

Recyclable Ag/TiO₂@PDMS Coated Cotton Fabric with Visible-Light Photocatalytic for Efficient Water Purification

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Research Article

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Abstract

Multifunctional materials for water purification have attracted great attention due to the increased water pollution problems. However, fabricating the low-cost and recyclable separation material is still a challenge. Herein, we developed an Ag/TiO₂@PDMS coated cotton fabric with self-clean ability, high flux, superior visible-light photocatalysts ability, and recyclability via the “powder + glue” strategy. The composites exhibit superhydrophobic (water contact angle 157°), and high separation efficiency. The separation efficiency of 20 times of repeated use remains 16322 Lm⁻²h⁻¹ and the degradation rate of methylene blue (MB) remains almost no change. The high oil purification, catalytic property, excellent stability in harsh condition and recyclability enables the material as a satisfactory candidate for water purification.

Introduction

Water pollution, including frequent crude oil leakages and the discharge of the organic solvent, has become a serious threat to marine species, human beings, and the ecological environment.(Fan et al. 2021) Efficient, selective, economical, and eco-friendly materials for water purification are highly required. (Ahmad et al. 2019) Currently, the oil/water separation materials with distinct opposite affinities toward water and oil have gained increasing attention (Dong et al. 2019). Materials with special wettability were designed and fabricated by regulating the structure and controlling the material’s surface energy (Chen et al. 2019). Inspired by the nature superhydrophobic phenomenon, different kinds of super wetting materials(Su et al. 2016; Ueda and Levkin 2013), including polymer membranes(Jin et al. 2021; Nayak et al. 2021), metallic meshes(Liu and Jiang 2011), textiles(Cao et al. 2016; Chauhan et al. 2019; Cheng et al. 2019; Lin et al. 2019; Yang et al. 2020), and sponge-based 3D absorbents(Chi et al. 2021; Nong et al. 2021; Qu et al. 2021b) were investigated. However, wastewater contains various kinds of oils with different components but water-soluble dyes (Bonigari et al. 2018), most of the material can't satisfy the requirement of the micro-nano scale pore sizes for effective separation of oil-water emulsion (Ma et al. 2020a; Ma et al. 2020b; Yu et al. 2020; Zhan et al. 2020b). Importantly, separation materials are easily contaminated by oily and dye contaminations in the treatment of oily wastewater process, causing secondary pollution to the environment and the high comprehensive cost of post-treatment (Ma et al. 2020b). The poor stability of corrosion resistance, low reusability, complex and time-consuming fabrication process greatly restricted the practical application of the oil/water separation materials.

Photocatalytic techniques, induce reactive oxygen species to degrade pollutants into harmless low molecular weight molecules, are an effective approach to resolve water pollutions. (Li et al. 2021; Pan et al. 2020) TiO₂(Pan et al. 2019), α-Fe₂O₃(Zheng et al. 2018), ZnO (Lee et al. 2021), CeO₂ (Zhao et al. 2021), BiVO₃(Benaissa et al. 2021), and BiOBr (Liu et al. 2021b) are the most widely used nanoparticle photocatalytic materials. Titanium dioxide (TiO₂), fabricating efficient charge transport pathways, and generating long-lived charges for efficient photocatalysis has widely applied in the photocatalyst field; (Yu et al. 2021) The photocatalytic activity of anatase type TiO₂ is higher.(Arumugam et al. 2021; Fotiou

et al. 2016; Liu et al. 2021a; Qu et al. 2021a) However, the wide bandgap photocatalysts' light absorption is only achieved in the ultraviolet region, which greatly limits its application potential.

