In situ growth of MnO₂ on pDA-templated cotton fabric for degradation of formaldehyde

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Abstract Degradation of formaldehyde (HCHO) in interior decoration has been an urgent issue due to its toxicity nature and potential threats to human health. In this work, manganese dioxide nanoparticles (MnO₂ NPs) were in situ grown on the polydopamine (pDA)-templated cotton fabrics for environmentally friendly HCHO degradation applications. The morphology, elemental composition, and crystal structure of the cotton/pDA/MnO₂ were characterized by scanning electron microscopy–energy dispersive X-ray spectrum, Fourier transform infrared, X-ray diffractometer and X-ray photoelectron spectroscopy, respectively. The degradation of HCHO by the as-developed cotton/pDA/MnO₂ was measured in a self-made quartz reactor, and the stability of adsorption was evaluated by cyclic experiments. The results showed that the HCHO removal efficiency reached to 100% within 20 min after three cycles, suggesting that the as-prepared fabrics exhibited good stability for the degradation of HCHO. The development of MnO₂ NPs coated fabrics provides new strategies in degradation HCHO in interior decoration.

Keywords MnO₂ NPs · Cotton fabric · pDA · HCHO · Removal efficiency

Introduction

Decorative materials, furniture boards and building materials are widely used in interior decoration, resulting in an inevitable problem of indoor formaldehyde (HCHO) pollution. Long-term exposure to HCHO may cause serious harm to human respiratory tract, skin diseases and nervous system, and even increased incidence of cancer (Songur et al. 2010; Kim et al. 2011; İnci et al. 2013). Therefore, it is of great significance to develop efficient and stable HCHO scavenging technology for indoor air purification. At present, physical adsorption (Chen...
et al. 2017a; Falco et al. 2018), green planting (Chen et al. 2017b), ozone (Zhu et al. 2017a) and catalytic oxidation (Quiroz et al. 2013; Nie et al. 2016; Bai et al. 2016) are the widely applied methods to remove HCHO. Physical adsorption method is simple and easy to perform, but the performance of the adsorbent is not stable with issues of adsorption saturation and secondary pollution. Green planting can decompose HCHO by photosynthesis, but its removal efficiency is low and there is no adsorption efficacy when dealing with high concentrations of HCHO. Ozone’s effect on HCHO is only limited to that in air state but not to the pollution source. In the catalytic oxidation method, HCHO is firstly oxidized to formic acid under the action of catalyst followed by conversion into nontoxic CO2 and H2O. Among these methods, catalytic oxidation has the advantages of simple operation, high conversion efficiency and no secondary pollution, demonstrating itself to be the most effective method in removal of indoor HCHO pollution.

Manganese dioxide (MnO2) as a transition metal oxide is an efficient catalyst for the catalytic oxidation of HCHO due to its low-cost, abundant surface hydroxyl groups and variable manganese valence (Rong et al. 2018; Wang et al. 2019; Dai et al. 2020; Ji et al. 2020; Zhu et al. 2017b) reported that Ce-modified MnO2 showed great activity for HCHO oxidation at a low temperature. Wang et al. (2017) designed layered-structure MnO2 with different amounts of manganese vacancy for catalytic oxidation of HCHO. Lu et al. (2016) fabricated graphene-MnO2 hybrid nanostructure as a new catalyst for HCHO oxidation. Although several highly active MnO2 catalysts have been successfully synthesized, they cannot be used directly for practical applications. The reason for this is mainly due to the powder form of MnO2 catalysts, and a carrier is usually needed to support them for subsequent catalytic oxidation. Because of its unique porous structure, the fabric has good air permeability, demonstrating itself as ideal carriers for adsorb formaldehyde by loading particle catalyst (Memon et al. 2017; Han et al. 2017; Yuan et al. 2019; Xu et al. 2019). Unfortunately, the interaction between catalyst and fibers is weak (Zhu et al. 2019; Xiao et al. 2021). Therefore, how to expose the active sites of the catalysts to maintain its high activity and stability is still a great challenge.

