Photocatalytic self-cleaning cotton fabrics coated by Cu₂(OH)PO₄

under Vis/NIR irradiation

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Abstract

In the present work, we designed a mild strategy to make Cu₂(OH)PO₄ (CHP) nanoparticles on cotton fabrics (CFs) to achieve multi-functionalities. The phytic acid (IP6) assisted method was employed to synthesize nanoparticles (CHP-IP6). Under Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray (EDX), transmission electron microscope (TEM), X-ray photoelectron spectroscopy (XPS) as well as thermogravimetric analysis (TGA), we characterized the coated cotton fabrics. The CHP-IP6 treated fabrics showed prominent photocatalytic activity, excellent photocatalytic stability and thorough discoloration of methylene blue (MB) stain under sunlight irradiation.

Keywords: cotton fabric; Cu₂(OH)PO₄; photocatalysis; self-cleaning

1. Introduction

Energy shortages and environmental pollution are two major challenges of the 21st century, limiting human society and economic development, particularly in developing countries [1]. Accordingly, it is urgent to find renewable energy sources rather than fossil fuels [2]. Compared with many other resources, solar energy is clean and inexhaustible, causing no pollution. Thus, it arouses increasing attention from people, which can be used either directly or indirectly [3]. Human activities that consume and contaminate large quantities of water are becoming increasingly acute in many places. Effective ways are therefore urgently required to reduce water consumption and to abate water pollution.

Traditional catalysts are difficult to recycle and separate from the reaction system. By immobilizing these catalysts onto solid supports, we can overcome this drawback [4]. As a supporting material, renewable resources of cotton fabric are characterized by good moisture absorption, air permeability, durability and biodegradability. Fabrics treated with self-cleaning technology can degrade contaminants or remove organic materials in wastewater. Such technology is very promising and attractive by its high catalytic efficiency, low cost, easy recycling and environmental sustainability [5, 6].

Though TiO₂ or ZnO modified fabrics aroused huge attention in the past few years, the wide band gap of these catalysts limits the efficiency of the solar-energy utilization [7-10]. Accordingly, it is the most urgent to develop an active and stable visible-light-responsive even near-infrared-driven photocatalysis fabric. Among the photocatalysts, Cu₂(OH)PO₄ has gained special attention primarily by its unique photocatalytic properties [11-13]. Recent studies show that CHP is a near-infrared-activated photocatalyst capable of directly generating photo-induced carriers under NIR irradiation. Also, CHP has been proven a promising Fenton reagent by its unique structure. Yet CHP photocatalysts reported in previous literatures

are difficult to recycle, limiting their further development [14, 15].

In the present work, an economical and 'green' reagent-phytic acid (IP6) serve as a soft template to prepare CHP. Next, a mild, versatile and green method was employed to immobilize of CHP on cotton fabric. Subsequently, we also studied photocatalytic activity of CHP and CHP coated cotton fabrics for the degradation of methylene blue (MB) under visible light and infrared light irradiation. Furthermore, by monitoring the removal of blue ink stain, we also evaluated self-cleaning property of CHP coated cotton fabrics under sunlight.

2. Experimental2.1.Materials and reagents

Plain weave 100% cotton fabric (50 mm \times 50 mm) in white color, purchased from Yancheng Kaiyuan Textile Co., Ltd. (China), was washed with hot deionized water several times and dried at 60 °C for 2 h. (3-aminopropyl) triethoxysilane (KH550) was purchased from Nanjing Chuagshi Chemical Company (China). All the chemical reagents were purchased from Sigma Aldrich (China), which include Dopamine (DA), Glutaric dialdehyde, copper (II) nitrate trihydrate (Cu(NO₃)₂·3H₂O), disodium hydrogen phosphateand methylene (Na₂HPO₄·2H₂O), phytic acid (IP6), blue (MB). All chemicals applied in this work were of analytical grade. All the chemicals were of analytical grade and used without further purification.

