

Recent advances in cotton fabric-based photocatalytic composites for the degradation of organic contaminants

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Abstract

Cotton is one of the oldest and most widely used natural fibers in the world. It enables a wide range of applications due to its excellent moisture absorption, thermal insulation, heat resistance, and durability. Benefiting from current developments in textile technology and materials science, people are constantly seeking more comfortable, more beautiful and more versatile cotton fabrics. As the second skin of body, clothing not only provides the basic needs of wear but also increases the protection of body against different environmental stimuli. In this article, a comprehensive review is proposed regarding research activities of systematically summarise the development and research of cotton fabric-based photocatalytic composites for the degradation of organic contaminants in the area of self-cleaning, degradation of gaseous contaminants, pathogenic bacteria or viruses, and chemical warfare agents. Specifically, we begin with a brief exposition of the background and significance of cotton fabric-based photocatalytic composites. Next, a systematical review on cotton fabric-based photocatalytic composites is provided according to their mechanisms and advanced applications. Finally, a simple summary and analysis concludes the current limitations and future directions in these composites for the degradation of organic contaminants.

Keywords: cotton, photocatalysts, self-cleaning, gaseous contaminants, pathogens, chemical warfare agents.

1. Introduction

Ongoing industrialization, outbreaks of epidemics and localized disputes pose a severe threat to human health and the remediation of the environment, as evidenced by continuously declining air quality, prolonged viral attacks and unforeseen chemical weapons leaks (He et al. 2019, Jabbour et al. 2021, Smith et al. 2022). In response to these threats, there has been an increased focus on personal hygiene and protection, resulting in diverse masks, sorbent materials and personal protective equipment (PPE) (Shi et al. 2021). However, most of these materials and equipment do not radically degrade or eliminate these gaseous, liquid pollutants or pathogenic threats, and thus there is enormous potential in seeking the solutions to fundamentally address these threats. Photocatalysis is an environmentally friendly process that utilizes the unlimited source of solar energy and convert ambient O₂ or H₂O into reactive oxygen species (ROS), which efficiently react with pollutants to degrade them into non-toxic degradation products such as water or carbon dioxide (Sudhaik et al. 2022). As an effective and sustainable catalytic method, photocatalysis has been widely used in the field of environmental remediation, like air and water treatment. As the core of photocatalysis, photocatalysts have also made great a progress from semiconductor homogeneous to heterogeneous catalysis. However, most photocatalysts are solid powders and they are difficult to be recycled sustainably. Incorporating the photocatalysts into other substrates not only gives the photocatalysts more long-term catalytic performance but also retains the benefits of the substrate.

Cotton is one of the most commonly used natural fabrics materials to produce apparel and industrial products. The great characteristics of cotton fabrics, including softness, comfort, hypoallergenicity, better breathability, and versatility have captured an amazing place in textile products. However, cotton fabrics are prone to staining, bacterial growth and inability to cope with changing environments during actual usage. Therefore, incorporated solid photocatalysts with cotton fabrics through innovative means not only increase the added value of the fabrics, but also give them higher flexibility to be functionalized.

Currently, many reviews focus on some specific photocatalysts or applications in a particular area. For example, Fujishima provided a comprehensive summary of titanium dioxide (TiO₂) photocatalysis and their surface phenomena (Fujishima et al. 2008). Ong et al. detailed graphitic carbon nitride (g-C₃N₄)-based photocatalysts and their applications in environmental remediation (Ong et al. 2016). Dhakshinamoorthy

summarised the effect of linkers and metal nodes on the photocatalytic performance of MOFs, and compared them with conventional semiconductor photocatalysts (Dhakshinamoorthy et al. 2018). Shayegan reported the application of TiO₂ photocatalysts in the photodegradation of indoor volatile organic compounds (VOCs) as well as outlined the techniques used to improve the activity of TiO₂ (Shayegan et al. 2018). Ma et al. summarised the applications of zirconium-based metal–organic frameworks (Zr-MOFs)/ fiber composites for the protection against chemical warfare agents (CWAs) and for biological protection against pathogenetic bacterial and viruses (Ma et al. 2023). However, there is a lack of review regarding the photocatalytic composites based on cotton fabrics substrates. Therefore, we systematically summarise the progress in the study of cotton fabric-based photocatalytic composites, especially concerning applications in self-cleaning, degradation of gaseous contaminants, pathogenic bacteria or viruses, and CWAs (as shown in Figure 1).

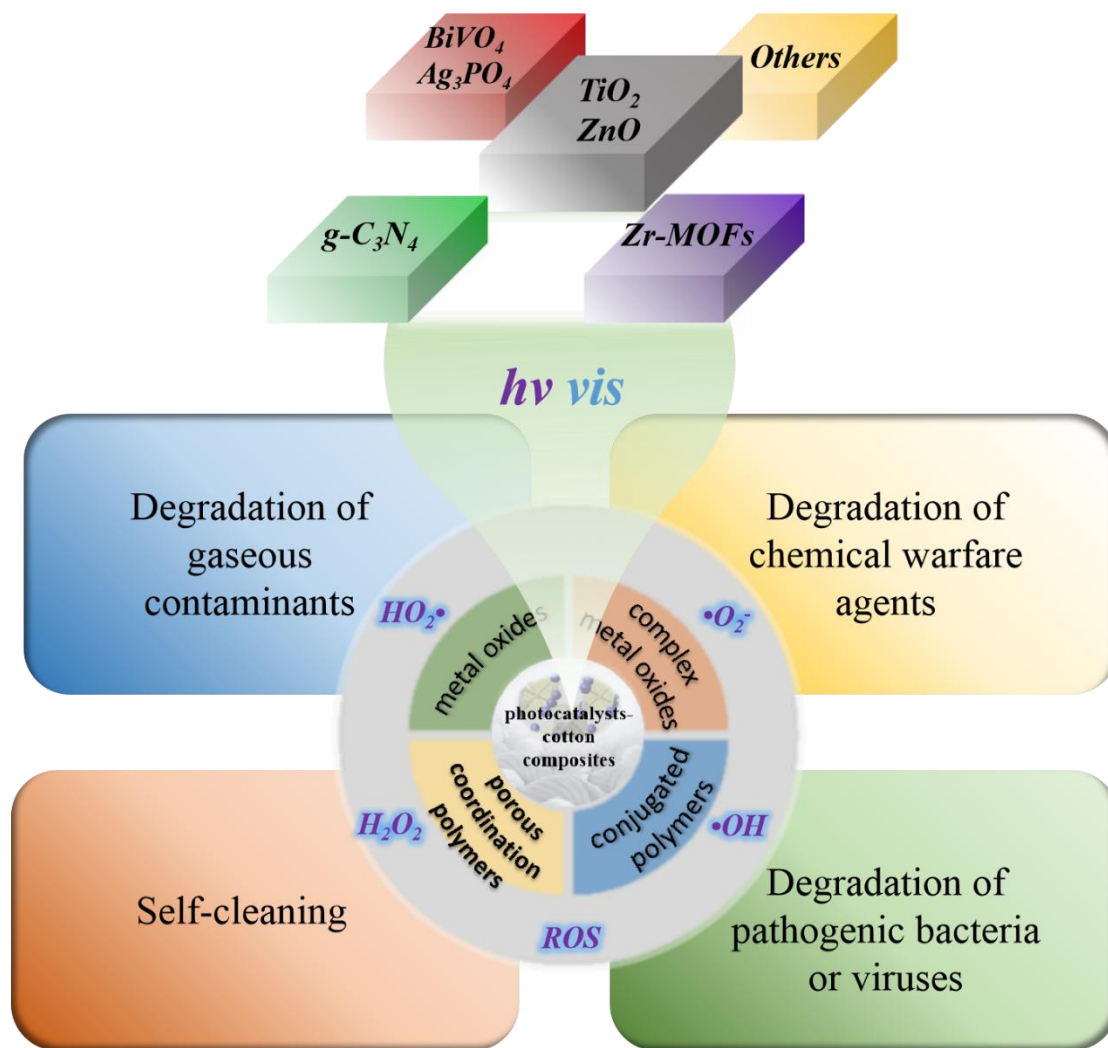


Figure 1. Summary of the recent advancements in cotton fabric-based photocatalytic composites for diverse applications.