In this work, MnO2 NPs were synthesized on pDA-templated cotton fabrics via a facile hydrothermal route. Due to the abundant catechol functional groups of pDA which can chelate with Mn metal ions, the MnO2 nanoparticles were uniformly dispersed on the surface of cotton fibers. The MnO2-loaded fabrics had rich porosity and highly exposed active sites, leading to a thorough and quick conversion of HCHO into CO2 under light conditions. The stability of the MnO2-loaded fabrics in HCHO removal was evaluated by performing repeated adsorption-degradation cycles. The possible reaction mechanism of HCHO removal by MnO2-loaded fabric was also explored.

**Experimental**

**Materials**

Cotton fabrics with a density of 135 g/m2 were supplied by Wuhan Yudahua Textile Co., Ltd (Wuhan, China). Hydroxytyramine hydrochloride (dopamine hydrochloride) was provided by Aldrich Chemical Co. (Milwaukee, USA). Potassium permanganate (KMnO4), tris(hydroxymethyl) aminomethane (Tris), sodium hydroxide (NaOH) and acetone were purchased from Aladdin Chemical Co., Ltd (Shanghai, China).

**Preparation**

MnO2 NPs coated cotton fabrics was fabricated by in situ growth method, as shown the preparation process in Fig. 1. Initially, cotton fabrics were immersed into a freshly dopamine solution (2 mg/mL, pH = 8.5) in an overhead shaker at 30 rpm. After self-polymerization for 24 h, the fabrics were washed with deionized water and dried. The obtained cotton fabrics are coded as cotton/pDA/MnO2.

**Characterization and measurements**

The morphology of the coated fabrics was characterized by scanning electron microscopy (SEM) (JSM-5600LV, JEOL, Japan) with an energy dispersive X-ray spectrum (EDS, Oxford Instruments, Oxford,
UK). Fourier transform Infrared (FT-IR) spectra were measured using a TENSOR 27 FT-IR spectrometer (Bruker, Germany). The crystal structure of the fabrics was examined on an X-ray diffractometer (D/max 2500, Rigaku, Japan) using Cu Kα radiation in the 2θ range of 10°–80°. The elemental composition of the cotton/pDA/MnO₂ was analysed by X-ray photoelectron spectroscopy using a Mg Kα source at 14.0 kV and 25 mA (PHI-5000 C ESCA, America). Thermogravimetry analysis was recorded on a thermal analyzer with a heating rate of 10 °C/min from 30 to 700 °C under nitrogen atmosphere (Netzsch TG209 F1, Germany). The washing durability of the cotton/pDA/MnO₂ was washed using a automatic washing machine (Haier, China) according to the GB/T 3923-013 with a stretching velocity of 50 mm/min.

**HCHO adsorption test**

The HCHO adsorption test of the as-prepared fabrics was carried out in a self-made quartz reactor (Fig. 2). The cotton/pDA/MnO₂ was cut into 10 × 10 cm² pieces and suspend in the center of the reactor. Then, HCHO vapor was quickly introduced into the reactor by heating a 1 mL HCHO solution (38 wt%). After 2 min, the HCHO solution was absolutely volatized at 90 °C with a stable concentration of HCHO vapor at 22.7 ppm. The concentrations of HCHO and CO₂ in the reactor were monitored in real time by respective detectors mounted on the upper panel of the reactor. The stability of the as-prepared fabrics in removal of HCHO was evaluated by performing repeated
adsorption-degradation cycles. Before each HCHO adsorption test, the adsorbed fabrics were exposed to light source for 3 h to ensure an thorough oxidization of HCHO into CO₂. The removal efficiency (E) of HCHO was evaluated according to the following Equation:

\[ E = \frac{C_0 - C}{C_0} \times 100\% \]  

(1)

where \( C_0 \) and \( C \) are corresponding to the initial and current concentration of HCHO, respectively.