2.2. Methods

2.2.1. Preparation of Cu₂(OH)PO₄ photocatalysts

We synthesized $Cu_2(OH)PO_4$ photocatalysts under a facile hydrothermal process [16]. For a typical hydrothermal synthesis procedure, 2 mmol $Cu(NO_3)_2 \cdot 3H_2O$ was dissolved in 45 mL water, and 5 mL 0.005 mol·L⁻¹ IP6 solution was added to the noted solution. Next, before 1 mmol Na₂HPO₄·2H₂O was added under vigorous stirring, the solution was heated to boiling point. Then, the solution was transferred into a Teflon-lined stainless-steel autoclave (100 mL) and heated at 120 °C for 8 h. Subsequently, the samples obtained were rinsed with ethanol and water at least 3 times, and dried in a vacuum oven at 60 °C for 12 h. For comparison, Cu₂(OH)PO₄ photocatalysts were prepared using the above noted methods without adding IP6. The samples prepared with and without IP6 were labeled as CHP-IP6 and CHP, respectively.



Figure 1. Schematic illustration for the fabrication process of CHP in the presence of IP6.

2.2.2. Fabrication of Cu₂(OH)PO₄ photocatalysts coated cotton fabrics

First, the cotton fabrics (5 cm \times 5 cm) were immersed to the solution containing ethanol(45 ml), deionized water (2.5 ml) and KH550 (2.5 mL) under constant stirring for 2 h. Next, the cotton fabrics were dried at 60 °C for 2 h. Then, 0.1 g of as prepared Cu₂(OH)PO₄ photocatalysts were dispersed in 50 ml DA aqueous solution (0.2 mg/mL) under constant stirring for 1h. Subsequently, the mixed solution was centrifuged and washed with deionized water 3 times. Finally, the Cu₂(OH)PO₄ photocatalysts and fabrics were added to the glutaraldehyde solution (10%) under vigorous stirring. After being stirred for 2 h, the fabrics were washed with deionized water, and the sample named as CHP-IP6/Cotton was dried at 60 °C for 60 min.

2.3. Materials Characterization

We tested the X-ray diffraction (XRD) of the samples on an X-ray diffractometer (D8 Adv. Bruker, Karlsruhe, Germany), with monochromatized CuKa (λ =0.15418 nm) radiation at 2θ angles ranging from 10 to 80. Using an IRPrestige-21 spectrometer (Shimadzu, Japan), we recorded FTIR spectra of uncoated and coated cotton fabrics. The morphologies of the prepared samples were taken under the scanning electron microscope (FESEM, JOEL, JSM-6700F) as well as transmission electron microscopy (TEM, Philips, and CM120). In the meantime, the X-ray energy dispersive spectroscopy (EDS, X-Max, Oxford Instruments) installed on the SEM was employed to verify the components of CHP-IP6/Cotton composites. We analyzed the surface chemical composition of CHP-IP6/Cotton composites under X-ray photoelectron spectroscopy (XPS, PHI Quantum 2000). Diffuse reflectance spectra (DRS) of the samples were recorded using a UV-Vis-NIR spectrophotometer (U4100, Hitachi) with an integrating sphere attachment ranging from 200 to 2500 nm and with BaSO4 as the reference standard. By conducting thermogravimetric analysis (TGA, Q500) and using nitrogen as the purging gas over a temperature range of 30-600 °C at a heating rate of 10°C/min, we investigated the decomposition of the coated cotton fabrics.

2.4. Photocatalytic activity

The photocatalytic activity of the samples was evaluated by photodegradation of

MB at ambient temperature under visible and infrared light illumination, respectively. 50 mg of the obtained samples were particularly added into 60 mL MB with an initial concentration of 20 mg L^{-1} aqueous solution, and the mixed solution was magnetically stirred in dark for 30 min to build an adsorption-desorption equilibrium. Next, 1.0 mL of 30% hydrogen peroxide solution was added. Subsequently, the photodegration was performed using 300W xenon lamp with a 420 nm or 800 nm cut-off filter. Using UV-Vis spectrophtotometer (Hitachi, UV-1080, Japan) at a wavelength of 665 nm, we determined the concentration of MB in the solution at given time intervals. The degradation efficiency was defined as C/C_o, where C₀ denotes the concentration of the MO after equilibrium, and C is the concentration at different time intervals after irradiation. For the composites of CHP-IP6/cotton, the fabric was fixed on the stainless-steel bracket with one side of the fabric facing upward and the other side facing downward. Then, 60 mL MB aqueous solution (5mg L^{-1}) with 1.0 mL of 30% hydrogen peroxide were applied for the photocatalytic evaluation.

