Since January 2020 Elsevier has created a COVID-19 resource centre with free information in English and Mandarin on the novel coronavirus COVID-19. The COVID-19 resource centre is hosted on Elsevier Connect, the company's public news and information website.

Elsevier hereby grants permission to make all its COVID-19-related research that is available on the COVID-19 resource centre - including this research content - immediately available in PubMed Central and other publicly funded repositories, such as the WHO COVID database with rights for unrestricted research re-use and analyses in any form or by any means with acknowledgement of the original source. These permissions are granted for free by Elsevier for as long as the COVID-19 resource centre remains active.
In-situ synthesis of Cu$_2$O on cotton fibers with antibacterial properties and reusable photocatalytic degradation of dyes

Xiuping Su (Doctor Degree)$^{a,b}$*, Wei Chen$^b$, Yanna Han$^a$, Duanchao Wang$^b$, Juming Yao$^b$

$^a$ Shaoxing University Yuanpei College, Shaoxing, Zhejiang 312000, China
$^b$ College of Textile Science and Engineering, Zhejiang Sci-Tech University, Hangzhou 310018, China

**ABSTRACT**

In this study, the cotton fabrics/cuprous oxide-nanocellulose (Cu$_2$O-NC) flexible and recyclable composite material (COCO) with highly efficient photocatalytic degradation of dyes and antibacterial properties was fabricated. Using flexible cotton fabrics as substrates, Cu$_2$O were in-situ synthesized to make Cu$_2$O uniformly grew on cotton fibers and were wrapped with NC. The photocatalytic degradation ability of COCO-5 was verified by use methylene blue (MB), the degradation rate was as high as 98.32%. The mechanism of COCO-5 photocatalysis and the process of dye degradation were analyzed by using electron paramagnetic resonance (EPR) spectrum, transient photocurrent response (TPR) spectrum, Fourier transform infrared (FTIR) spectroscopy and ion chromatography (IC). This study analyzed the complete path from electron excitation to dye degradation to harmless small molecules. Qualitative and quantitative experiments demonstrate that COCO-5 has high antibacterial activity against *S. aureus* and *E. coli*, the highest antibacterial rate can reach 93.25%. Finally, the stability of COCO-5 was verified by recycling and mechanical performance tests. The textile-based Cu$_2$O functionalized material has photocatalytic degradation and antibacterial properties, and the preparation process is simple and convenient for repeated use, so it has great potential in wastewater treatment containing dyes and bacteria.

**1. Introduction**

The citizens of the bustling metropolis drink clean, non-toxic tap water, but water pollution is still a major threat to human survival in underdeveloped areas [1,2]. There is always a tendency for industrial areas to migrate to less developed regions because of low labor costs and relatively weak environmental regulations [3,4]. In particular, the recent COVID-19 outbreak reminds people that the threat of microorganisms and viruses to humans is also huge. It is better to develop an inexpensive material to eliminate the source of disease, that is, water pollution. The dyes in wastewater can kill aquatic plants and plankton, causing ecosystem collapse, which is very difficult to recover. If organism (including humans) drink wastewater containing dyes for a long time, even at lower concentrations, they can cause cancer [5–8]. Wastewater containing a large amount of bacteria is a hotbed of disease, which not only causes various diseases, but also promotes bacterial growth and contaminates more water and water containers [9–11]. Therefore, researchers have been investing a lot of energy in the research of wastewater treatment materials.

Nanocellulose (NC) is an ideal environmentally and friendly material, it is green, sustainable and cheap. NC can be derived from plants, bacteria and marine shellfish, which have the advantages of being degradable, flexible, hydrophilic and rich in surface groups [12–13]. NC has used as an interface “bridge” between inorganic nanomaterials and polymer materials, so NC is an ideal choice in interface chemistry of composite materials [14–18]. Cu$_2$O is a semiconductor material because it has a narrow band gap and a suitable conduction band to facilitate absorption of visible light and exhibits photocatalytic properties, which can be used in the field of photocatalytic degradation of dyes [19–20]. On the other hand, Cu is abundant in nature, inexpensive, and is suitable for a large amount of synthesis. These advantages make Cu$_2$O industrial applications more preferred than similar photocatalysts such as TiO$_2$ [21–24]. Yu et al. [25] used solvothermal method to prepare Zn-doped Cu$_2$O nanoparticles with various crystal structures, and explored the effect of Zn doping on the structure and properties of Cu$_2$O. Their samples used for photocatalytic degradation of ciprofloxacin, and the highest degradation rate reached 94.6%. However, the crystal structure of Zn-doped Cu$_2$O is not clearly resolved, and it is difficult for the nanoparticles to be recycled result in secondary pollution. Nie et al. [26] incorporated Cu$_2$O nanoparticles and

https://doi.org/10.1016/j.apsusc.2020.147945

Received 8 June 2020; Received in revised form 13 September 2020; Accepted 17 September 2020
Available online 26 September 2020
0169-4332/ © 2020 Published by Elsevier B.V.
graphene oxide (GO) nanosheets into microcrystalline cellulose (MCC) foam for photocatalytic degradation of MB. The use of GO improves the dispersibility of Cu2O and promotes itself stratification. Although the degradation rate is improved, the dispersion of physically mixed nanoparticles is still not satisfactory and the cost of GO is too high.