**Result and discussion**

**Characterization of cotton/pDA/MnO₂**

The morphology of the pristine cotton, pDA coated cotton, and cotton/pDA/MnO₂ were detected by a scanning electron microscope. It can be seen from Fig. 3a that untreated pristine cotton exhibits a smooth surface, and the ribbon-like profile of cotton fibers are clearly observed. In Fig. 3b, the deposition and polymerization of dopamine has resulted in a rough surface of the fibers. The evenly distributed nanoparticles can be observed from Fig. 3c, and this is due to the incorporation of MnO₂ into the deposited pDA film on cotton fibers. In the SEM image captured under a high magnification (Fig. 3d), MnO₂ NPs are densely deposited on the surface of the cotton fibers without obvious aggregations. After the in situ growth process, the color of the cotton/pDA sample shifted from brown to black due to the loading of MnO₂ NPs (Insets of Fig. 3).

As a contrast, MnO₂ was grown on the surface of the cotton fiber without pDA pretreatment, as shown in the SEM of Fig. S1. The loading of MnO₂ on the fiber surface was heterogeneous, and significant clustered phenomenon was also observed. The main advantages of cotton fabric modified with dopamine are as follows: Firstly, the abundant phenolic hydroxy active functional group can be well cooperated with Mn ions, thus to promote the uniform and dense growth of MnO₂ on fiber surface. Secondly, the polydopamine exhibits strong adhesion, which can anchor nanoparticles on the fiber surface, and to improve the stability of fabric for better formaldehyde adsorption. Finally, pDA is a similar substance to melanin, which

![Fig. 3 SEM images of pristine cotton (a), cotton/pDA (b), and cotton/pDA/MnO₂ with different resolutions (c-d) (Insets: optical photos of corresponding samples); SEM–EDS elemental map of Mn (e), and EDS patterns collected from the cotton/pDA/MnO₂ (f)](image-url)
can adsorb sunlight therefore to promote the decomposition of formaldehyde.

The EDS mapping (Fig. 3e) and spectrum (Fig. 3f) of the cotton/pDA/MnO$_2$ show four peaks for carbon (C), oxygen (O), manganese (Mn) and potassium (K) elements with the weight% of 22.26%, 54.78%, 18.91% and 4.05%, respectively. The high content of Mn element indicates that large amounts of MnO$_2$ NPs have been anchored onto the fabric surface. The dense loading of MnO$_2$ NPs is due to the abundant phenolic hydroxyl groups of pDA through chelation effects, which promotes the uniform growth of MnO$_2$ NPs in the pDA film. These SEM and EDS results demonstrate that MnO$_2$ NPs have been uniformly dispersed on the surface of cotton fabrics.

The chemical structures of the pristine and nanocomposite deposited cotton fabrics were characterized by FTIR spectroscopy in the spectral ranges of 400 to 4000 cm$^{-1}$. The FT-IR spectra are shown in Fig. 4a. It can be observed that pristine cotton exhibits an obvious wide peak at 3330 cm$^{-1}$ arising from –OH stretching vibration in hydroxyl groups. The peak at 2900 cm$^{-1}$ corresponds to –CH bending absorption bands in methylene groups. The peaks at 1720 cm$^{-1}$ and 1435 cm$^{-1}$ are assigned to C=O stretching vibration and –CH$_2$ bending vibration, respectively. The peaks at 1330 cm$^{-1}$ and 1030 cm$^{-1}$ are resulted from O–H in-plane deformation vibration and C–O stretching vibration, respectively (Ran et al. 2019; Cheng et al. 2021). Similar characteristic peaks are appeared in the FTIR pattern of cotton/pDA. Besides, the extra peak at 1660 cm$^{-1}$ is due to the stretching vibration effects of benzene ring groups, which can be attributed to the polymerization of dopamine on cotton surface (Ran et al. 2019). In addition, the intensity of the absorption peak at 3330 cm$^{-1}$ is stronger than the original cotton, which is mainly due to the increase of reactive OH groups on the fiber surface after modification with dopamine. After MnO$_2$ is anchored on the surface of cotton fibers, the pristine characteristic peaks of cotton have been obviously weakened, and the characteristic peak for MnO$_2$ appears. For example, the peak (725 cm$^{-1}$) detected below 800 cm$^{-1}$ is attributed to metal-oxygen (Mn–O) stretching (Li et al. 2011). These results have confirmed the successful modification of cotton substrate through pDA templating and MnO$_2$ nanocomposite deposition.