Herein, we deposited an eco-friendly and low-cost method to fabricate recyclable Ag-TiO₂@PDMS coated cotton fabric for oil/water separation and organic contaminants degradation. By combining the advantages of silver nanoparticles (Ag), we fabricated a heterojunction structured photocatalyst, which changed the light absorption range of TiO₂ and improved photocatalytic performance. After, polydimethylsiloxane (PDMS) was introduced as a "glue" attached the Ag-TiO₂ particles to form a micro-nano structure on the surface of cotton fabric, endowing with the superhydrophobic properties and high photocatalytic activity. The superhydrophobic/superlipophilic fabric can effectively separate the oil/water mixture and emulsion with high flux and high purity. Importantly, large-scale water-soluble organic contaminants are transferred into the photocatalytic activity sites due to the high photocatalytic effect. The separation efficiency of oil/water emulsion is as high as 16482 Lm⁻²h⁻¹, and the purity of separated oil is 99.98%, the tensile strength is 74.785 MPa. Moreover, the tightly attached Ag-TiO₂@PDMS on the flexible cotton fabric makes it easy to recycle and reuse after sunlight irradiation. Hence, the environmentally friendly, easy accessibility composite with high oil-water separation efficiency and visible-light photocatalytic activity, provides a novel approach to deal with the water pollution problems.

Experimental Section

Materials

Nano titania powder (Titanium(IV) oxide, 98%, anatase powder), Silver nitrate, cetyltrimethoxy silane (85%), Anhydrous ethanol (99.9%), cyclohexane (99.5%), tetrahydrofuran (99.0%), sodium Borohydride (98%), and Methylene blue (95%) were purchased from Shanghai Titan technology co. LTD. Sylgard 184 was obtained from Down Corning.

Preparation of silver decorated TiO₂ (Ag/TiO₂) particles

TiO₂ (0.2 g) and silver nitrate (5%, 10%, 15%, 20% and 25% of TiO₂ mas ration) were dispersed in distilled water (100 mL) and ultrasonic for 5 min. Then the pH of the solution was adjusted to 10 with ammonia and magnetic stirring for 10 min to get liquid A. The same molar amount of sodium borohydride as silver nitrate was weighed and dissolved in distilled water (10 mL) to obtain liquid B. Then, liquid A and liquid B were mixed and dispersed by ultrasonic for 30 min. The precipitate was collected and the precipitate was cleaned and then dried overnight in a drying furnace at 50°C to get Ag- TiO₂ powder. Then, the as-prepared Ag-TiO₂ was dispersed in 50 mL tetrahydrofuran, followed by adding 10uL, 20uL, 30uL, and 40uL cetyltrimethoxy silane with ultrasonic for 15 min, and then the fully stirred solution was filtered and the powder was dried in the oven at 50°C for 6 h. The prepared samples were named 5% Ag-TiO₂, 10%

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Ag-TiO₂, 15% Ag-TiO₂, 20% Ag-TiO₂, and 25% Ag-TiO₂ according to the mass ratio of silver nitrate in titanium dioxide.

Preparation of superhydrophobic cotton-based material

The modification process of TiO₂ particles and the fabrication schedule of Ag-TiO₂@PDMS coated fabric as illustrated in Scheme 1. The polydimethylsiloxane (PDMS) and curing agent were mixed with the mass ratio of 10:1 and dispersed into 50 mL cyclohexane and stirred for 30 min. Then, a certain amount of Ag/TiO₂ particles was added to cyclohexane containing PDMS and ultrasonic dispersion for 30 min. The cotton fabric was cut into 6×6 cm² size and put into Ag-TiO₂/PDMS solution with magnetic stirring for 2 h at 500 rpm. Finally, the soaked fabric was dried at 135°C for 3 h to obtain the Ag-TiO₂@PDMS coated cotton fabric.

Characterization

The micro morphologies and structure of the as-prepared coated fabric were observed by scanning electron microscopy (SEM) (JEOL SU8010) and transmission electron microscopy (TEM, Tecnai F20, Japan), and atomic force microscopy (AFM, Bruker edge). Chemical compositions of the composites were measured by energy dispersive spectra (EDS, KeveX), Fourier transform infrared spectra (FT-IR, Nexus 670), and X-ray photoelectron spectra (XPS, Thermo ESCALAB 250XI) and X-ray diffraction (XRD). Thermogravimeter (Diamond TG/DTA, PerkinElmer) was used to test the thermal stability by heating from 30°C to 800°C at a heating rate of 10 °C/min in an N₂ atmosphere. The water contact angles (WCAs) were carried out with a contact angle meter (OCA40 Micro, Data Physics, Germany). The droplet sizes of the feed and filtrate were tested by a dynamic laser scattering (DLS) analyzer measured (Malvern Zeta ZS). The ultraviolet-visible spectroscope (UV-vis, UV-2550) was used to assessing the MB concentrations in the feed and filtrate.