This work in propose to provide a solution that is simple to fabricate, low in cost, and recyclable. In this study, Cu2O was synthesized in-situ on cotton fabrics, NC as a “bridge” to make the dispersion of Cu2O very uniform, and not too fast to fall off. The use of cotton fabrics as a substrate allows the composite to be easily reused. Among them, COCO-5 was capable of photocatalytic degradation of 98.32% MB and was capable of degrading 85% MB after repeated use for 5 times. On the other hand, COCO-5 can deal with a wide range of dyes and exhibits strong recyclable photocatalytic degradation of complex dye wastewater. The mechanisms of photocatalytic degradation were analyzed using techniques such as EPR, TPR, FTIR and IC. Combine multiple test results to demonstrate a complete dye degradation pathway. Further, COCO-5 showed excellent antibacterial ability, and the antibacterial rates against S. aureus and E. coli reached 93.25 and 89.73%, respectively, and the antibacterial rate after 5 cycles of S. aureus was still 80.99%. Through the mechanical property test, the cotton fabrics as the base material did not exhibit mechanical failure during the recycling process. In summary, this study developed a kind of recyclable cotton fabrics/Cu2O-NC composite materials with promising capabilities for dye wastewater treatment and antimicrobial applications. In-situ synthesis of nano-functional particles based on textile materials is a promising process route, and the ideal recyclable nanocomposites can be prepared by combining different organic–inorganic materials.

2. Experimental section

2.1. Materials.

Cotton fabrics were fabricated in our textile laboratory. Acrylic acid (AA), acrylamide (AM), Cellulose powder, hydroxylamine hydrochloride (HH, NH2OH·HCl), copper sulfate (CuSO4), ammonium persulfate (APS), ethanol, urea, sodium hydroxide (NaOH) and methylene blue (MB) were purchased from Aladdin Chemistry Co. Ltd (Shanghai, China).

2.2. Chemical modification of cotton fabrics and preparation of NC.

Immersed 2 cm × 2 cm cotton fabrics in the mixed solution containing 3 M AA and 3 M AM, stirred the reaction at 45 °C for 1 h, then taken out the cotton fabrics, washed it gently 5 times with deionized water, and put it in a vacuum oven to dry for 4 h. NC was obtained by dissolving cellulose powder in an alkaline urea solution (7 wt% NaOH and 12 wt% urea solution). After the reaction, the NC solutions were filtered and freeze-dried (−70 °C, 72 h) to obtain dry NC.

2.3. In-situ synthesis of octahedral Cu2O on cotton fibers.

First prepare 5, 10, and 15 mM CuSO4 solutions, immersed the three chemically modified cotton fabrics in these three solutions, and then used NaOH to adjust the pH of all solutions to about 12, correspondingly added 1, 3 and 5 g NC to the CuSO4 solution in the above order (the amount of NC added were determined after preliminary experiment optimization). Next, prepared 5, 10, and 15 mL of 0.8 M HH solution, added them to the corresponding precursor solution described above, and stirred the reaction at 45 °C for 1 h. In this process, CuSO4 were reduced to Cu2O in brick-red by HH. After the reaction, the brick-red cotton fabrics were taken out, and the three samples were gently washed three times with ethanol, and then transferred to a vacuum oven for drying for 12 h. Finally, according to the added amount of NC mass, the three samples were named as COCO-1, COCO-3, COCO-5. The reaction mechanism is shown in Fig. 1.

2.4. Characterizations.

The microscopic morphology and elemental composition of the synthesis were characterized using an Ultra 55 field emission scanning electron microscope (FE-SEM) with energy dispersive X-ray spectroscopy (EDS). The composite structure of Cu2O/NC was characterized using a JEOL 2100 transmission electron microscope (TEM). The contents of Cu2O on textile fabric were quantified through Sollar M6 atomic absorption spectrometry (AAS) with air-acetylene flame. Separate hollow cathode lamps radiating at wavelengths of Cu 224.8 Å were used to determine the amount of Cu. The crystal structure was characterized using a D8 Advance X-ray diffractometer (XRD). The chemical functional group structure was characterized using a Nicolet 5700 Fourier transform infrared spectrometer (FTIR). X-ray photoelectron spectroscopy (XPS, K-Alpha) data was obtained using an electronic spectrometer. The ultraviolet absorption spectrum was characterized using a UV-visible (UV-Vis) spectrometer. The ion chromatography (IC) was carried out with instruments of Metrohm. Free radicals in the system were detected using a Bruker A300 electronic paramagnetic resonance (EPR). The transient photocurrent response (TPR) spectrum was tested using a Zahner Zennium electrochemical station. The mechanical properties were measured on Instron mechanical testing equipment.