The crystalline structure of the different cotton samples was investigated by XRD (Fig. 4b, c). In Fig. 4b, the pristine cotton exhibits four obvious diffraction peaks at 20 angle of 14.1°, 16.5°, 22.5° and 34.2°, which are attributed to the crystal faces (1–10), (110), (200), and (004) of cellulose I$\beta$, respectively (French and Cintrón 2013; French 2014; Cheng et al. 2018). The cotton/pDA fabrics present a similar XRD pattern to pristine cotton, suggesting the negligible effects of the pDA layer on the crystalline structure of cotton. According to reported studies, this is mainly due to the amorphous structure of pDA (Wang et al. 2018; Cheng et al. 2020). With respect to cotton/pDA/MnO$_2$ (Fig. 3c), the characteristic peak intensity of pristine cotton phase is decreased, which is possibly due to the growing of MnO$_2$ NPs on the surface of cotton fabrics. Furthermore, four extra diffraction peaks at 20 = 12.1°, 24.8°, 36.6° and 65.4° corresponding to the characteristic peaks (001), (002), (006) and (119) crystal planes of δ-MnO$_2$ (JCPDS No. 18-0802), respectively can be observed (Ma et al.

Fig. 4 FTIR (a) and XRD (b, c) pattern of pristine cotton, cotton/pDA, and cotton/pDA/MnO$_2$
The XRD results proved the presence of δ-MnO₂ NPs on the surface of cotton fabrics.

The surface chemical state of the as-prepared samples was further investigated by XPS. The XPS wide scan spectrum of cotton/pDA/MnO₂ proved the presence of C, O, Mn, and K elements on the cotton/pDA/MnO₂ (Fig. 5a). The K element is from the reactant KMnO₄, which is in good agreement with EDX results. The high resolution C1s spectrum in Fig. 5b can be deconvoluted into three peaks at 288.1 eV, 286.2 eV and 284.8 eV corresponding to the C=O, C–O/C–H, C–C bonds, respectively (Qi et al. 2021). Mn 2p XPS core level spectrum is shown in Fig. 5c, in which two peaks at 653.7 eV and 642.2 eV are attributed to Mn2p 1/2 and Mn2p 3/2 of Mn⁴⁺, respectively (Miao et al. 2021). Additionally, the spin-energy separation of 11.5 eV has agreed well with previously measured spectra of MnO₂ (Lu et al. 2017; Shi et al. 2018). The O1s spectrum can be fitted into three peaks at 533.7 eV, 531.5 eV, 529.7 eV, which are attributed to C–O/C = O, Mn–O–H, and Mn–O–Mn, respectively (Fig. 4d) (Wang et al. 2016).

After the modification of dopamine, polydopamine layers with several nanoscale thickness were formed on the fabric surface. The N element has not been observed at 400 eV, which can be attributed to the relatively thin polydopamine layer and low content. In Fig. 2d, the fiber surface is nearly completely covered by MnO₂ NPs. This has indicated that the fiber surface stack exhibited thick manganese dioxide layer, which might be leading to the invalid detection of N elements. XPS analysis indicated that MnO₂ NPs were successfully coated on the cotton fabric surface by in-situ growth.