2. Photocatalysts and the mechanisms of photodegradation

2.1 Photocatalysts

Like photosynthesis in plants of nature (Cao et al. 2012), photocatalysts convert solar energy into chemical energy, resulting in a catalytic effect that excites the surrounding oxygen and water molecules into reactive oxygen species (ROS) with great oxidising power. It can be utilized to decompose almost all organic substances that are harmful to humans and the environment. With the continuous development of photocatalytic chemistry, a wide variety of photocatalysts (e.g. semiconductor metal oxides (Hoffmann et al. 1995), complex metal oxides (Byrne et al. 2018), conjugated polymers (Dai and Liu 2020), and porous coordination polymers (Wang Qi et al. 2020)) have emerged and many have been combined with cotton fabrics to form cotton/photocatalyst composites.

2.1.1 Semiconductor metal oxides

Semiconductor metal oxides are one of the most extensively studied classes of photocatalysts due to their high catalytic activity, good chemical stability, abundantly available, and low cost (Byrne et al. 2018). As photocatalysts, they have demonstrated the ability to degrade a wide range of environmental pollutants, including oils, dyes, gaseous toxic gases, bacterial, viruses and chemical toxins. There are several common semiconductor metal oxides including TiO_2 , ZnO , WO_3 , SnO_2 , and Fe_2O_3 have been applied to cotton fabrics to degrade environmental pollutants. Among them, research on TiO_2 plays a dominant role. There are three main common structural types of TiO_2 : rutile, anatase and brookite. Of these, rutile and anatase are the two most dominant structures. The most stable particle size for rutile phase is above 35 nm, while that for anatase is below 11 nm (Zhang Hengzhong and Banfield 2000). In addition to the crystalline form, the band gap (E_g) is another important concept for semiconductor photocatalysts. Based on the principle of conventional semiconductor photocatalysts, photocatalysts can be directly excited by light with energy greater than the E_g . The E_g of these common semiconductor photocatalysts are summarised in Figure 2c.

2.1.2 Complex metal oxides

Various new complex metal oxides such as bismuth vanadate (BiVO_4), silver phosphate (Ag_3PO_4), cesium tungsten bronze (Cs_xWO_3), bismuth oxyhalide (BiOBr), and their nanoparticles, have been used to treat cotton fabric for photocatalytic applications. BiVO_4 with a narrow E_g (~2.5 eV, as shown in Figure 2c) is suggested to be a promising candidate for fabricating photocatalytic cotton composites because of its low cost, good biocompatibility, and high photocatalytic stability (Chen Jiayi et al. 2021b). Another promising photocatalyst with relatively narrower E_g (~2.4 eV), high positive valence band (+2.9 V versus NHE), and good visible light photocatalytic activity is Ag_3PO_4 (Yan et al. 2022). However, the uncontrollable photocorrosion and relatively high cost limit its application. Cs_xWO_3 (Peng et al. 2019), as a typical non-stoichiometric compound, can be applied to full-spectrum photocatalytic materials due to its unique hexagonal structure and broad-spectrum absorption properties. BiOBr is a visible-light-responsive semiconductor with an E_g of about 2.7 eV. BiOBr coupled with other metal oxides can further accelerate light-induced electron transfer to enhance photocatalytic efficiency (Yang Hao et al. 2018).

2.1.3 Conjugated polymers

Conjugated polymers are organic macromolecules that are characterized by a

photoactive π -system, and thus they represent an attractive platform for a variety of photocatalytic applications (Dai and Liu 2020). Common conjugated polymers includes linear, porous, water-soluble polyelectrolytes, covalent organic framework materials (COFs) and g-C₃N₄. Graphite-like carbon nitride (g-C₃N₄) has been intensively studied in the field of photocatalysis owing to its narrow band gap (~ 2.7 eV) and visible light absorption at about 450-460 nm as well as its unique optical and electronic properties (Fan et al. 2018). At present, g-C₃N₄ is mainly employed in the production of self-cleaning cotton whereas other conjugated polymers are less commonly found in photocatalytic cotton components.

2.1.4 Porous coordination polymers

Porous coordination polymers, also termed metal-organic frameworks (MOFs), are comprehensively studied in photocatalysis due to their high specific surface area, rich topology and semiconductor-like photocatalytic properties. The photoactive site can be a coordinatively unsaturated metal ion, a substituent on an organic linker, or a guest species located within the pore or their combinations (Dhakshinamoorthy et al. 2018). Unlike conventional metal oxide semiconductors with a delocalized valence band (VB), conduction band (CB) and E_g , MOFs can be considered as molecules located in a crystalline lattice. Similar to conventional semiconductor photocatalysts, electrons in MOFs can be transferred from the highest occupied orbital (HOMO) to the lowest unoccupied orbital (LUMO) under light radiation, leaving holes (h^+) in the HOMO (Wang Qi et al. 2020). Therefore, in order to effectively activate the MOFs, the incident light energy E_{light} requires to be larger than the $E_{\text{HOMO-LUMO}}$ of the MOFs. The E_g of MOF-801, UiO-66, UiO-66-NH₂, UiO-67, MOF-808, NU-1000, and MOF-525 were 4.4 eV, 3.3 eV, 2.76 eV, 3.63 eV, 4.1 eV, 2.8 eV, and 1.67 eV, respectively (Choudhuri and Truhlar 2020, Gao et al. 2021, Gayathri et al. 2022, Ghasemzadeh and Akhbari 2023, Zhang Xiansheng et al. 2023).

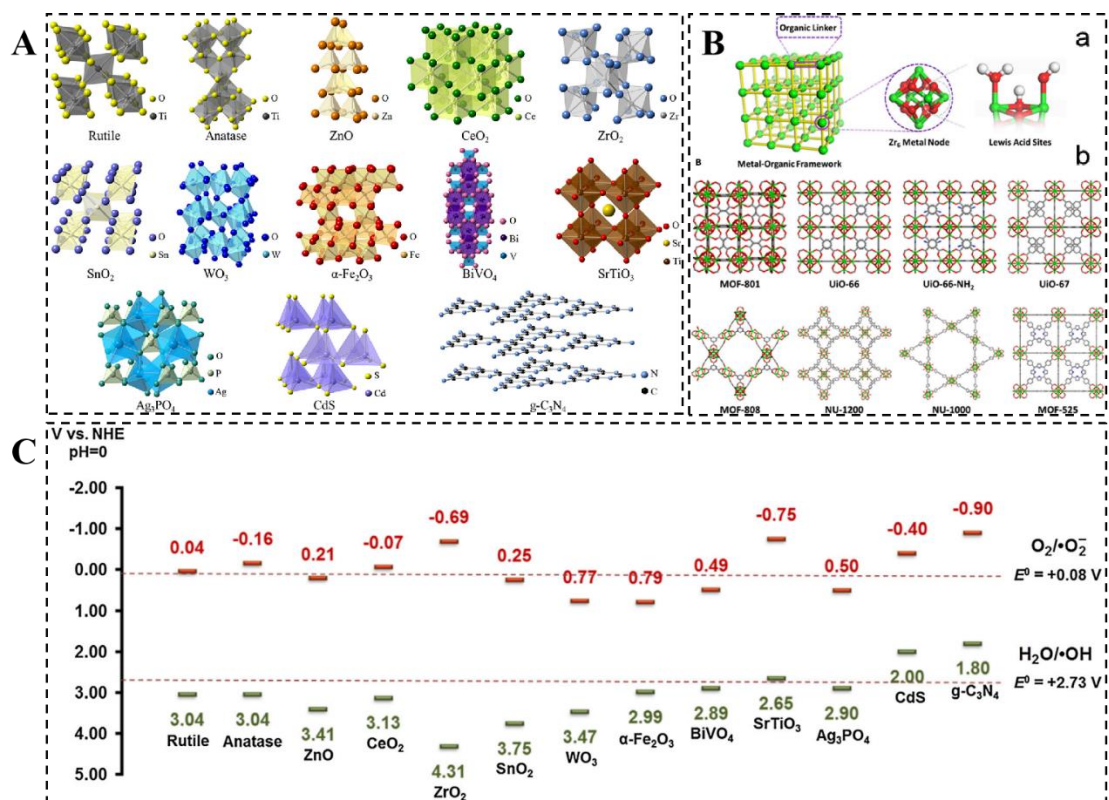


Figure 2. (A) Crystal structures of common photocatalytic materials (Ren et al. 2017). (B) Structures of representative Zr-MOFs(Ma et al. 2021). (a) construction of Zr-MOF with metal clusters and organic linkers. (b) structures of Zr-MOF catalysts. (C) E_g of the VB maximum (green) and the CB minimum (red) of the corresponding materials in Figure 2a (Ren et al. 2017), which calculated at theoretical pH = 0 (V is voltage; NHE is normal hydrogen electrode potential); the redox potentials (E⁰) for O₂/•O₂⁻ and H₂O/•OH at pH = 0 were calculated on the basis of data at pH = 7.