To study the effects of relevant active species, we investigated hydroxyl radicals ('OH), superoxide radicals (' O_2^-) and holes (h⁺) by adding 1 mM tert-butanol (t-BuOH), 1 mM p-benzoquinone (BQ) or 1mM ethylenediamine tetraacetic acid disodium salt (EDTA-2Na) into the MB solution before adding the photocatalyst, respectively. The experiment was similar to the photodegradation experiment.

2.5. Self-cleaning property

According to the discoloration of blue ink, we assessed self-cleaning property of the samples. One drop of blue was dropped onto fabric samples (2.5 cm×2.5 cm). The

stained specimens were irradiated under solar light in a clear day. Also, their photographs were taken at different intervals.

3. Results and discussion

3.1. Raman and FTIR analysis

Raman spectra of the as-prepared CHP-IP6 powders are shown in Figure s1. The lattice OH^{-1} vibration bands were observed at 816 cm⁻¹. The Raman bands at 976⁻¹ and 453 cm⁻¹were attributed to the v_1 and v_2 mode of the phosphate vibration, respectively. The v_3 mode was observed at 1020 cm⁻¹, and the v_4 modes were at 646, 627 and 557 cm⁻¹. The stretching modes of -OH, symmetric stretching vibrations of PO₄³⁻ and vibrations of Cu-O bond were observed from infrared spectrum of the CHP-IP6 powders (Figure s2), also confirming the formation of pure copper hydroxyphosphate [17].



Figure 2. FTIR spectra of the pristine and the coated cotton fabric.

The FTIR spectra of the pristine and the coated cotton fabric are shown in Figure 2. Figure 2 shows that the broad absorption bands at 3340 cm^{-1} and 3275 cm^{-1} of the

coated fabrics were assigned to the O-H stretching vibration of cotton, proving the reduction of hydroxyl groups on the surface of fiber. This can also be confirmed by the reduction of peaks at 1158.0 cm⁻¹ and 1107.0 cm⁻¹, representing the C-O stretching vibration of the primary and the secondary alcohol, respectively. The absorption peak at 1052.9 cm⁻¹ was slightly increased, resulting from the v_2 mode of the phosphate vibration [18]. Absorption bands at 994 cm⁻¹ represented P-O stretching vibrations of PA [19].

3.2. XRD analysis

The XRD pattern (Figure s3) shows the highly crystalline structure of as-prepared samples. The characteristic diffraction peaks of CHP and CHP-IP6 agreed with the JCPDS File no. 36-0404 with the chemical formula $Cu_2(OH)PO_4$, crystallized in an orthorhombic system with the lattice constants: a=8.43 Å, b=8.08 Å, and c=5.90 Å.



Figure 3. XRD patterns of the pristine and the coated cotton fabric.

Figure 3 shows that for both the original and coated cotton fabrics, the characteristic peaks of a crystalline cellulose structure in the cotton fabric appeared at

peak $2\theta = 14.8$, 16.7, 23.1 and 34.6° [20]. The characteristic peak of CHP from the coated fabrics at $2\theta=30.17^{\circ}$ can be indexed to (220) of JCPDS No. 36-0404.

3.3. SEM images and EDS analysis

The typical FESEM images of the as-prepared products obtained are given in Figure s1. It is further observed under TEM that the morphology of CHP (Figure s4a) is microrod with a length of 200µm and width of 300nm, and CHP-IP6 (Figure s4b) is aquasi-uniform flake-like structures with the width of 30-100nm (Figure s4c). The morphological properties of untreated and CHP-IP6 coated fabric are shown in Figure 4, respectively.