Thermal properties

The thermal properties of cotton, cotton/pDA, and cotton/pDA/MnO₂ were characterized by TG analysis, as shown in Fig. 6. It can be observed that the residual weight of all samples exhibited a slight decrease in the initial stage (as shown the TG curves in Fig. 6a), which can be attributed to the water evaporation phenomenon. The temperature of TG analysis is up to 800°C, and the TG curve of cotton/pDA/MnO₂ fabric was gradually smoothed and remained unchanged. With the heating temperature of increasing to higher than 400 °C, the residual weight decreased rapidly with only 10% residue at 800 °C. Compared with the pristine cotton, the cotton/pDA shows a similar thermal decomposition
behavior due to the amorphous structure of pDA. The residual weight of the cotton/pDA is slightly higher than original cotton. After loading of MnO₂ NPs, however, the TG curve is totally different from either cotton or cotton/pDA. The residual weight of cotton/pDA/MnO₂ is 40.0% higher than cotton/pDA, and it has proven the excellent thermal stability of cotton/pDA/MnO₂. As it is known to all, the melting point of manganese dioxide is 535 °C. The MnO₂ NPs will be dissolved when the thermal treated temperature is higher than melting point, thus makes the measured curve gradually slow down. The enhanced thermal stability can be attributed to the enhanced carbonization and invigoration effect of cellulose chain as a result of MnO₂ NPs deposition.

According to DTG curves (Fig. 6b), the maximum thermal degradation temperature (DTG_max) of cotton fabric and cotton/pDA is very similar (355 °C and 354 °C, respectively). This is mainly because the amorphous structure of pDA has little influence on the thermal properties of cotton fibers. For cotton/pDA/MnO₂ sample, the DTG curve has two main weight loss stages occurring over 200 °C. The first DTG_max representing the decomposition of polymers was detected at 233 °C, which was much lower than the original cotton sample. This is mainly due to the existence of MnO₂ NPs, as the catalytic nanoparticles has reduced the activation energy and accelerated the depolymerization reaction. The second DTG_max was at 378 °C, which was related to phase transition from MnO₂ to Mn₃O₄ by the losing of oxygen from MnO₂ lattice (JCPDS No. 24-0734) (Yang et al. 2021).

HCHO adsorption property

The HCHO adsorption test of the cotton/pDA/MnO₂ was carried out in a sealed quartz reactor. In the presence of the as-prepared fabrics, the concentration of HCHO decreased from 22.7 ppm to 0 (Fig. 7a). The drop of HCHO concentration is due to the complete absorption of the HCHO by the coated MnO₂ NPs.

As shown in Fig. 7b, due to the higher concentration of HCHO, the removal efficiency of HCHO gradually increased and the adsorption rate of cotton/pDA/MnO₂ was faster at the initial stage. With the removal of HCHO, the adsorption rate became slower, and finally the HCHO was completely adsorbed in about 20 min.

In order to evaluate the effect of air circulation on the adsorption of HCHO by the cotton/pDA/MnO₂, the parameter of air flowing rate was introduced by turning on a fan mounted on the floor of the reactor. As shown in Fig. 7c, the concentration of HCHO from the 1 mL liquid formaldehyde after gasification was slightly less than 22.7 ppm after adding the fan. This phenomenon is due to the accelerated movement of HCHO molecules that leads to the backflow of HCHO. Obviously, the rate of HCHO adsorption by cotton/pDA/MnO₂ is faster after adding a fan, as the HCHO molecules will move faster to promote absorption.
The HCHO adsorption efficiency was studied before and after washing treatment (Fig. 7d), and it has indicated that the HCHO adsorption rate was slightly decreased after ten washing cycles. However, the HCHO can still be completely adsorbed, and this has proved that most MnO₂ NPs are still loaded on the fiber surface. This is due to the strong binding between MnO₂ and fiber, and the cooperation between pDA and Mn ion has enhanced the adhesion of loading MnO₂ with fiber matrix.

