ability of F-CuO@PVDF to photocatalyze the degradation reaction of RhB has been demonstrated. The F-CuO@PVDF membrane possessing 0.1 mg CuO is effective to almost totally degrade 10<sup>-5</sup> M RhB aqueous solution of 0.35 L. Cycled degradation tests demonstrate the photostability of the flower-like CuO crystals. Moreover, catalyst separation, recovery, and regeneration are not necessary for F-CuO@PVDF in the cycled tests.

## Acknowledgements

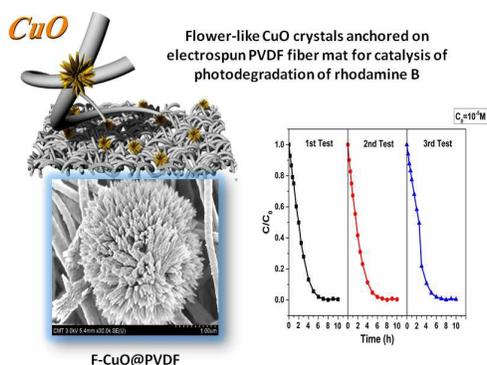
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# Redox Reaction Mediated Direct Synthesis of Hierarchical Flower-Like CuO Spheres Anchored on Electrospun Poly(vinylidene difluoride) Fiber Surfaces at Low Temperatures

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Flower-like CuO spheres anchored on electrospun PVDF fiber surfaces as catalytic membranes for photodegradation of rhodamine B aqueous solutions.