Water-in-oil immiscible emulsion separation

The Span 80, deionized (DI) water and oil were mixed at the weight ratio of 1:10:100 and vigorously stirred for 6 h. During the water-in-oil emulsion separation experiments, the as-prepared superhydrophobic fabric was fixed inherently between two tubes. The water-in-oil emulsions were poured into the container and permeated through the superhydrophobic coated cotton fabric. After separation, pure oil was flowed down and collected in the bottom vessel. The flux was calculated by calculating the volume of the collected oil within unit time by the following equation:

$$Flux = \frac{V}{A_t}$$

where V is the volume of collected emulsion permeated through the coated cotton fabric, A is the valid test area of the fabric, and t represents the valid time.

Photocatalytic Performance measurements

To evaluate the photocatalytic performance of Ag-TiO₂@PDMS coated cotton fabric, MB was used as the model pollutants probes. Photocatalysts (40 mg) were added into MB dye solution (50 mg/L, 100 mL). The solution was placed in the dark for 30 min to achieve adsorption equilibrium. Then, the photodegradation test was employed using a 300 W Xe lamp (BL-CHI-Xe-300) without any filter (320–2500 nm). A series of reaction solutions were collected at 10min intervals. The percentage of degradation is expressed as C/C_0 . Here, C_0 is the original concentration of the dye solution, and C is the dye concentration obtained each time.

Self-cleaning properties and reuse ability

The modified cotton fabric's self-cleaning property was tested by removing the dust and MB particles sprinkled on the cotton fabric using water droplets. For recycle and reuse ability measurement, the coated cotton fabric after oil/water separation was placed in the sunlight for a photocatalytic reaction for 1h and then again for filtration separation, repeated 20 times to verify the recycling performance of the separation material. Each analyzed sample was filled back for the next period of irradiation.

Results And Discussion

Hydrophobic Ag-TiO₂ particles with high visible light photocatalytic ability

The morphology and structure of the original TiO₂ particles (Fig. S1) and the hydrophobic 15% Ag-TiO₂ were observed by SEM and TEM imaging. TEM analysis shows that the silver particles in hydrophobic 15%Ag-TiO₂ are uniformly attached upon the TiO₂ particles and both Ag and TiO₂ nanoparticles presented nearly spherical shapes. In addition, the diameter of TiO₂ particles is about 100 nm while the diameter of silver particles is about 5 nm to 40 nm and mainly concentrates on 20 nm (Fig. 1a). The uniform distribution of silver particles on the surface of TiO₂ reduces the bandgap width of TiO₂ and the recombination rate of photogenerated electron-hole pairs thus improves the photocatalytic activity of the particles(Ibrahim et al. 2020). In HRTEM, the distance of the two adjacent planes corresponding to the (101) plane (d value = 3.52 Å) and Ag nanoparticles were identified the (111) plane (d value = 2.35 Å) (Fig. 1b). The ring electron diffraction patterns are presented in Fig. 1c.(Karimi-Maleh et al. 2020) Fig. 1d shows the (110), (101), (111), and (211) crystal faces of anatase type TiO₂ are respectively corresponding. In general, the sharp diffraction peak of silver nanoparticles can be found in the XRD

Loading [MathJax]/jax/output/CommonHTML/jax.js surface of modified titanium dioxide is deposited with good

crystalline silver nanoparticles. The FTIR spectrum in Fig. S2 also demonstrated the Ag presence. The 15% Ag-TiO₂ presents hydrophobic property (CA=157°) and the water droplets can slide freely on the filter cake, while the TiO₂ particles easy to absorb water (Fig. S3).