MnO₂ has been reported as a catalyst for decomposing HCHO. Herein, the efficiency of cotton/pDA/MnO₂ photocatalytic degradation of HCHO under the condition of sunlight and ultraviolet lamp was evaluated by the yield of CO₂ (Fig. S2). At the initial stage, the concentration of CO₂ was about 1000 ppm due to the presence of CO₂ in the air. Under the irradiation of sunlight and UV lamp, the concentration of CO₂ was increased with the irradiation time, and finally reached the maximum threshold of the detector (5500 ppm). In details, the concentration of CO₂ under sunlight irradiation rose faster and took less time to reach the maximum value than that under UV irradiation. The high solar intensity and temperature (2021.06.24, 3:00 p.m., 36 °C, Wuhan, China) of sunlight accelerated the decomposition of HCHO molecules, thus leading to the high efficiency of photocatalytic decomposition of HCHO. On the other hand, the concentration of CO₂ under UV irritation was slow at first and then increased sharply. The temperature in
the closed environment was low at the beginning of UV irradiation, resulting in a relatively slow decomposition rate of HCHO molecules. After irradiation for a certain time, the temperature rose and the decomposition of HCHO molecules was accelerated. Overall, cotton/pDA/MnO2 demonstrated its potential of being used as a catalyst to decompose the adsorbed HCHO into CO2 under the irradiation of either sunlight or UV lamp.

Further, a comparison of cotton/pDA/MnO2 with other fabric-based materials for the adsorption efficiency of formaldehyde is given in Table 1S. The as-prepared cotton/pDA/MnO2 exhibits outstanding adsorption efficiency of formaldehyde when compared to currently available fabric-based formaldehyde adsorption materials.

Proposed reaction mechanism

Based on the above-mentioned discussions, a possible reaction mechanism of HCHO removal on the cotton/pDA/MnO2 is proposed here as shown in Fig. 8. Firstly, the surface of MnO2 catalyst is oxidized by O2 in the air to form surface adsorbed oxygen, which then oxidizes HCHO as-adsorbed on the catalyst surface to methylene dioxygen (DOM) (as shown in Eq. ①) (Lin et al. 2019; Wang et al. 2020; Lam et al. 2021). Then, the DOM will be rapidly transformed into formate (HCOO–) species on the cotton/pDA/MnO2 (as shown in Eq. ②) (Huang et al. 2017). Finally, the formate species decompose into CO, which further oxidizes into CO2 (as shown in Eq. ③) (Sun et al. 2019; Ye et al. 2020). The excellent HCHO oxidation efficiency of the cotton/pDA/MnO2 catalyst can be mainly attributed to the following two aspects. First, cotton fabrics have a large specific surface area and porous structure, as can be observed from the microscope images, which is conducive to the HCHO diffusion to catalyst surface. In addition, pDA exhibited a similar structure to natural melanin pigment, which can absorb sunlight and facilitate the decomposition of various formate species into CO2. In summary, the cotton/pDA/MnO2 can adsorb HCHO, and followed by the reutilization.

Tensile property

The strain-stress tests were performed on cotton fabric before and after loading MnO2, as shown in Fig. S3. It can be seen that the strength of the fabric decreases obviously after loading MnO2, which is mainly due to the hydrothermal growth temperature is 80 °C, and potassium permanganate has been used as strong oxidant. The oxidant effect and high temperature can cause the damage of fiber, resulting in decreasing strength of yarn. However, in practical applications, MnO2 loaded fabric is mainly used to absorb and decompose formaldehyde for interior air, and the mechanical performance is not a key factor for removing HCHO.

Conclusions

In conclusion, pDA modified cotton fabrics with abundant phenolic hydroxyl groups served as anchoring points for MnO2 NPs deposition. The SEM, XRD and XPS results have demonstrated that δ-MnO2 NPs were uniformly dispersed on the surface of cotton fabrics after in-situ growth. The HCHO adsorption test results have indicated the excellent catalytic activity cotton/pDA/MnO2, applicable to effectively
adsorb and decompose the HCHO into CO₂ under the irradiation of either sunlight or UV lamp. The HCHO removal efficiency reached to 100% within 20 min after three cycles, suggesting the good stability of the as-prepared fabrics in the degradation of HCHO. The possible reaction mechanism of HCHO removal on the cotton/pDA/MnO₂ was also explored. The high adsorption and degradation efficiency are attributed to the high specific surface area and porous structure of cotton fabrics together with the natural melanin pigment like structure of pDA film. The in-situ growth of MnO₂ NPs on pDA-templated cotton fabrics is a promising strategy to solve the increasingly urgent problem of HCHO in interior decorations.

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