2.5. Photocatalytic performance of dyes degradation.

Prepared 200 ppm MB solution, take three 200 mL MB solution into the beaker, put as-prepared COCO-5 (2 × 2 cm) into the beaker respectively and were stored in the dark under magnetic stirring for 120 min to reach absorption–desorption equilibrium. Subsequently, the photocatalytic reaction was performed by exposing the solution to the 350 W xenon lamp coupled with the UV cutoff filter (λ > 400 nm). The photocatalytic reactions were carried out for 120 min under irradiation. Degradation rate (%) of MB, calculated as:

\[
D(\%) = \frac{C_0 - C_t}{C_0} \times 100
\]

where \(C_0\) is the initial MB concentration (ppm), and \(C_t\) is the MB concentration (ppm) at time \(t\). The photocatalytic degradation process of other dyes (i.e. cationic yellow, cationic red, anionic yellow, neutral red) is consistent with this. All experiments of photocatalytic degradation of dyes were carried out three times, and the average value was taken.

2.6. Antibacterial performance

Escherichia coli (E. coli, ATCC 25922) and Staphylococcus aureus (S. aureus, ATCC 27217) were used as model Gram-negative and Gram-positive bacteria. The plate colony counting method is used to study the antibacterial ability of samples. All materials used in the antimicrobial activity test need to be sterilized in an autoclave, and the experimental operation should be carried out in a clean bench. Approximately 5 × 10^7 CFU/mL for bacteria and 1 × 10^7 CFU/mL for yeast at 37 °C for 14 h to count the amount of viable microorganism colonies. Transfer 50 μL of bacterial strains to 50 mL liquid culture medium and add Incubate in a shaking incubator at 37 °C at 100 rpm for 24 h. Then, the activated bacteria were dispensed into 50 μL of liquid culture medium, which respectively contained 0.2 mg samples, and nothing was used as a blank sample for another 24 h culture. Dilute various bacterial solutions to 100 times, and then spread 20 μL of the diluted bacterial solutions evenly on the LB agar plate. The antibacterial activity of these substances can be observed by the number of colonies, and all tests are repeated at least 3 times. Microbial colonies or average colony forming units (CFU), the equation is as follows [27,28]:

\[\text{Antibacterial rate} = \frac{N_{control} - N_{sample}}{N_{control}} \times 100\%\]
where $N_0$ is the mean number of bacteria on the pure liquid medium with full cells, and $N_1$ is the mean number of bacteria on the COCO-5.

### 3. Results and discussions

#### 3.1. Morphological observation

Firstly, the Cu$_2$O-NC composite sample without cotton fabrics was prepared, and its micro composite structure and crystal structure were analyzed by TEM. As can be seen from Fig. 2a, Cu$_2$O were dispersed in the middle of the NC and had quadrilateral or elliptical structures of varying sizes, with Cu$_2$O having diameter of about 20–40 nm. The (1 0 0) and (2 0 0) crystal planes of Cu$_2$O were observed under high resolution TEM, and their interplanar spacings were 0.30 and 0.21 nm, respectively (Fig. 2b). The above observations prove that the Cu$_2$O prepared by the research method has good structures and NC assists in the dispersion of Cu$_2$O.

In order to explore the optimal synthesis conditions, the concentration of CuSO$_4$ and NC were adjusted to prepare Cu$_2$O in-situ on the surface of cotton fabrics. Some significant differences in Cu$_2$O content of three samples was observed by FE-SEM (Fig. 3). The COCO-1 cotton fibers were loaded with only a small amount of Cu$_2$O-NC, and most of the cotton fibers were bare. At high magnification, it can be seen that the Cu$_2$O of octahedral structure were scattered on the surface of the fibers and is not wrapped by the NC (Fig. 3a-a2). Fig. 3b-b2 showed that the Cu$_2$O on the cotton fiber of COCO-3 were obviously increased, and the distribution was relatively uniform. The Cu$_2$O portion of the cotton fibers were wrapped by the NC, which helped prevent Cu$_2$O from falling off easily, but some of the Cu$_2$O were exposed. COCO-5 achieved an ideal composite structure, cotton fibers had been densely attached by Cu$_2$O-NC, while NC coated most of the Cu$_2$O on the surface of the fiber with some pores (Fig. 3c-c2). NC were clustered together again through the hydrogen bonds network on the cotton fibers, leaving some pores while constructing the NC three-dimensional network, which was conducive to the reaction of the liquid phase with the encapsulated Cu$_2$O. Furthermore, the AAS was utilized to accurate analyze content of Cu$_2$O on composite sample for COCO-1, COCO-3 and COCO-5 was 15.78, 21.38, and 30.27 mg/g, corresponding to the FE-SEM analyses. Notably, sample COCO-5 showed the highest Cu$_2$O content when obtained with the highest concentration of synthetic raw material. On the other hand, combined with some preliminary experiments (including photocatalytic degradation of dyes and antibacterial tests), the COCO-5 was the idea sample for the recyclable photocatalytic and antimicrobial applications.