Figure 4. SEM images of (a) cotton fabrics, (b) CHP-IP6 coated cotton fabrics and (c) EDS of CHP-IP6 coated cotton fabrics.

In comparison with the CHP-IP6/cotton fabric, cotton fabric has a smooth surface before the coating process (Figure 4a). Yet the surface of the fabrics coated with CHP-IP6 is relatively rough and composed of many particles, as shown in Figure 4b. This proves that CHP-IP6 was successfully coated onto the fabric surface. It has been proven from Figure 4c that elemental C, O Cu and P can been found in the coated fabrics with the results consistent with the SEM images. 3.4. XPS analysis



Figure 5. XPS spectra of the coated cotton fabrics, (a) survey spectrum; (b) Cu 2p; (c) P 2p; (d) O

1s.

The surface composition and chemical states of the Cu, P and O atoms in CHP-IP6/cotton(Figure 5a-d). The survey spectrum (Figure 5a) shows the copper photoelectron peaks (Cu 2p), the silver peaks (Ag 3d), the oxygen peaks (O 1s), the silicon peaks (Si 2p), the nitrogen peaks and the carbon (C 1s). This suggests that the CHP-IP6 particles are successfully grafted on the surface of cotton fabrics. It is proven from Figure 5b that the Cu $2p_{1/2}$ and Cu $2p_{3/2}$ spinorbital photoelectrons are located at binding energies of 956.5 eV and 936.5 eV, respectively, suggesting the Cu²⁺ state in the sample. Besides, the peaks observed at ca. 963.9 and 944.2 eV are characteristic of samples that contain Cu²⁺ ions with d⁹ configuration in the ground

state [17]. The peak at 134.3 eV in Figure 5c corresponds to P 2p, suggesting that the valence value of P atoms are all +5. The O 1 s peaks centered at the binding energies of 531.4 and 533.2 eV are shown in Figure 5d. The peak at 533.2 eV is associated with the Cu-O bond in CHP, while the other peak at 531.4 eV is probably correlated with the adsorbed oxygen.

3.5. UV-vis-NIR diffuse reflectance spectra



Figure 6. DRS spectra of the coated fabrics.

The optical absorption properties of the pristine and the coated cotton fabrics are shown in Figure 6. The pristine cotton fabrics show any obvious optical absorption. Yet the cotton coated fabrics show significant absorption in the whole range of wavelength. Moreover, CHP-IP6 coated cotton fabrics show stronger photoresponse compared with the CHP coated fabrics. The UV/Vis/NIR absorption spectrum of the Cu₂(OH)PO₄ samples derived from its diffuse reflectance spectrum is shown in Figure 6. As the results suggest, the CHP-IP6 has very broad absorption band and higher intensity. It is noteworthy that there is no obvious absorption when the wavelength is greater than 1500nm. The NIR absorption of CHP-IP6 can fit into four Gaussian peaks centered at 670, 864, 1121 and 1349 nm, respectively). The absorption observed beyond 2000 nm is attributed to the lattice and OH stretching modes [21].

3.6. Photocatalytic performance

The photodegradation efficiencies for CHP and CHP-IP6 under Vis-NIR are shown in Figure s5a. The CHP-IP6 showed very high efficiency and could degrade MB by 62% in merely 5min under Vis-NIR irradiation. In comparison with CHP, the degradation efficiency for CHP-IP is increased by 1.3 times in 20 min. The transient photocurrent responses of CHP and CHP-IP6 are shown in Figure s5b. As the results suggest, CHP-IP6 showed a less significant improvement photocurrent response than CHP. The CHP-IP6 or its coated fabrics showed good photocatalytic activity, which primarily resulting from the increased surface area, the stronger absorption strength as well as the higher photocurrent response of CHP-IP6. In the meantime, BET measurements show that CHP-IP6 has a larger specific surface area $(3.05 \text{ m}^2/\text{g})$, which is 1.7 times higher than that of the CHP. The trapping experiments were performed to explore the major active species of the catalyst in the photocatalytic process. Figure s4c shows that the decomposition efficiency was not changed significantly when BQ scavengers were added. Yet the catalytic activity decreased by 57% after the addition of t-BuOH which can trap •OH radicals. Besides, the reaction rate was reduced by 25% after the addition of EDTA-2Na that can capture holes (h+). The results of the trapping experiments confirm that •OH species and photogenerated holes are critical for the photocatalytic process [22].