UV–vis diffuse reflectance spectra (UV–vis DRS) were used to assessing the light absorption property and electronic band structure of pure TiO₂ and Ag-doped TiO₂ particles. As shown in Fig. 1e, a wide and strong redshift of the absorption edge to the visible light (200–800 nm) reflection was observed of Ag-TiO₂ particles, which can be attributed to the electronic interactions between Ag and TiO₂, leading to good photocatalytic activity of Ag-TiO₂ under visible light.(Yu et al. 2021) (Xu et al. 2021) The effect of Ag deposition is observed on metal oxides bandgap through the differential reflectance spectroscopy (DRS) surface analysis. The modified metal oxides were absorbed in the visible region, and redshift (higher wavelength) is predicted in the bandgap of the metal oxides (Fig. 1f). It is to be noted that pure metal oxides have a wide bandgap TiO₂ = 3.2 eV and the bandgap of Ag-TiO₂ nanoparticles is identified as 2.78 eV. The modification of the band gap was assigned to the Ag deposition on the surface of the metal oxide nanoparticles. The nanocomposite materials showed longer wavelengths due to the SPR phenomenon and indicating the strong interfacial coupling between TiO₂ and the adjoining Ag in the metallic state. The bandgap energy (E_g) was calculated based on the Kubelka–Munk equation and Tauc's plots(Huo et al. 2021).

As shown in Fig. 1g, the as-prepared Ag-TiO₂ particles exhibit excellent photocatalytic activities for MB degradation under visible light irradiation. The photocatalytic performance increase to 80% as the Ag amount increased from 5 and 10 %, and the 15% Ag-TiO₂ particles show the best photocatalytic activity for visible light photocatalytic tetracycline degradation, which is far superior to commercial TiO₂. However, the photodegradation activity decreased while further increasing the Ag doping, the reason is that small amounts of Ag-doping increase the specific surface area and decreasing the nanoparticle size, providing a higher number of reactive sites for photocatalytic processes. But a higher Ag content strongly reflected the incident UV beam, decreasing the generation of electron-hole pairs, leading to a declination of the photocatalytic degradation ability.

The simultaneous photocatalysts experiments of TiO₂ and Ag-TiO₂ particles were carried out on the 50 mL of mixture solution of MB under visible light. As shown in Fig. 1h, there is almost no MB degradation of irradiation for TiO₂ under visible light. After modification, the 15% Ag-TiO₂ particles displayed enhanced dye degradation activity relative to TiO₂ both under sunlight (Fig. 1i). The intensity of the absorption peak at 628 nm weakened drastically with increasing photocatalytic time and completely disappeared after 50 min of irradiation for Ag-TiO₂ under UV-light while the degradation rate was 50.4% under visible light, indicating the enhanced photocatalysis properties.(Yu et al. 2021) (Wang et al. 2021) (Yan et al. 2020)

Hydrophobic Ag-TiO₂@PDMS coated cotton fabric

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The morphologies of Ag-TiO₂@PDMS coated cotton fabric obtained under different weight ratios of PDMS to Ag-TiO₂ are shown in Fig. S5, S6. As shown in Fig. 2a, a rough hierarchical surface was formed via attached the Ag-TiO₂ particles upon cotton fabric through PDMS polymer. The EDX elemental mappings also demonstrated the C, O, Ag, Ti, and Si elements are uniformly distributed in the prepared Ag-TiO₂@PDMS coated fabric, indicating the successful fabrication of superhydrophobic Ag-TiO₂@PDMS coated fabric (Fig. 2b). The FTIR spectrum of cotton fabric before and after coating modification was shown in Fig. 2c. It is evident that the hydrophobic treated fabric maintains the spectral characteristics of cotton fiber, and all three fabrics have characteristic peaks of cotton fiber at 3340 cm⁻¹, 2890 cm⁻¹, 1314 cm⁻¹, and 1020 cm⁻¹, corresponding to the -OH tensile vibration, the C-H contraction vibration, and the C-O contraction vibration in the cotton fabric. The infrared peak strength of the hydrophobically modified fabric at 1100 cm⁻¹ is related to the tensile vibration of Si-O in the PDMS contained in the first two hydrophobic modified fabrics. In addition, the infrared spectrum of the hydrophobic 15%Ag-TiO₂ fabric is the same as that of the 15% Ag-TiO₂ fabric because the content of hexadecyl trimethoxy silane is too little. Infrared peaks were observed at 795 cm⁻¹, 1260 cm⁻¹, and 2962 cm⁻¹, related to the symmetric contraction of Si-O-Si, the bending vibration of Si-C, and the asymmetric tensile vibration of -CH₃, respectively. The result indicates that PDMS has been successfully arranged on the fiber and the internal structure of cotton fiber has not been changed.