#### 3.2. Crystal structure and chemical composition analysis

As shown in Fig. 4, XRD patterns and XPS spectra were used to analyze the crystal structures of Cu$_2$O and the composite structures of...
Cu$_2$O/ cotton fabrics. Fig. 4a clearly shows the XRD patterns of the crystal structures of COCO-5 and pure Cu$_2$O. The diffraction peaks observed at 2θ = 29.36°, 36.45°, 42.38°, 61.57°, 73.69° and 77.65° correspond to the (110), (111), (200), (220), (311) and (222) crystal planes of Cu$_2$O (JCPDS no: 77–0199) [31,32], respectively, as indicated in the Fig. 4a. This is the XRD diffraction patterns of the crystal structures of octahedral Cu$_2$O [33,34]. At the same time, the growth of octahedral Cu$_2$O in the FE-SEM images was verified (Fig. 3c2). The intensities of the diffraction peaks of COCO-5 is higher than that of pure Cu$_2$O, which because the cotton fiber as a growth substrate promotes the formation of better Cu$_2$O crystal structures [35]. The TEM images of Fig. 2 also confirmed this phenomenon, in the absence of cotton fabrics as a growth substrate, the crystal structures of Cu$_2$O were close to an ellipse rather than a regular octahedron. In contrast, there is no Cu$_2$O crystal diffraction peak on the cotton fabrics because the pure cotton does not carry any Cu$_2$O [36]. Fig. 4b is XPS analysis of cotton fabrics,
Fig. 5. (a) UV–vis spectra and (b) optical image of MB after different photocatalytic degradation time, (c) UV–vis standard curve with concentrations corresponding to absorbance. The right color ruler is the correspondence between colors and concentrations.

Cu₂O and COCO-5. The peaks of C 1 s, N 1 s and O 1 s were detected at 285.4, 399.7 and 532.2 eV in cotton fabrics, and the peaks of O 1 s and Cu 2p were detected at 529.5 and 931.7 eV in Cu₂O, and the above four peaks appeared simultaneously in COCO-5 [37,38]. In detail, on the XPS spectrum of Cu 2p (Fig. 4c), the peaks located at 932.3 and 952.4 eV are ascribed to the Cu 2p1/2 and Cu 2p3/2 [39]. In Fig. 4d, the O 1 s can be fitted into 529.5 and 534.0 eV, which were attributed to lattice oxygen of Cu–O bonds and surface-adsorbed oxygen species [40]. The results of XRD and XPS prove that Cu₂O and cotton fabrics can be well combined with the assistance of NC.

3.3. Photocatalytic degradation of MB and its mechanism analysis

COCO-5 verified its photocatalytic performance by degrading MB under irradiation with a xenon light, and the concentration of MB was monitored by UV–vis, as shown in Fig. 5. Five reaction times were set to degrade MB using COCO-5, which were 0, 10, 20, 40 and 60 min, respectively (Fig. 5a). The concentration of MB after degradation was then calculated from the corresponding absorption intensity in the standard curve (Fig. 5b-c). From the UV–vis absorption peak (Fig. 5a), the absorption peaks at 664 nm of MB were weaker and blue-shifted, and the color of the MB solution also changed from blue to colorless. This indicates that the reduction of the chromophore group can de-generate MB using COCO-5, which were 0, 10, 20, 40 and 60 min, respectively (Fig. 5a). The concentration of MB after degradation was then calculated from the corresponding absorption intensity in the standard curve (Fig. 5b-c). From the UV–vis absorption peak (Fig. 5a), the absorption peaks at 664 nm of MB were weaker and blue-shifted, and the color of the MB solution also changed from blue to colorless. This indicates that the reduction of the chromophore group can determine the occurrence of degradation, and the blue shift of the peak indicated that the energy required for the electronic transition increases to form an intermediate product [41]. After 60 min, almost no MB was left in solution (1.68%), COCO-5 shown excellent photocatalytic degradation property. More importantly, COCO-5 can be easily taken out because it is easy to remove the COCO-5 from the liquid. Six photodiode reactions are as follows:

\[ \text{Cu}_2\text{O} \rightarrow 2\text{e}^- + \text{2h}^+ \rightarrow \text{O}_2^- + \text{2H}^+ \quad (4) \]

\[ \text{H}_2\text{O} + \text{2h}^+ \rightarrow \text{2H}_2\text{O}_2 \quad (5) \]

\[ \text{H}_2\text{O}_2 + \text{e}^- \rightarrow \text{HO}_2^- + \text{H}_2\text{O} \quad (6) \]

\[ \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2 \quad (7) \]

ii, firstly, the •OH radical attacks the -S = bond and the -N = bond of MB to interrupt the MB molecule. Secondly, under the function of •O₂⁻ and •OH, the MB split product is oxidized to phenol, diphenol, etc., because phenol and diphenol have an electron donor –OH present on the benzene ring, which is beneficial to •OH electrical attacks, especially in the presence of –OH on the ortho and para positions. Phenol can be oxidized to hydroquinone, catechol, resorcinol, etc., and diphenol can be quickly oxidized to benzoquinone. In the third step, the intermediate product of the aromatic ring is further oxidized by •OH into a short-chain carboxylic acid such as fumaric acid, oxalic acid, formic acid, etc., and these short-chain carboxylic acids can be rapidly degraded into CO₂ and H₂O [46–49]. Analysis of the IC verified this degradation process (Fig. 6d). Eventually, under this series of physicochemical reactions, MB is degraded and water is harmless. The gradual degradation process is shown in Fig. 7.

One of the advantages of this study is that it can be easily reused because it is easy to remove the COCO-5 from the liquid. Six photocatalytic degradation cycles were set to test the stability of COCO-5. We performed the cycling tests of sample by simply washing with distilled water for the next cycle of photocatalytic. It can be seen from Fig. 6a that the photocatalytic activity of COCO-5 can still be maintained above 85% after 6 cycles, which indicates that it has good durability.
performance is significantly better than the Cu$_2$O photocatalytic material without the cotton fabrics [50,51], which indicates that the cotton fiber is a good matrix to promote stability, and NC helps Cu$_2$O to anchor better on the fiber. Fig. 8b shows the photocatalytic degradation properties of COCO-5 for a variety of dyes, including CY (cationic yellow), CR (cationic red), AR (anionic red), AY (anionic yellow) and NR (neutral red). At first step, the concentration of the five dyes decreased by 10–50% when in the dark treatment environment (purple part). In this 120 min, COCO-5 mainly showed the ability to adsorb dyes. In the second step (light blue part), the species dye were rapidly degraded under visible light irradiation, and COCO-5 mainly exhibited photocatalytic degradation properties. This situation indicates that COCO-5 can degrade the chromophore groups (azo group) of a variety of dyes [52], thereby having the potential to handle complex dye wastewater.

3.4. Antibacterial performance test

Generally, Cu$_2$O has strong antibacterial properties, so the samples in this study have also been tested for antibacterial. Similarly, the antibacterial properties of COCO-5 in the aqueous phase can be easily reused. S. Aureus and E. Coli were used to represent Gram-positive and Gram-negative bacteria, respectively. COCO-5 was tested for antimicrobial property using plate colony counting method. Fig. 9a shows that the CFU on the medium after being treated with COCO-5 for 30 min had dropped to 107 (S. Aureus) and 143 (E. Coli), and the blank (nothing on it) CFU were still 1050 and 984 (Fig. 9c). At the same time, we prepared pure cotton and cotton-NC composite fabrics to test the antibacterial properties. The results showed that the antibacterial
properties of pure cotton and cotton-NC composite fabrics were not excellent. Although their tested CFU was lower than that of the blank control group, they were all at a high CFU value, which did not achieve the desired antibacterial effect. The antibacterial rates (AR) of COCO-5 to \textit{S. Aureus} and \textit{E. Coli} reached 93.25 and 89.73\%, respectively (Fig. 9b). This indicates that the cotton fabrics loaded with Cu$_2$O had a strong antibacterial activity. Usually, the Cu$_2$O surface could generate hydrogen peroxide (H$_2$O$_2$) with antibacterial effect, and H$_2$O$_2$ binds to the bacterial cell membrane to affect its permeability and respiratory function, leading to bacterial apoptosis [53]. Photos of CFU reduction of \textit{S. aureus} and a significant inhibition zone of \textit{E. Coli} can be seen in Fig. 9c. The maximum inhibition zone of COCO-5 against \textit{E. Coli} was 8.6 cm, showing an excellent antibacterial effect. The COCO-5 reuse ability was verified by 5 \textit{E. Coli} antibacterial cycles (Fig. 9d). After 5 cycles, the antibacterial rate of COCO-5 to \textit{E. Coli} was still maintained at 80.99\%, showing excellent stability.