2.2 Mechanisms of photodegradation

Photocatalytic materials for the degradation of organic contaminants are based largely on the principle that photocatalysts can absorb light radiation of suitable wavelengths, which generates ROS that can further decompose contaminants. As shown in Figure 3, the electrons (e⁻) on the surface of photocatalyst were activated when photocatalysts being bombarded with photons from light. The electrons in the VB or LUMO can bridge the energy barrier and are excited to the CB or HOMO to form excited electrons (e_{CB}⁻), leaving the same number of holes (h⁺) behind in the VB or LUMO. This process involves charge separation. The e_{CB}⁻ may react with oxygen (O₂) and produces superoxide radicals ((•O₂⁻) or hydroperoxide radicals (HO₂•). The oxidation of water can take place with the photogenerated hole (h⁺) and then transforms to an oxidizing hydroxyl radical (•OH). Hydrogen peroxide (H₂O₂) can also be formed

during these reactions. These typical ROSs, like $\cdot\text{OH}$, $\cdot\text{O}_2^-$, $\text{HO}_2\cdot$, and H_2O_2 , can potentially decompose organic and inorganic contaminants. Another important outcome is that the photogenerated e^- may meet the h^+ during diffusive transfer, resulting in recombination and therefore the loss of catalytic activity. It is worth mentioning that the recombination time and rate have a great impact on the efficiency of the photocatalyst.

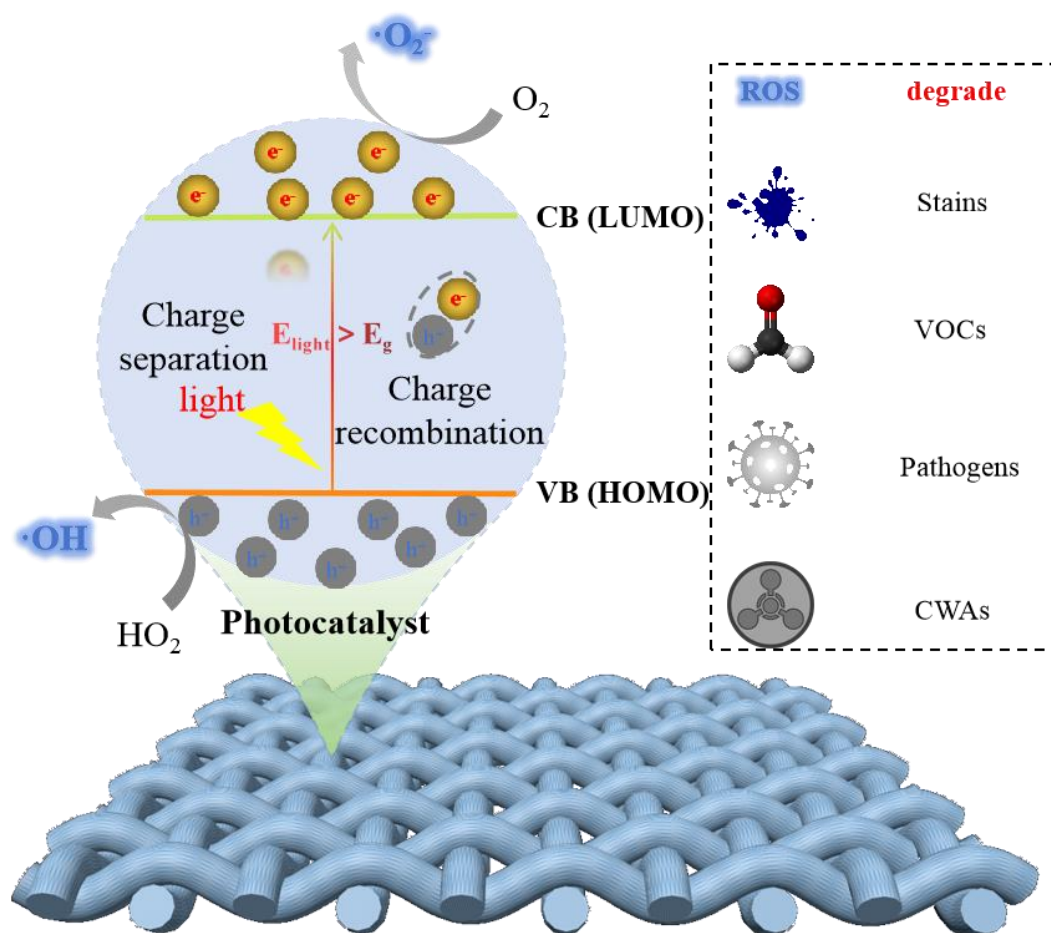


Figure 3. Photocatalytic mechanism of cotton fabric-based photocatalytic composites and schematic illustration of its photocatalytic applications.

3. Applications of cotton fabric-based photocatalytic composites

The combination of cotton fabrics and photocatalysts not only exploits the supportive and sustainable working properties of the fabrics, but also utilises the catalytic activity of the catalysts and improves their processability and reusability. Cotton can be in the form of cotton fibers, yarns, cloth and fabrics, while photocatalysts come in flexible categories from the most common metal semiconductors, metal composite components, nitrogen carbide, organic frameworks and polymers. Of course, their applications vary significantly, and here we summarise only some of the most

advanced applications, such as photocatalytic self-cleaning, deactivation of pathogenic bacteria and viruses, degradation of airborne toxic gases and degradation of CWAs.

3.1 Self-cleaning

Although self-cleaning is also used in a wide range of applications in construction, glass, electronics and medical devices, this review only discusses the application of self-cleaning on cotton fabrics. Maintaining the hygiene and aesthetics of fabrics is a prerequisite for clothing uses. Self-cleaning fabrics are a novel technology that enables the automatic removal of contaminants from fabrics to achieve neatness and long-term use. There are two types of conventional self-cleaning (Wu Qingshan et al. 2023). One is static self-cleaning, of which typically employs a hydrophobic coating on the surface of the fabric to reduce staining and impregnation caused by liquids contaminants. A considerable number of these coatings are inspired by nature, including the water repellent lotus leaves and tree leaves. Another is dynamic self-cleaning, of which uses a photocatalyst to degrade and remove contaminants on the fabric surface in the presence of a light source. Photocatalytic self-cleaning is widely studied due to its excellent smart cleaning properties. As a hydrophilic polymer, cotton fabrics are prone to be stained by oils, dyes and other organic contaminants. This often reduces the aesthetics and neatness of the garment, and some of these contaminants are difficult to be removed from the fabric surface, significantly affecting its usability. Hence, self-cleaning cotton shows promising prospects for practical use.

The first self-cleaning photocatalysts developed were semiconductor metal oxides, which are TiO_2 , ZnO , ZrO and SnO_2 . These metal oxides can create h^+ and peroxides under light irradiation and these reactive species then come into contact with the pollutants, causing a redox reaction of the organic pollutants and their subsequent degradation to small molecules that can be easily removed.

Among these inorganic photocatalysts, TiO_2 is the most predominantly researched and industrially employed metal oxides. Different methods have been developed to fabricate crystalline TiO_2 on self-cleaning substrate surfaces, such as physical vapor deposition (PVD), chemical vapor deposition (CVD), and atomic layer deposition (ALD)(Zhang Liwu et al. 2012). However, these methods usually require very high temperatures to produce highly catalytically active crystalline TiO_2 on the substrate surface. They are not suitable to be used on fabric substrates, especially cotton fabrics

with poor heat resistance. Some research groups have proposed new strategies to fabricate cotton/TiO₂ composites. Walid and Xin produced anatase nanocrystalline TiO₂ coatings on cotton fabrics using a low-temperature (100 °C) sol-gel process under ambient pressure (Daoud and Xin 2004). Kiwi's group bonded TiO₂ to cotton fabrics via chemical spacers and investigated the photocatalytic properties of TiO₂ against stains such as wine, cosmetics, sweat and coffee on cotton fabrics (Meilert et al. 2005). Bozzi, A., et al. anchored TiO₂ on the cotton surface via pre-activated cotton by RF-plasma, MW-plasma and UV-irradiation(Bozzi et al. 2005).