The chemical compositions and states before and after irradiation were further analyzed by XPS. The elements C, O, Ag, Ti, and Si were detected in the full spectrum of the Ag-TiO₂@PDMS coated cotton fabric while there are no Ti, Ag, and Si elements in the cotton fabric (Fig. 2d). Fig. 2e demonstrates that three different carbon chemical environments existed in the C1s spectrum of Ag-TiO₂@PDMS. The binding energies of 284.8 eV, 286.4, and 288.2 eV attributed to the C-C/ C = C bond, C-O bonds, and C-O-Ti bonds, respectively. As shown in Fig. 2f, the high-resolution O1s spectrum of the Ag-TiO₂@PDMS coated cotton fabric exhibited two peaks at 530.3 eV and 532.0 eV, which were assigned to Ti-O bonds and oxygen vacancies, respectively. The Si-O and Si-O-Si bonds indicating the successful attaching of PDMS on the cotton fabric (Fig. S8). Exhibited in Fig. 2g are the two different presence of titania state of Ti2p, divided into the Ti 2p_{3/2} for TiO-H at 459.1 eV and Ti 2p_{1/2} for TiO₂ with BEs of 464.8 eV, respectively. The Ti 2p_{1/2} - Ti 2p_{3/2} splitting (5.7 eV) is related to the Ti⁴⁺ oxidation state, implying the existence of Ti-O bonds (Pérez-González and Tomás 2021). The two peaks of the Ag spectrum at 373.58 and 367.68 eV are attributed to Ag 3d_{5/2} and Ag 3d_{3/2} respectively (Fig. 2h). The difference between the two peaks is 6.0 eV, indicating the metallic Ag form. Hence both TiO₂ and Ag existed with their own identity in TiO₂/Ag nanocomposites. (Karimi-Maleh et al. 2020) (Ma et al. 2020b) The results demonstrated the PDMS was successfully attached to the surface of the cotton fabric.

Durable hydrophobic and stable mechanical properties

The wettability is a critical property of wastewater treatment, which is determined by the surface structure and chemical composition. Fig. 3a demonstrated the superhydrophobic mechanism of coated fabric, the PDMS functioned as a “glue” to embedded the Ag-TiO₂ particles on the cotton fabric surface to form superhydrophobic filter materials. The surface roughness of the Ag-TiO₂@PDMS coated fabric was also measured by AFM. The micro-sized roughness is evident on the coated cotton fabric compared with the pristine cotton fabric (Fig. S9). As shown in Fig. 3b, the increase of the mass ratio of Ag-TiO₂ to PDMS leading to a higher water contact angle.