3.5. Mechanical stability test

The stability after multiple cycles of COCO-5 was also verified by mechanical performance testing (Fig. 10). Divided into two groups tested mechanical properties of cotton fabrics, unused COCO-5 and COCO-5 used five times. In the first group (Fig. 10a), compared to cotton fabrics and unused COCO-5, the stress and strain of COCO-5 after photocatalytic degradation (5 times) decreased slightly, which may be due to the visible light radiation that reduces the mechanical properties of the cotton fibers[54,55]. In the second group (Fig. 10b), the stress and strain of COCO-5 decreased slightly after antibacterial experiments (5 cycles) compared to the unused COCO-5. This may be because the bacterial medium weakened the strength and toughness of cotton fibers. However, compared with pure cotton fabric, the difference in COCO-5 stress and strain after 5 antibacterial experiments was slight, which verified the durability of COCO-5 in mechanical properties.

Fig. 8. (a) Cycle photocatalytic degradation of MB by COCO-5, and (b) photocatalytic activity of COCO-5 to a variety of dyes (CY: cationic yellow; CR: cationic red; AR: anionic red; AY: anionic yellow; NR: neutral red).

Fig. 9. (a) Bacterial reduction of COCO-5, cotton fabrics, cotton fabrics-NC and blank (nothing on it) samples, (b) antibacterial rate of COCO-5 against \textit{S. Aureus} and \textit{E. Coli}, (c) Photos of the bacterial CFU reduction of \textit{S. Aureus} and the zone of inhibition of \textit{E. Coli}, and (d) antibacterial ratio to \textit{E. Coli} of COCO-5 after 5 cycles.
Fig. 10. Stress–strain curves: (a) cotton fabrics, unused COCO-5 and COCO-5 after 5 photocatalytic degradation cycles of dyes, (b) cotton fabrics, unused COCO-5 and COCO-5 after 5 antibacterial cycles.

4. Conclusion

In this study, Cu$_2$O was synthesized in-situ on cotton fabrics and used NC as “bridge”, which ensured the good dispersion of Cu$_2$O and allowed it to be recycled. The fabricated cotton fabrics/Cu$_2$O-NC composite material can efficiently degrade the dye by photocatalysis, and is also an ideal antibacterial material. A variety of technical tests have analyzed the photocatalytic degradation mechanism of cotton fabrics/Cu$_2$O-NC, and the practicality of this research strategy has been illustrated by recycle use. In-situ synthesis of nano-functional particles based on textile materials is a promising process route, and the ideal recyclable nanocomposites can be prepared by combining different organic-inorganic materials.

5. Credit author statement

Xiuping Su: synthesized the composite materials and wrote the paper. Wei Chen: measured the antibacterial experiments. Yanna Han: designed and supervised the experiments. Duanchao Wang: designed and supervised the experiments. Juming Yao: designed and supervised the experiments.

Declaration of Competing Interest

The authors declared that there is no conflict of competing interest.

Acknowledgments

This work was supported by Technology Planning Project of Shaoxing (2018C30012; 2017B70069), the National Science Foundation of Zhejiang Province (GG19E030011), and the Project of Shaoxing University Yuanpei College (KY2018Z01).

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apsusc.2020.147945.