Then, different methods of synthesis and modification of TiO₂ on cotton fabrics were outlined. In 2009, Mejia et al. developed the methods of UVC-light (185 nm) and RF-plasma under atmospheric pressure to prepare self-cleaning modified TiO₂-cotton(Mejía et al. 2009). The experimental results showed that this method had good reproducibility and the self-cleaning cotton demonstrated decent decolourisation kinetics for red wines. Wu et al. developed a facile and effective method for producing TiO₂-coated cotton fabrics at ambient temperature, and 3-5 nm well-crystallised TiO₂ nanoparticles were obtained by dipping the cotton fabrics in an aqueous TiO₂ nanosol (Wu Deyong et al. 2009). Lacombe et.al developed a simple and reproducible one-pot process for the elaboration of cotton fabrics coated with anthraquinone-2-carboxylic acid sensitized TiO₂ (Rahal et al. 2011). Examination by scanning electron microscope of treated cotton tissues showed that the coating of TiO₂ particles on cotton fibers was stable and homogeneous. The cotton coated with sensitized TiO₂ displayed self-cleaning properties towards wine stain, either under solar or even indoor light. The possible mechanism for the higher efficiency of sensitized TiO₂-coated cotton is attributed to the synergistic effect between TiO₂ and anthraquinone-2-carboxylic acid, enhancing the formation of ROS.

In around 2013, the research of photocatalytic self-cleaning cotton proceeded rapidly, more research progress of photocatalytic TiO₂ has been emphasized on the applications on cotton fabrics. In the next decade, the research of TiO₂ photocatalytic self-cleaning cotton mainly focused on two aspects. a) To improve the photocatalytic activity of TiO₂ by doping with other materials. b) To improve the durability of the TiO₂ on cotton fabric.

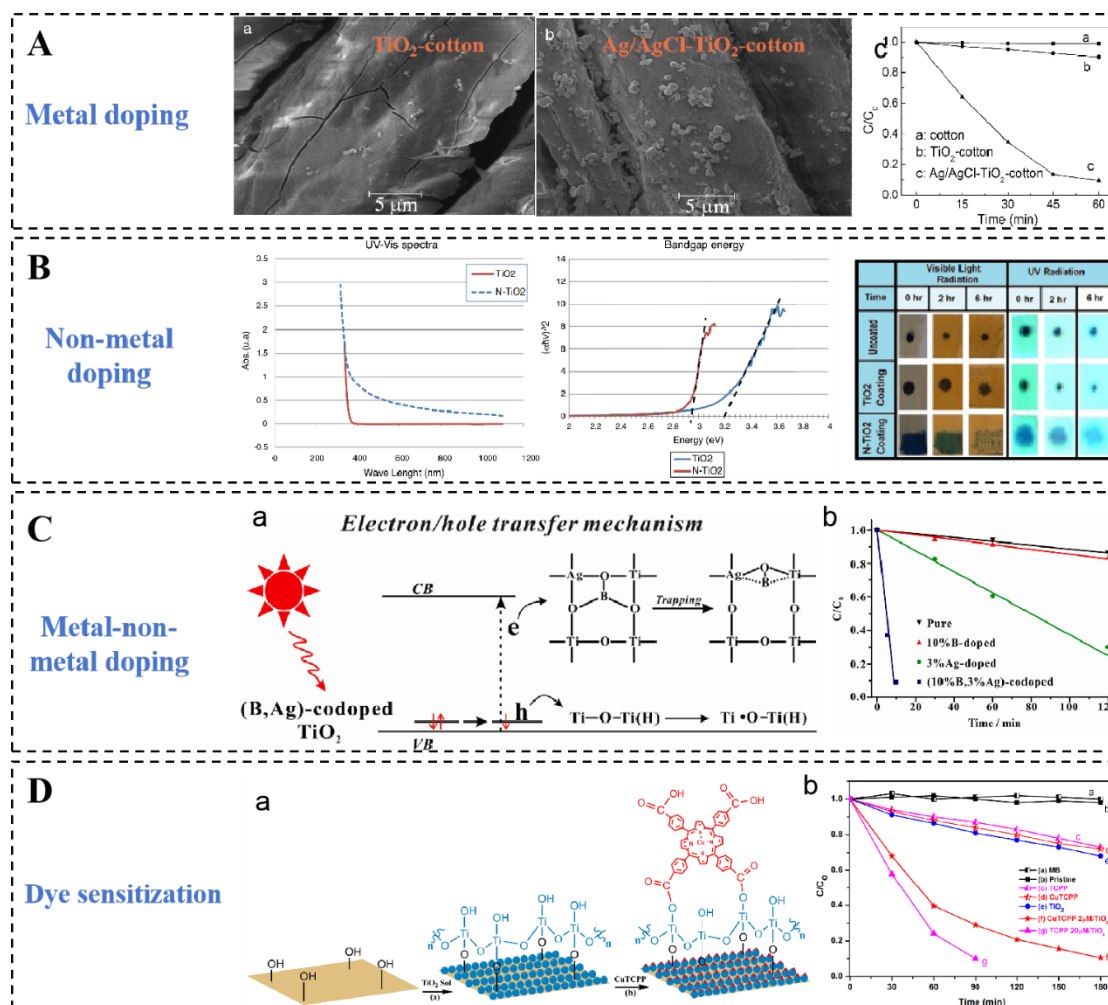


Figure 4. Strategies for improving the photocatalytic activity of TiO₂. (a) Metal doping TiO₂ with Ag/AgCl nanoparticles and Ag/AgCl-TiO₂-cotton for degradation of methyl orange (Wu Deyong et al. 2013). (B) N-doped TiO₂ coating onto cotton fabric and its photocatalytic performance in photodegradation of dyed ink (Katoueizadeh et al. 2018). (C) (B, Ag)-codoped TiO₂ catalysts and its photodegradation curves of methylene blue (Feng et al. 2013). (D) Dye sensitisation to improve self-cleaning properties of TiO₂-cotton fabric (Afzal et al. 2013a).

Since the E_g of TiO₂ is about 3.2eV, the light absorption is mainly in the ultraviolet region ($\lambda < 390\text{nm}$) that only accounts for 3%-5% of the solar energy, while 45% of the solar energy lined in the visible light cannot be fully utilised. Therefore, reducing the E_g of TiO₂ and expanding the light-absorbing region of TiO₂ are effective ways to increase the light energy available for driving the photocatalytic performance of TiO₂ and its composites.

In order to improve the efficiency of TiO₂ photocatalytic self-cleaning property, diverse strategies have been adopted including metals doping, non-metals doping,

metal-non-metal co-doping as well as the incorporation of sensitized dyes, as shown in Figure 4. Different mechanisms such as narrowing E_g , prolonging the life of the photoinduced charge carrier, formation of more excited intermediates, formation of intrinsic defects oxygen vacancies have been suggested to be potential approaches for promoting the activity of doped TiO_2 photocatalysts.

Modification of TiO_2 with metals (eg. Au, Ag, Pt, etc.) has received increasing attention attributing to their unique optical properties exhibited by metal nanoparticles through surface plasmon resonance. The surface plasmon resonance of metals can significantly enhance the absorption of visible light, which would induce electron transfer from metals surface to the CB of TiO_2 , and thus the photocatalytic performance of TiO_2 under visible light can be significantly improved. Apart from assisting the charge transfer, the doping metals on the surface of TiO_2 could also promote the separation of photogenerated charges as electron sinks (Long et al. 2016). Wu et al. loaded Ag/AgCl nanoparticles onto TiO_2 -coated cotton (Figure 4A), and the Ag/AgCl- TiO_2 -cotton showed higher photocatalytic degradation activity for methyl orange under visible light when compared with TiO_2 (Wu Deyong et al. 2013).

Inorganic non-metallic doped TiO_2 is another effective way to endow TiO_2 with photocatalytic activity under visible light irradiation. Asahi et al. calculated the density of states of C, N, F, P, S and O doped TiO_2 , and the results have showed that N is the most efficient dopant for doping TiO_2 (Asahi et al. 2001). Katoueizadeh et al. have found that N-doped TiO_2 not only exhibits high absorption in visible light range, but also reduces the E_g of TiO_2 to 2.98 eV, which increases its photocatalytic activity under visible light (Katoueizadeh et al. 2018), as shown in Figure 4B. Pakdel et al. developed a flower-like N-doped TiO_2 /PDMS coating over cotton fabrics by dip-coating method. This N-doped TiO_2 coating greatly improves the photocatalytic activity of cotton fabrics and effectively degrading adsorbed oil stains under sunlight stimuli (Pakdel et al. 2021).