To illustrate the superhydrophobic durability and stability of the Ag-TiO₂@PDMS composite, we investigated the WCAs under harsh conditions, including chemical oxidation, strong light, and physical rubbing. As presented in Fig. 3c, the WCAs of the composite was remained larger than 150° and almost unchanged under different pH, indicating the chemical stability of the coated fabric. (Zhang et al. 2021) The mechanical stability of Ag-TiO₂@PDMS coated fabric was conducted by cyclic abrasion. (Chen et al. 2021) As shown in Fig. 3d, after 50 cycles of sliding on a sandpaper substrate (80 grit, 100 g), the WCA and sliding angle of the modified cotton fabric remained above 150° and below 10° respectively, indicating the superior stability of hydrophobicity of the modified cotton fabric.(Yang et al. 2019) (Cheng et al. 2020) Additional testing also evidenced that the as-prepared Ag-TiO₂@PDMS coated fabric resists high-temperature treatment and air storage, even after 200 min of air exposure (Fig. 3e) and 150 °C of high-temperature heating (Fig. 3f). As illustrated in Fig. 3g. the Ag-TiO₂@PDMS cotton fabric shown improved thermal stability compared with the pristine cotton fabric. The thermal stability of the Ag-TiO₂@PDMS composite was also confirmed by TG testing. The weight decreased 15.05% for cotton fabric and 24.09% for coated cotton fabric after 412 °C, and about doubled weight remained for coated fabric compared with pristine cotton fabric at 800 °C (Fig. 3g). The DTG curves (Fig. S10) show that the peak degradation temperature of the cellulose is 392.16 °C in the natural balsa, and shifts to 419.87 °C after coating.

The pore structure and pore size are critical parameters that influence the separation efficiency of the water purification materials. We investigated the pore structure of the cotton fabric and Ag-TiO₂@PDMS coated cotton fabric by using nitrogen adsorption/desorption measurements. As illustrated in Fig.s 3h, the nitrogen physisorption isotherm features type-IV behavior, suggesting the coated cotton fabric maintained a hierarchical porous structure.(Zhou et al. 2021) The pore sizes are distributed continuously, and the adsorption average pore diameter is 5.1 nm for the cotton fabric and 6.1 nm for coated cotton fabric.(Lei et al. 2021) This interconnected hierarchical porous architecture would provide more catalytic sites and improved photocatalytic performance of Ag-TiO₂@PDMS coated cotton fabrics. In addition, the tensile measurement was conducted to study the stretching deformation of Ag-TiO₂@PDMS coated fabric. It is found that the tensile force reaches 74.785 MPa after modification (Fig. 3i).

Separation efficiency of oil/water mixtures and water in oil

The super-hydrophobic/super-oleophilic Ag-TiO₂@PDMS coated cotton fabric has low adhesion to water droplets but selectively allows oil pollution to pass through, leading to a high separation efficiency for oil-water mixtures. The was evaluated. A series of oil/water mixtures were applied to evaluate the potential oil/water separation performance of the composite for the complex effluents system.

The separation fluxes of Ag-TiO₂@PDMS coated cotton fabric for various oil/water mixture (Fig. 4a) and water-in-oil emulsions (Fig. 4b) were measured. The results revealed the modified cotton fabric present a higher separation flux. For example, the flux of hexane/water mixture and hexane in water emulsion were $14592 \pm 32.1 \text{ Lm}^{-2}\text{h}^{-1}$ and $11397.2 \pm 66.5 \text{ Lm}^{-2}\text{h}^{-1}$, respectively. Moreover, the oil purity of all coated cotton fabrics was greater than 99.9% (Jiang et al. 2019). As shown in Fig. 4c, a mixture of dichloromethane and pure water was poured for separation. The dichloromethane quickly passed through the fabric and fall into the container driven by gravity, while the blue water was retained upon the coated cotton fabric. The separation process of the oil/water mixture and the optical microscopy images of feed emulsion and the associated filtrate was shown in Fig. 4d. Numerous micro-scaled water droplets were observed under the optical microscope in the original emulsion while the mixture became transparent after separation and no water droplets were observed, indicating the high separation efficiency of Ag-TiO₂@PDMS coated cotton fabric. (Zhan et al. 2020a) (Jiang et al. 2019)