References

[1] J. Barnett, S. Rogers, M. Webber, B. Finlayson, M. Wang, Sustainability: transfer project cannot meet China’s water needs, Nature 527 (2015) 295–297.
[2] M. Song, R. Wang, X. Zeng, Water resources utilization efficiency and influence factors under environmental restrictions, J. Cleaner Prod. 184 (2018) 611–621.
[3] T. Hashino, K. Onaka, Industrial districts in history and the developing world, Springer, 2016.
[4] T.H. Ngo, T.T. Hien, N.T. Thuan, N.H. Minh, K.H. Chi, Atmospheric PCDD/F concentration and source apportionment in typical rural Agent Orange hotspots, and industrial areas in Vietnam, Chemosphere 182 (2017) 647–655.
[5] D. Miklos, C. Remy, M. Jekel, K.G. Linden, J.E. Drewes, U. Hubner, Evaluation of advanced oxidation processes for water and wastewater treatment – A critical re-
view, Water Res. 139 (2018) 118–131.
[6] J. Hu, P. Zhang, W. Ai, L. Liu, Y. Liang, W. Cui, In-situ Fe-doped g-C$_3$N$_4$ heterogeneous catalyst via photocatalysis–Fenton reaction with enriched photocatalytic performance for removal of complex wastewater, Applied Catalysis B-environ-
mental 245 (2019) 130–142.
[7] W. Shi, H. Ren, M. Li, K. Shu, Y. Xu, C. Yan, Y. Tang, Tetracycline removal from aqueous solution by visible-light-driven photocatalytic degradation with low cost red mud wastes, Chem. Eng. J. 382 (2020) 122876.
[8] Y. Sun, M. Chen, H. Liu, Y. Zhu, D. Wang, M. Yan, Adsorptive removal of dye and antibiotic from water with functionalized zirconium-based metal organic frame-
work and graphene oxide composite nanomaterial Uio-66-OH/GO, Appl. Surf. Sci. 525 (2020) 146614.
[9] E.D. Brown, G.D. Wright, Antibacterial drug discovery in the resistance era, Nature 529 (2016) 336–343.
[10] H.M. Hegab, A. Elmekawy, L. Zou, D. Mulcahy, C.P. Saint, M. Ginic-Markovic, The controversial antibacterial activity of graphene-based materials, Carbon 105 (2016) 362–376.
[11] J. Podporska-Carroll, A. Myles, B. Quilty, D.E. McCormack, R. Fagan, S.J. Hinder, D.D. Dionysius, S.C. Pillai, Antibacterial properties of F-doped ZnO visible light photocatalyst, J. Hazard. Mater. 324 (2017) 39–47.
[12] H.J. Kim, E.C. Yim, J.H. Kim, S.J. Kim, J.Y. Park, I.K. Oh, Bacterial nano-cellulose triboelectric nanogenerator, Nano Energy 33 (2017) 130–137.
[13] W. Li, B. Li, M. Meng, Y. Cui, Y. Yu, Y. Zhang, H. Dong, Y. Feng, Bimetallic Au/Ag decorated TiO$_2$ nanocomposite membrane for enhanced photocatalytic degradation of tetracycline and bactericidal efficiency, Appl. Surf. Sci. 487 (2019) 1008–1017.
[14] D.C. Wang, H.Y. Yu, D. Qi, M. Ramasamy, J.M. Yao, F. Tang, K.C. Tam, Q.Q. Ni, Supramolecular self-assembly of 3D Conductive Cellulose Nanofiber Aerogels for Flexible Supercapacitors and Ultrasensitive Sensors, ACS Appl. Mater. Interfaces 11 (2019) 24435–24446.
[15] S. Wang, A. Lu, L. Zhang, Recent advances in regenerated cellulose materials, Prog. Polym. Sci. 53 (2016) 169–206.
[16] O. Nechyporchuk, M.N. Belgacem, J. Bras. Production of cellulose nanofibrils: A review of recent advances, Ind. Crop. Prod. 93 (2016) 2–25.
[17] F. Rol, M.N. Belgacem, A. Gandini, J. Bras. Recent advances in surface-modified cellulose nanofibrils, Prog. Polym. Sci. 88 (2019) 241–264.
[18] D. Kracher, S. Schellbrandner, A.K. Felske, E. Brezinmayr, M. Preimis, K. Ludwiczka, D. Haltrich, V.G. Eijjk, R. Ludwig, Extracellular electron transfer systems fuel cellulose oxidative degradation, Science 352 (2016) 1098–1101.
[19] J. Luo, L. Steier, M.K. Son, M. Schreier, M.T. Mayer, M. Grätzel, Cu$_2$O nanowire photocathodes for efficient and durable solar water splitting, Nano Lett. 16 (2016) 1848–1857.
[20] C.G. Morales-Guio, L. Liardet, M.T. Mayer, S.D. Tilley, M. Grätzel, X. Hu, Photoelectrochemical hydrogen production in alkaline solutions using Cu$_2$O coated with earth-abundant hydrogen evolution catalysts, Angew. Chem. Int. Ed. 54 (2015) 664–667.
[21] S. Kumar, C.M. Parlett, M.A. Isaacs, D.V. Jowett, R.E. Douthwaite, M.C. Cockett, A.P. Lee, Facile synthesis of hierarchical Cu$_2$O nanocubes as visible light photo-
catalysts, Appl. Catal. B 189 (2016) 226–232.
[22] A. Lee, J.A. Libera, R.Z. Waldman, A. Ahmed, J.R. Avila, J.W. Elam, S.B. Darling, Conformal nitrogen-doped TiO$_2$ photocatalytic coatings for sunlight-activated membranes, Adv. Sustainable Systems 1 (2017) 1600041.
[23] A. Errokh, A.M. Ferraria, D.S. Conceicao, et al., Controlled growth of Cu$_2$O nanowires on copper substrates using a facile hydrothermal method, J. Mater. Sci.: Mater. Electron. 29 (2018) 15271–15281.
[24] Y.M. Xia, Z.M. He, J.B. Su, B. Tang, Y. Liu, Enhanced photocatalytic performance of Z-scheme Cu$_2$O/Bi$_5$O$_7$I nanocomposites, J. Mater. Sci.: Mater. Electron. 29 (2018) 13019–13028.
[25] X. Yu, J. Zhang, J. Zhang, J. Niu, J. Zhao, B. Yao, Photocatalytic degradation of ciprofloxacin using Zn-doped Cu$_2$O particles: analysis of degradation pathways and intermediates, Chem. Eng. J. 374 (2019) 316–327.
[26] J. Nie, C.Y. Li, Z.Y. Jin, W.T. Hu, J.H. Wang, T. Huaz, Y. Wang, Fabrication of
Enhanced photocatalytic performance of ZnO-based photocatalysts has been extensively studied, with various modifications and combinations to improve their performance. For instance, the use of Ag3Bi2Te57 plasmonic photocatalyst with enhanced photocatalytic activity for degradation of tetraethyl lead, ACS Appl. Mater. Interfaces 7 (2015) 17061–17069.