Metal/non-metal co-doping can combine the advantages of metals and non-metals to exhibit high photocatalytic activity under the visible light irradiation due to the synergistic effect of metal/non-metal dopants narrowing the E_g and facilitating the separation of h^+ (Banerjee et al. 2015). Feng et al. found for the first time that B-Ag-co-doped TiO_2 exhibit exceptionally high photocatalytic activity under solar-light irradiation. The results have shown that the embedment of dopant B into the interstices of TiO_2 lattice simultaneously facilitates the embedment of dopant Ag

into the lattice. As a result, the presence of [the tricoordinated interstitial B–O–Ag] species (as shown in figure 4C) effectively trap photoinduced electrons and prolong the lifetime of the photoinduced carriers (Feng et al. 2013). However, co-doping cannot guarantee the improvement of photocatalytic efficiency of TiO₂. Long et al. modified cotton fabric by Pt-TiO₂ and Pt-N-TiO₂ nanosols, and the results showed that Pt-TiO₂ significantly enhanced the photocatalytic activity, while Pt-N-TiO₂ had poor photocatalytic activity. This is because the N species adsorbed on TiO₂ surface block the adsorption of PtCl₆²⁻, and this reduce Pt present on Pt-N-TiO₂ coatings (Long et al. 2016).

Dye sensitization allows TiO₂ to gain visible light absorption more effectively compared with other methods. This is because photosensitive dyes such as porphyrins have extensively delocalized π electrons, contributing to strong absorption in the visible light region. When photosensitisation occurs, light-induced electrons are transferred from the excited dye to the TiO₂ and form electron holes. These electrons holes can react with O₂ to form superoxide radical anions(O^{2•-}), and oxidise the organic pollutant subsequently. Porphyrins have excellent photophysical properties and their photophysical properties can be readily improved by modifying peri-phenyl substituents and/or by metal complexation. Afzal et al. developed a range of porphyrin-sensitised TiO₂ cotton fabrics (Afzal et al. 2013a, b, 2014). These cotton fabrics showed superior self-cleaning performance comparing with other TiO₂-coated cotton fabrics. Among different porphyrin metal couplings, copper porphyrin-sensitised TiO₂ showed the highest catalytic activity.

In the early stages of self-cleaning cotton research, researchers mainly addressed the low-temperature growth of TiO₂ nanoparticles onto cotton fabrics, but less studies have addressed the issue of wash resistance. It is worth mentioning that the wash durability of self-cleaning fabrics is one of the most important criteria for garment application. To tackle the existing limitations, some studies have been conducted to improve the washing resistance of self-cleaning cotton fabrics. Xin et al. first strengthened the wash-resistant photocatalytic performance of self-cleaning cotton by the introduction of Au/TiO₂/SiO₂ nanocomposites, the self-cleaning properties under visible light irradiation could be retained after 20 washes according to the standard of Australian/New Zealand AS/NZS 4399: 1996 (Wang RongHua et al. 2010). Additional work by Qi and Xin presented a more facile method to synthesize single-phase anatase TiO₂ nanocrystallites on cotton at room temperature (Qi Kaihong

and Xin 2010). The adhesion fastness of cotton/TiO₂ composite was studied by standard accelerated washing method of AATCC 61-2003 Test No. 2A. The result showed that the photocatalytic self-cleaning ability could be maintained after 20 times of repeated launderings. Subsequent studies have been carried out to improve the washing resistance of photocatalytic self-cleaning cotton by different methods.

Yu et al. first introduced a carbon-carbon double bond on the surface of TiO₂ by maleic anhydride (MAH), and then the TiO₂-g-MAH and 2-hydroxyethyl acrylate were co-grafted onto cotton fabrics under γ -ray irradiation (Yu Ming et al. 2013). The finished cotton fabric showed excellent photocatalytic self-cleaning properties with washing resistance. After 30 accelerated washes (equivalent to 150 home washes), a large amount of TiO₂ was still remained on the surface of the cotton fabrics, and their photocatalytic degradation of organic stains was insignificantly changed. Wang reported a method to obtain amino-functionalized reactive TiO₂ (TiO₂/KH550), which was then bonded to cotton fabrics via an exhaust dyeing method (Qi Zhenming et al. 2021). The cotton fabrics loaded with TiO₂/KH550/SAT exhibited durable self-cleaning activity. In addition to washing resistance, self-cleaning cotton fabrics demonstrated ability to adapt to different conditions and even harsh environments. Yang et al. developed a flexible method to prepare cotton fabrics co-coated with TiO₂ and fluorosilanes. The self-cleaning property of cotton could sustain under various washing conditions with different pH and organic solvents (Yang Maiping et al. 2019).

ZnO is another promising alternative to TiO₂ for photocatalytic self-cleaning owing to its non-toxicity, low cost and strong photochemical activity. However, ZnO generally exists as a solid powder and there are also problems with recycling after use. Anchoring ZnO on cotton fabrics is a potential approach for developing practical self-cleaning applications. In 2004, Wang et al. (Wang Ronghua et al. 2004) developed an effective method to grow ZnO nanorod on cotton fabrics at low temperature, the treated cotton fabrics provided an excellent UV protection factor rating of 50+, implying high photocatalytic activities. However, ZnO has an energy band gap 3.37 eV in the UV region ($\lambda < 387$ nm) that limits its photocatalytic applications under visible light irradiation. Therefore, many studies have focused on doping other materials to enhance the photocatalytic activity of ZnO under visible light. A bioinspired mineralization route to assemble nanostructured Ag@ZnO on the surface of cotton fabrics was proposed by Manna (Manna et al. 2015). In this process,

the coating of ZnO was formed on substrate directly from water-soluble zinc salts under mild conditions, while the presence of polyamine in the ZnO matrix acted as reducing agent to generate Ag (0) from Ag(I) at room temperature. The presence of Ag nanoparticles could boost photocatalytic property as well as visible-light-driven activities of ZnO-coated fabrics. Yang et al. (Yang Hao et al. 2018) developed ZnO/BiOBr functionalized cotton fabrics by a simple and time-saving ultrasonic-microwave combined method. Compared with ZnO coated cotton fabric, the photocatalytic activity of ZnO/BiOBr fabric was remarkably improved without sacrificing its antibacterial activity. The introduction of BiOBr nanoflakes on cotton fabrics improved the visible light absorption and reduced the recombination rate of electron-hole (e^-/h^+) pairs, thus obviously improving the photocatalytic self-cleaning performance under visible light irradiation. Kumbhakar (Kumbhakar et al. 2018) reported a green synthesis method to synthesize 2D rGO-ZnO (rGZn) nanocomposites from zinc acetate and apple juice. The cotton fabric coated with rGZn could efficiently degrade dyes and tea stains under sunlight irradiation.

Some other metal composite materials are also used as catalytic components of self-cleaning cotton. Peng et al. (Peng et al. 2019) developed a kind of Cs_xWO_3 -coated cotton fabric, which exhibited UV/NIR shielding and full spectrum (ranging from UV, Vis to NIR) self-cleaning properties. SnO_{2-x}/GO photocatalyst modified cotton fabrics were developed by Qi et al. (Qi Zhenming et al. 2019), and the as-prepared cotton fabrics displayed productive and durable self-cleaning activity. The results showed that the existence of oxygen vacancies greatly improves the light absorption, and the presence of GO effectively enhanced the separation of photoinduced e^-/h^+ pairs. A surface functionalization of cotton fabric was developed using Ag_3PO_4 by the dip-padding process, the Ag_3PO_4 finished fabric demonstrated better photocatalytic activity than Ag_3PO_4 . This was contributed by the synergetic effect of the Ag constituent with the carboxyl groups on the modified fabric (Yan et al. 2022). Chen's group illustrated the loading of self-dispersive and reactive $BiVO_4$ onto cotton fabrics, the results showed that the modified cotton fabrics possessed better ultraviolet protection and self-cleaning performance (Chen Jiayi et al. 2021b). A zeolitic imidazolate framework-8 (ZIF-8)- modified cotton fabric was fabricated by Ran et al. (Ran et al. 2020), and the finished ZIF-8/cotton fabrics revealed remarkable photolysis of methylene blue under ultraviolet light. Due to the wide band gap (5.22 eV) of ZIF-8, another work by Chen (Chen Hang et al. 2021a) deposited $MoS_2/ZIF-8$

composite on cotton fabrics. The MoS₂/ZIF-8 composite lowered the bandwidth of ZIF-8, and thus greatly increased the catalytic performance under visible light. In addition to metal-component photocatalysts, two-dimensional graphite-like carbon nitride (g-C₃N₄) is known to be an emerging and high-performance photocatalyst. It can also be used to prepare photocatalytic cotton. Fan et al. assembled g-C₃N₄ nanosheets onto cotton fabrics by electrostatic interaction. The treated cotton fabrics presented distinguishable photocatalytic activity and superior self-cleaning performance. The complete degradation of Rhodamine B as well as the removal of wine and coffee stains could be achieved accomplished under xenon irradiation.