Figure 4e presents the emulsion separation procedure of the Ag-TiO₂@PDMS coated cotton fabric. The superhydrophobic property (WCA=157°) corresponding to a positive ΔP ($\Delta P_w > 0$), render the coated cotton fabric with excellent water respell ability. In the contrast, oil can spontaneously permeate through the Ag-TiO₂@PDMS coated cotton fabric due to the Laplace pressure of the oil is negative ($\Delta P_o < 0$) (Chen et al. 2019; Gu et al. 2017; Li et al. 2020). Water in the emulsion was filtered out because of the excellent water repellency and size-sieving effect of the Ag-TiO₂@PDMS coated cotton fabric. As a proof of concept, the contact status between oil and the coating was evaluated. According to the Cassie–Baxter model, the contact status between the liquid and the rough surface can be expressed as:

$$\Delta P = \frac{4 \gamma_{SL} \cos \theta_{liquid}}{D_{pore}}$$

where ΔP is the Laplace pressure, θ_{liquid} is the CA of the liquid, and D_{pore} stands for the pore diameter.

Photocatalytic ability and recycling performance

Organic dyes are ubiquitous in wastewater, not only posing a challenge in wastewater treatment but causing membrane contamination. We glue the photophobic Ag-TiO₂ particles to cotton fabric by low-energy PDMS polymer to construct a superhydrophobic surface. Simultaneously, the particles endow the composites with excellent visible light catalytic degradation performance. UV–vis diffuse reflectance

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spectroscopy (DRS) was used to investigate the optical property of the Ag-TiO₂@PDMS coated cotton fabric and MB was used as a target organic pollutant to conduct photocatalytic degradation.

As shown in Fig. 5a, the traditional cotton fabric has almost no photocatalytic degradation ability while the modified cotton fabric completely degrades MB in about 50 min. Meanwhile, it can be seen that the photocatalytic performance of the modified cotton fabric is better than that of the fabric without Ag modification (70%). The results illustrate that the combination between Ag nanoparticles and TiO₂ can enhance the photocatalytic property under simulated sunlight. The main absorption peak at 464 nm gradually weakened with the increase of irradiation time, indicating the decomposition of MB (Fig. 5b), which is also confirmed by the statistics of the absorption spectrum in Fig. 5c. The enhanced photocatalytic degradation abilities can be explained by the following reasons: 1) the Ag doping upon TiO₂ lower the band-gap energy, rendering the electrons transfer from the valence band to the particles conductive band more easily; 2) the Ag-TiO₂ particles longer the wavelength, extended adsorption peak from UV-light wavelength to visible light; 3) the porous cotton fabric with Ag-TiO₂ nanoparticles homogenously immobilized, providing more catalytic sites (Zhou et al. 2021).

The pollutants attached to the surface always lower the photocatalytic activity and separation efficiency of the separation material. Thus, self-clean property and reuse ability are critical for water purification materials. Fig. 5d shows the anti-pollution performance of the coated cotton fabric (methylene blue and vegetable oil were chosen as the pollutants). The pollutants attached to the surface of the separation materials have been effectively degraded by visible light catalytic degradation of the composite materials prepared in this study, and the recycling of the materials has been realized. No obvious residues remained on the surfaces of the Ag-TiO₂@PDMS coated cotton fabric, indicating that the Ag-TiO₂@PDMS coated cotton fabric exhibited excellent anti-pollution properties (Cai et al. 2020; Tang et al. 2021).

The photocatalytic degradation mechanism of the Ag-TiO₂@PDMS coated cotton fabric for oil and MB is displayed in Fig. 5e. The Ag-TiO₂ particles attached to the cotton fabric demonstrated a decreasing radius and increasing peak intensities, leading to the strong interaction between MB and the Ag-TiO₂@PDMS coated cotton fabric. When Ag-TiO₂@PDMS coated cotton fabric absorbs optical energy equal to or higher than its bandgap under visible light irradiation, the electrons (e⁻) in the valence band (VB) are excited and jumped to the conduction band (CB), generating electron-hole (e⁻/h⁺) pairs with high activity. (Wang et al. 2020) Then, the electron-hole (e⁻/h⁺) pairs migrated to the surface and react with the H₂O and O₂ molecules around it to generate numerous produce superoxide radicals of ·O²⁻, reacts with H⁺ to form H₂O₂, i.e., hydroxyl (·OH) radicals. The ·OH and ·O²⁻ are responsible for the oxidization of the oil and MB dye molecules into CO₂ and H₂O, contributing to their high oxidation ability.(Yang et al. 2021) From the perspective of environmental protection, the Ag-TiO₂@PDMS coated cotton fabric is a promising candidate in the application of wastewater treatment.(Ma et al. 2020b)