Figure 7. (a) & (c) Photocatalytic MB degradation under Vis-NIR and NIR irradiation,

respectively; (b) cycling tests of under Vis-NIR irradiation.

The degradation efficiency of the CHP-IP6 coated fabrics shown in Figure 7a proves the higher photocatalytic efficiency (ca. 99%) in 30min. To determine the photocatalytic stability of CHP-IP6 coated fabrics, we performed the repeated degradation experiments to degrade MB under Vis-NIR irradiation five times. Figure 7b shows that 6.4% decrease of the photocatalytic activity for MB degradation was obtained after five consecutive cycles, suggesting the high stability of the CHP-IP6 coated fabrics in the photocatalytic process for MB degradation. Besides, we tested catalytic properties of the coated fabrics under infrared irradiation (Figure 7c). The photodegradation ratios of MB over CHP and CHP-IP6 coated fabrics were 40% and 72% after 12 h under NIR irradiation. This suggests that the sample has certain catalytic activity under infrared light.

3.7. TGA analysis



Figure 8. TGA curves of pristine cotton and coated fabrics

Thermogravimetric analysis was conducted to evaluate the thermal stability and degradation behaviour of the fabrics (Figure 8). TGA curve fell into primary, core and char decomposition regions, respectively [23]. In the primary region between 30-150 °C, mass weight of the cotton fabric resulted from the evaporation of water in the amorphous region. In the core region, due to the single stage degradation process of polymer chain, there was a sudden drop between 250 and 380 °C for all the samples.

In the final stage, complete decomposition of polymer chains appeared at 400 and 600 °C for unmodified and coated cotton fabrics, respectively. The CHP-IP6 coated layer improved the thermal stability of the cotton fabrics. The residue for the coated fabrics was found as 18.7wt%, while the pristine cotton was found only 8.5wt%.



3.8. Self-cleaning properties



The images of stain degradation on fabrics after 3, 6, 9 and 18 h of sunlight in the self-cleaning test are given in Figure 9. It is clear from the figure that the stain of the pristine fabrics remained after being irradiated for 12 h. Both CHP and CHP-IP6 coated cotton fabrics showed good catalytic effect for stain degradation, suggesting the excellent photocatalytic property of the coated fabrics. In comparison with CHP coated fabrics, the color of stains on CHP-IP6 fabrics is much lighter at the same time, suggesting the consistence with the effect of photocatalysis presented earlier.

4. Conclusions

In conclusion, we have successfully prepared the novel CHP-IP6/CFs with different using a facile and mild method. We prepared CHP-IP6 nanoparticles and then coated them effectively on the surface of the cotton fibers. Whether under Vis-NIR or NIR irradiation, both CHP-IP6 and CHP-IP6 coated fabric showed high catalytic efficiency. Furthermore, the CHP-IP6/CFs showed a excellent sunlight driven self-cleaning properties, suggesting their bright application prospect in multifunctional textiles.

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Figure captions:

Figure 1. Schematic illustration for the fabrication process of CHP in the presence of IP6.

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Figure 4. SEM images of (a) cotton fabrics, (b) CHP-IP6 coated cotton fabrics and (c)

EDS of CHP-IP6 coated cotton fabrics.

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Figure 9. Photocatalytic degradation of MB stain on pristine (a), CHP (b) and CHP-IP6 (c) cotton fabrics under solar irradiation.