3.2 Degradation of gaseous contaminants

In modern society, the use of products like construction materials, decorative furniture, auxiliaries, adhesives and cosmetics often involve the release of certain toxic and harmful gases. Furthermore, the industrial waste gas, vehicles pollution or chemical gas leakage often pose negative health impact on humans. Common indoor (as shown in Figure 5A) and outdoor air gaseous pollutants include volatile organic gases (VOCs), carbon monoxide, nitrogen oxides and sulphides (Ren et al. 2017). According to the World Health Organization, the annual premature deaths reach 7 million, and this is closely associated with the indoor and outdoor air pollution. Besides, more chronic and respiratory diseases occur as a result of the inevitable contact of these pollutants. Unlike solid airborne particles that can be simply filtered out, gaseous contaminants often require more complex treatment for removal. Alternative strategies mainly include physical adsorption and chemical degradation. Physical adsorption requires frequent handling of spent adsorbents, and the periodic cleaning, replacement or discarding of the adsorbent may result in recontamination. Therefore, there is an urge to the development of a safe, effective and long-lasting technology to degrade air gaseous contaminants.

Clothing has a large surface area for covering the human body, and this body's second skin plays an important role in regulating dermal exposure to chemicals. Hence, many fabric-based photocatalytic degradation of air pollutants have been fabricated (Yu Jie et al. 2022), but not many of them have focused on cotton fabrics. Here we highlight the cotton fabric-based photocatalytic materials for degradation of airborne gaseous pollutants.

Formaldehyde (HCHO) is the most common indoor air pollutant, commonly found in various building decoration materials, which causes serious harm to human health. In

order to reduce the harm associated with indoor HCHO to human body, various photocatalytic cotton component materials are developed. Wang et al. constructed TiO₂/potassium alginate-CNTs coating on cotton fabric via layer-by-layer self-assembly technique, the coated fabrics exhibited excellent photocatalytic degradation activity for HCHO with a degradation rate constant of 1.676 h⁻¹(Wang Yanyan et al. 2017). In addition, a facile modified strategy was proposed by Yao(Yao Chengkai et al. 2019) to spray a suspension of carbon nitride nanosheet(CNNS) onto cotton T-shirt, as shown in Figure 5B. Since the plentiful amino/ hydroxyl groups of CNNS are favorable for forming hydrogen bonds with cotton, contributing to the firm adhesion of CNNS on textile substrate. The photocatalytic properties of modified cotton could be retained after repeated washings. In addition to investigating the self-cleaning properties of the as-prepared samples, the photocatalytic degradation of gaseous HCHO was also evaluated using xenon lamp and LED lamp. Superior photocatalytic properties of CNNS modified cotton have been demonstrated by 100% of HCHO removal after 20 min under xenon lamp illumination. The photocatalytic repeatability and reproducibility were proven by similar photocatalytic behavior for successive 3 cycles. Another work by Zhang et al. developed a manganese dioxide nanoparticle (MnO₂ NPs)-loaded cotton fabric by growing metal oxide in situ on the polydopamine-modified cotton fabrics (Zhang Yali et al. 2022). A good HCHO removal efficiency and stability were obtained, giving 100% HCHO degradation within 20 min for more than 3 cycles. A possible reaction mechanism is proposed. Firstly, the MnO₂ catalyst is oxidized by oxygen on the surface to form surface adsorbed active oxygen, which oxidizes HCHO to methylene dioxygen (DOM). The DOM will be then converted to formate (HCOO⁻), which is then decompose into CO and eventually oxidizes to CO₂.

In order to eliminate indoor ammonia emitted from antifreeze admixtures in construction concrete, fibrous TiO₂- cotton photocatalysts were produced by Dong et al. using TiO₂ aqueous dispersion with silicone or acrylic additives, and these fabric photocatalysts showed effective decomposition of ammonia under UV light (Dong et al. 2007).

In addition, a number of TiO₂ co-catalysts have been investigated for their degradation of different VOCs in indoor air. For example, Han et al. synthesised [Mo₃S₁₃]²⁻ modified TiO₂ for the mineralization of acetone in air (Figure 5C). The [Mo₃S₁₃]²⁻/TiO₂ composite exhibited remarkable photocatalytic performance

doubling that of commercial TiO_2 (Han et al. 2019). Xu et al. combined white TiO_2 with three colored materials of red $\alpha\text{-Fe}_2\text{O}_3$, green CuPcCl_{16} , and blue CuPc by immobilization. Compared with pure TiO_2 -based fabric, the fabrics containing different colored components displayed better catalytic degradation of HCHO . Currently, the research focuses on the embedment of TiO_2 co-catalysts into synthetic fiber materials, and there is a lack of studies exploring the effect of these catalysts on cotton fabrics for air purification (Xu et al. 2019).

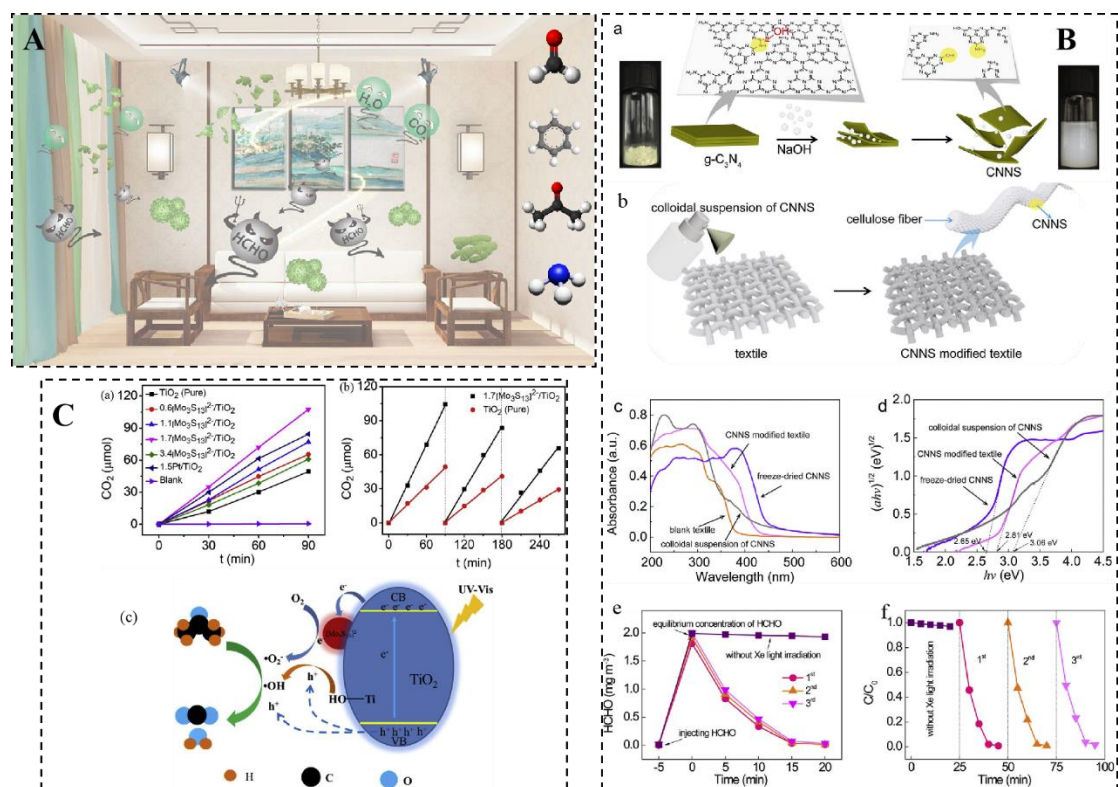


Figure 5. (A) Diagram of common gaseous pollutants indoor (Xu et al. 2019). (B) Degradation of gaseous HCHO using $\text{g-C}_3\text{N}_4$ (Yao Chengkai et al. 2019). (a) The process of alkali-treating exfoliation of $\text{g-C}_3\text{N}_4$ into CNNS . (b) preparation of CNNS modified textiles. (c-d) UV-vis absorption spectra and Tauc plots of the CNNS modified textile and referential samples. (e-f) The degradation of gaseous HCHO by CNNS -cotton textile under Xe lamp irradiation. (C) $[\text{Mo}_3\text{S}_{13}]^{2-}$ - TiO_2 coated cotton fabric for degradation of acetone (Han et al. 2019). (a-b) CO_2 production using different catalysts and cycle runs of photocatalytic degradation of acetone. (c) the mineralization process of acetone under $[\text{Mo}_3\text{S}_{13}]^{2-}/\text{TiO}_2$ composite.