Layer by layer assembly of nanosilver for high performance cotton fabrics, Fibers Polym. 17 (2016) 418–426.

Photocatalytic performance of Cu2O/CdS composites was enhanced through the construction of novel Cu2O/Bi24O31Br10 composites and excellent photocatalytic performance, J. Mater. Sci.: Mater. Electron. 29 (2018) 19544–19553.

The construction of novel Cu2O/PbBiO2Br composites with enhanced photocatalytic activity, Journal of Materials Science: Materials in Electronics: Mater Electron 30 (2019) 9843–9854.

Positive Onset Potential for Improved Water Reduction, ACS Appl. Mater. Interfaces 11 (2019) 38625–38632.

The Construction of Cu2O@TiO2 Composite photocatalysts with p-n heterojunctions formed on exposed Cu2O facets, their energy band alignment study, and their enhanced photocatalytic activity under illumination with visible light, ACS Appl. Mater. Interfaces 7 (2015) 1465–1476.

Efficient visible-light photocatalytic hydrogen evolution and enhanced photostability of core@shell Cu2O@g-C3N4 octahedra, J. Alloy. Compd. 753 (2018) 356–363.

A novel photocatalyst with enhanced photocatalytic activity for degradation of methyl orange in Cu2O system, Appl. Catal. A 512 (2016) 74–84.

Photocatalytic degradation pathway of methylene blue in water, Appl. Catal. B 31 (2001) 145–157.

Methylene blue degradation, Catal. Sci. Technol. 3 (2013) 1405–1414.

Photocatalytic degradation of methylene blue by CNT/TiO2 composites prepared from MWNT and titanium n-butoxide with benzene, J. Korean Ceram. Soc. 45 (2008) 651–657.

The effect of UV irradiation on methylene blue, Carbohydr. Polym. 223 (2019) 115101.

The antibacterial activity of Cu2O particles with controllable morphologies in acrylic coatings, Appl. Catal. A 512 (2016) 74–84.

Flower-like hierarchical h-Bi24O31Br10 particles and nanoframes with novel shapes, CrystEngComm 13 (2011) 6265–6270.

Photocatalytic performance enhancement of Cu2O/CdS heterostructures for photodegradation of organic dyes: Effects of CuO morphology, Applied Catalysis B Environmental 116 (2013) 81–86.

Flower-like hierarchical h-Bi24O31Br10 particles and nanoframes with novel shapes, CrystEngComm 13 (2011) 6265–6270.

3D Glasses/Polymers/Zeolites Nanocomposites with Enhanced Photocatalytic Activity, Microporous Mesoporous Mater. 211 (2017) 1–12.

Photocatalytic degradation of methylene blue by a nanocomposite system: synthesis, photocatalysis and degradation pathways, PCCP 17 (2015) 5345–5351.

Studies on the drastic improvement of photocatalytic degradation of acid orange-74 dye by TiPO capped CuO nanoparticles in tandem with suitable electron capturing agents, RSC Adv. 5 (2015) 45815–45823.

Fabrication of a Ag/Bi2Te57 plasmonic photocatalyst with enhanced photocatalytic activity for degradation of tetracycline, ACS Appl. Material Interfaces 7 (2015) 17061–17069.

IEEE Transactions on Nanotechnology, IEEE 20 (2019) 1–11.

Fabrication of a Ag/Bi2Te57 plasmonic photocatalyst with enhanced photocatalytic activity for degradation of tetracycline, ACS Appl. Material Interfaces 7 (2015) 17061–17069.

Fabrication of a Ag/Bi2Te57 plasmonic photocatalyst with enhanced photocatalytic activity for degradation of tetracycline, ACS Appl. Material Interfaces 7 (2015) 17061–17069.