The recyclability of Ag-TiO₂@PDMS coated cotton fabric is a pivotal criterion for the engineering application in the water purification area. The SEM images also illustrated the stability of morphology of Ag-TiO₂@PDMS coated cotton fabric, maintaining the properties of Ag-TiO₂@PDMS coated cotton fabric (Fig. 5f). The reusability of Ag-TiO₂@PDMS coated cotton fabric was evaluated by simultaneous removal of MB in five cycles. The Ag-TiO₂@PDMS coated cotton fabric still exhibits efficient photocatalytic ability after five consecutive cycles (Fig. 5g), thereby indicating promising recyclability. In summary, the Ag-TiO₂@PDMS coated cotton fabric photocatalyst possesses acceptable reusability and stability. As shown in Fig. 5h, ten cycles of the water-in-oil emulsion separation were performed. After each cycle of separation, the filter fabric was subjected to photocatalysis degradation. Though the separation flux decreased slightly, the separation efficiency after separation was maintained above 99 %, demonstrating the as-prepared cotton fabric could be used as a low-cost effective water purification material with recycling and reuse ability (Lei et al. 2021; Li et al. 2020).

Conclusions

In summary, we prepared an effective material for water purification via constructing the micro/nano hierarchy surface by immobilization of Ag-TiO₂ and PDMS on cotton fabric. The coated cotton fabric exhibits superhydrophobic properties (CA=157°), high flux (16482 Lm⁻²h⁻¹), high oil purity up to 99.98% and exhibits excellent durability in harsh conditions. In addition, the material demonstrated satisfactory photocatalytic activity and the combination of Ag and TiO₂, reducing the bandgap and enhances the photocatalytic efficiency under visible-light irradiation. Thus, the material could degrade the organic dyes in the wastewater and could be recycled and reused after photocatalysis without performance reduction after 20 cycles. The one-pot process, low cost, high efficiencies, outstanding stability, and can be reused to avoid the environmental pollution and resource waste during the water purification process of the coated cotton fabric, providing a new sight for the advanced materials for large-scale application on water purification area.

Declarations

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Table

Table 1

Comparison of separation efficiency and reuse ability.

Material	Contact angle	SA	Flux $L \cdot m^{-2} \cdot h^{-1}$	Oil purity	Recycle ability	Ref.
MS@TiO ₂ @PPy Monoliths	165	-	9549	-	>99.5% after 8 cycles	(Yan et al. 2020)
SCMs (cotton/PVA)	156±2	7.5±1	10,400 ± 400	>99.98	-	(Daksa Ejeta et al. 2020)
SiO ₂ /PS/PLA	152±2.1	-	8k-12k	-	10 cycles >90%	(Gu et al. 2017)
TiO ₂ /cotton	>150	-	36k-38k	>99.5	-	(Li et al. 2020)
UIO-66-F4@rGO composites	169.3 ± 0.6°	-	990.45 ± 36.28	-	10 cycles >99%	(Zhan et al. 2020a)
ZIF-8@GSH/PI membrane	130.64-153.25	-	2587.2-5632.9	-	20 cycles >99/8	(Ma et al. 2020b)
RGO-PI membrane	-	-	1273.88-2040.04	-	20 cycles	(Zhang et al. 2021)
SiO ₂ /PVDF membrane	130-160	-	16,400 ± 1500	99.95	20 cycles >99.95%	(Wei et al. 2018)
3D melamine sponge	157 ± 2.5	6.2 ± 1.5	-	-	20 cycles >99.87%	(Yang et al. 2019)
rGO@PPS	149.8	-	12903	99.98	10 cycles >99.9%	(Fan et al. 2021)
Ag/TiO ₂ @PDMS Composites	157±2.1	10.2±1.5	16482	99.98	10 cycles >99.9%;	This work

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