3.3 Degradation of pathogenic bacteria/viruses

The use of photocatalysts for the degradation of pathogens such as bacteria and viruses in air or water has been extensively researched and applied to practical production processes. Nevertheless, relatively little research has been conducted on

personal protection fabrics, especially cotton fabrics. With the outbreak of COVID-19 pandemic, there was a growing concern for personal hygiene and health protection. In the last few years, there has been a lot of research focusing on the antibacterial and antiviral properties of textiles. On the one hand, pathogen-resistant textiles can reduce human infections. On the other hand, they can increase people's personal hygiene. Photocatalytic degradation of pathogens in cotton textiles is a promising category of textiles, owing to its excellent performance and wide adoption.

The first antimicrobial activity of the Pt-doped semiconductor TiO_2 was reported by Matsunaga and coworkers (Matsunaga et al. 1985). They found that microbial cells in water could be killed by contacting with a TiO_2 -Pt catalyst under near-UV light for 60 to 120 min. Since then, various photocatalysts have been explored for their ability to degrade a variety of pathogens, including bacteria, fungi and viruses. This is because pathogens generally consist of ~99 wt% organic compounds including proteins, sugars, amino acids, polysaccharides, and nucleic acids (DNA and RNA)(Ren et al. 2017). Upon excitation by light, the photon energy generates an electron hole pair on the photocatalyst surface. The hole in the VB can react with H_2O or hydroxide ions adsorbed on the surface to produce hydroxyl radicals ($\text{OH} \cdot$), and the electron in the CB can reduce O_2 to produce superoxide ions (O_2^-). These ROS of holes and $\text{OH} \cdot$ are extremely reactive toward organic pollutants and pathogenic microorganisms (Maness et al. 1999).

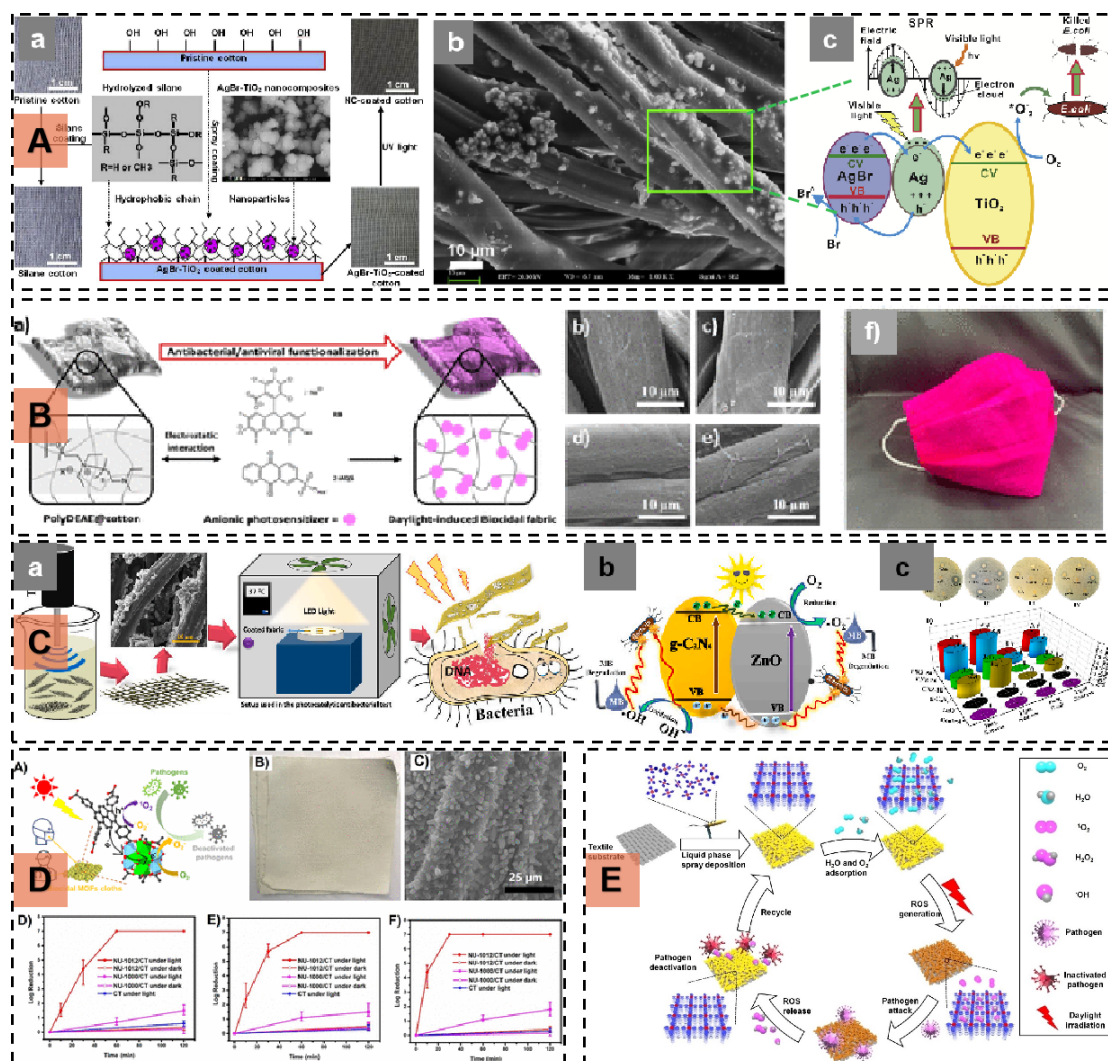


Figure 6. (A) Ag/AgBr-TiO₂-modified antibacterial cotton fabric (Rana et al. 2016). (a) The preparation process, (b-c) Morphology and proposed antibacterial mechanism of AgBr-TiO₂-coated cotton. (B) Anionic photosensitizers as photo-induced biocidal component (Tang et al. 2020). (a) Schematic illustration of the fabrication of antibacterial/ antiviral cotton, (b-f) SEM images and a face mask of modified cotton. (C) g-C₃N₄/ZnO-finished cotton fabric (Hosseini-Hosseiniabad et al. 2023). (a) The coating procedure, (b) Proposed mechanism, and (c) Antimicrobial property. (D) Zr₆Ti₄-based MOFs-cotton with photocatalytic biocidal performance (Wang Xingjie et al. 2022a). (E) The schematic of the preparation of HOF-101-F coatings on cotton fabrics and the process against pathogens (Wang Yao et al. 2022b).

TiO₂ is a good photocatalytic antimicrobial catalyst for cotton, and the incorporation of other components with TiO₂ can further improve the antimicrobial activity of cotton fabrics components under visible irradiation. Wu et al. prepared self-cleaning antibacterial cotton fabrics by depositing and grafting anatase TiO₂ nanoparticles (~3-5 nm) at low temperature, the TiO₂-coated cotton fabrics showed significant

inhibition of bacterial growth under UV light (Wu Deyong et al. 2009). In addition, Selishchev et al. modified cotton fabrics with nanocrystalline TiO₂, which improved adsorption and degradation of influenza A (H1N1) virus (Selishchev et al. 2022). The results showed potential applications of modified cotton in air disinfection and personal protective clothing against biochemical threats. In order to explore the photocatalytic antibacterial effect of different TiO₂ under visible light, various TiO₂ doped materials have been investigated. Rana et al. sprayed a coating of a mixture of Ag/AgBr-TiO₂ and organic silane on cotton for preparing antibacterial fabrics that were 81.43 % bacterial reduction in dark condition and 99.87 % bacterial reduction under the visible light irradiation (In Figure 6A). This high photocatalytic antibacterial effect could be attributed to various reactive species ($\cdot\text{O}_2^-$, $\cdot\text{OH}$, photo-generated holes and Br^0) formed. They could break down the cell wall of microorganisms by oxidation-reduction reactions, thus effectively inhibiting the bacterial growth. Another similar study (Zahid et al. 2018) used a simple technique to prepare antimicrobial cotton by spraying manganese (Mn) -doped TiO₂ with a silicon binder on cotton fabrics. The treated cotton fabrics showed a 100 % reduction of *Staphylococcus aureus* (*S. aureus*) and *Klebsiella pneumoniae* (*K. pneumoniae*) under the exposure to sunlight within 2 hours, demonstrating excellent antibacterial kinetics. Compared with TiO₂, ZnO has lower photocatalytic activity but higher antimicrobial properties (Yalcinkaya and Lubasova 2017). Yang developed an ultrasonic-microwave combined method to prepare ZnO/BiOBr functionalized cotton fabrics (Yang Hao et al. 2018). The inhibition rates of ZnO/BiOBr coated cotton against *S. aureus* and *Pseudomonas aeruginosa* (*P. aeruginosa*) were 96% and 76%, respectively, which was slightly lower than ZnO-coated cotton fabrics. This is may be because that ZnO has a smaller nano-size with higher surface area to interact with the bacteria, and therefore greater antimicrobial activity than ZnO/BiOBr. In addition to metal oxides, metal sulphides can also be used to prepare photocatalytic antimicrobial cotton. In the work by Kumar (Kumar et al. 2022), they sprayed micro-nano sized molybdenum disulfide (MoS₂) particles formulated with an adhesive onto cotton fabrics. 5% MoS₂ coated fabrics respectively reduced *Escherichia coli* (*E. coli*) and *S. aureus* by 96% and 98% over a bacterial contact time of 2 hours. The antimicrobial properties of the fabrics showed impressive laundry durability, still displaying more than 89 % bacterial reduction rate after 20 washes.

Apart from various semiconductor nanomaterials, a number of organic materials have

been employed in the fabrication of antibacterial and antiviral cotton. Graphitic-like carbon nitride (g-C₃N₄) is a novel two-dimensional metal-free photocatalyst that exhibits efficient and stable photocatalytic activity. Hosseinabad et al. directly coated as-synthesized g-C₃N₄/ZnO (CNZ) nanocomposite onto cotton fabric via sonication technique (Hosseini-Hosseinabad et al. 2023). The prepared cotton containing 30% ZnO (CNZ-30) exhibited significant photocatalytic inhibitory activity against both *E. coli* and *S. aureus*. The bacteriostatic inhibition of CNZ-30 coated fabrics was over 98% for both *E. coli* and *S. aureus* even after 18 washes. This excellent performance can be explained by the effective coupling of ZnO with g-C₃N₄, which improves the light absorption and reduces the e⁻/h⁺ pair recombination rate (In Figure 6C). Photosensitizers are agents that absorb light energy and generate ROS for inactivating pathogenic microorganisms. Tang et al. presented a novel method to fabricate photoinduced antibacterial and antiviral cotton (PIFs) by a chemisorption process. The anionic photosensitizers of rose bengal and anthraquinone-2-sulfonic acid sodium salt monohydrate (2-AQS) were employed to modify cationization cotton (In Figure 6B). The amount of ROSs were determined by N,N-Dimethyl-4-nitrosoaniline as a highly selective hydroxyl radical scavenger (Tang et al. 2020). The antibacterial and antiviral function were examined against *E. coli*, *Listeria innocua* (*L. innocua*), and T7 bacteriophage (T7 phage). The PIFs demonstrated highly efficient biocidal property against *E. coli* and *L. innocua* bacteria and T7 phage viruses, attaining microorganism reduction rates about 5-6 logs under sunlight exposure less than 60 min.

Porous materials such as metal-organic frameworks (MOFs), covalent organic frameworks (COFs), and hydrogen-bonded organic frameworks (HOFs) are very highlighted materials for photocatalytic components. Our group and co-workers have developed MOFs and HOFs for the deactivation of biological pathogens. In the work of Wang (Wang Xingjie et al. 2022a), a straightforward fabrication method was used to construct visible-light induced biocidal coatings on fabrics by utilizing photoactive MOF(NU-1012) with titanium/zirconium clusters and a pyrene linkers (In Figure 6D). Electronic structure characterization and experimental studies have shown that NU-1012 exhibits enhanced properties of reactive oxygen generation ([•]O²⁻ and ¹O²) under visible light. Besides, the NU-1012/cotton composite exhibited admirable antibacterial performance within a very short time of contact. For example, a 1.5 log (97%) reduction of *E. coli* and a 2.4 log (99.6%) reduction of *S. epidermidis* were

obtained after illumination of visible light for 10 min. Additional work by Wang (Wang Yao et al. 2022b) further investigated the process of ROS generation and storage. The authors developed a liquid phase spray deposition method to coat HOF onto cotton substrate (In Figure 6E). The HOF-cotton promoted the spontaneous ROS generation under daylight and long-term ROS storage in dark conditions. Compared with TiO₂ or g-C₃N₄ photocatalysts, the HOF-101-F showed a 10 to 60-fold increase of ROS generation and 10 to 20- fold enhanced ROS storage ability. The results pave the new way for the development of personnel protective clothing for rapid deactivation of pathogenic bacteria or viruses under both daylight and dark conditions.

Table 1. Summary of various materials used in photocatalytic degradation of pathogenic bacteria/ viruses on cotton fabrics.

Photocatalysts	Techniques	Anti-B/V mechanism	Tested pathogens	Antibacterial activity (performance)	Refs
TiO ₂	aqueous sol process	destruction of the bacteria cell wall and membrane by ROS ROS, Ag ⁺ , Br ⁰	A dose of bacteria	Inhibited the growth of bacteria	(Wu Deyong et al. 2009)
Ag/AgBr-TiO ₂	spray coating		<i>E. coli</i> ATCC-8739	reduction ratio of 99.87% under visible light and 81.43% in dark	(Rana et al. 2016)
Mn-TiO ₂	sol gel	ROS	<i>S. aureus</i> ; <i>K. pneumoniae</i>	100% reduction	(Zahid et al. 2018)
ZnO/BiOBr	Ultrasonic-microwave	Reduce e ⁻ /h ⁺ recombination rate	<i>S. aureus</i> and <i>P. aeruginosa</i>	The inhibition rates against <i>S. aureus</i> and <i>P. aeruginosa</i> were 96% and 76%	(Yang Hao et al. 2018)
Cationic cotton & Anionic photosensitizer	chemisorption	ROS	<i>E. coli</i> and <i>L. innocua</i> ; viruses (T7 bacteriophage)	99.9999% (6 log) reductions against Bacteria; more than 6 log reduction of plaque-forming units	(Tang et al. 2020)
Nano-crystalline TiO ₂	Impregnating	ROS	<i>Influenza virus(H1N1)</i>	destruction of all virion structures	(Selishchev et al. 2022)
MoS ₂	spray-coating	ROS	<i>E. coli</i> and <i>S. aureus</i>	10% MoS ₂ coated fabric reduced <i>E. coli</i> and <i>S. aureus</i> by about 98%	(Kumar et al. 2022)
g-C ₃ N ₄ /ZnO	Sonication coating	reduced e ⁻ /h ⁺ pair recombination rates	<i>E. coli</i> and <i>S. aureus</i>	The bacterial reduction rate for both was above 98%	(Hosseini-Hosseinabad et al. 2023)
Zr ₆ Ti ₄ -based NU-1012		enhanced ROS generation (•O ₂ ⁻ and ¹ O ₂)	<i>E. coli</i> ; <i>S. epidermidis</i> , and T7 phage.	1.5 log(97%) reduction of <i>E. coli</i> and a 2.4 log(99.6%) reduction of <i>S. epidermidis</i> after irradiation 10 min; 7-log(99.99999%) reduction of T7	(Wang Xingjie et al. 2022a)

HOF-101-F	liquid phase spray deposition	(ROS) generation upon daylight & longterm storage in dark conditions	<i>E. coli</i> ; <i>K. pneumoniae</i> ; <i>S. aureus</i> , and <i>Mycobacterium marinum</i> strain.	over 99.99% bactericidal efficacy	(Wang Yao et al. 2022b)
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3.4 Detoxification of chemical warfare agents

CWAs used for military operations are chemical substances of high toxicity which are capable of poisoning or killing enemy human beings, animals, and plants on a large scale. It is also one of the most brutal weapons of mass destruction compared to nuclear and biological weapons. In World War I, the use of phosgene, mustard gas, and lewis acid, caused 1.3 million casualties. During World War II, millions of innocent civilians were killed by hydrogen cyanide gas (Ganesan et al. 2010). Although the modern international community has generally legislated against the illegal use of CWAs, it has always posed a serious threat to human society due to the possibility of national conflicts and terror attacks.

There are more than 70 different chemicals or mixtures of chemicals were used or stockpiled as CWAs (Liu et al. 2017). According to the human physiological responses to the CWAs, the CWAs are classified as nerve agents, blistering agents, blood agents, choking agents, and psychomimetic agents etc (Ganesan et al. 2010). Based on their chemical structure, they can be classified as organophosphate, organosulfur, organic nitrogen compounds, arsenic lewisite and so on (Some as shown in Figure 7A). Decontamination of CWAs can be by physical removal or chemical neutralisation. Physical removal involves the adsorption of toxic CWAs using adsorbents such as activated carbon, kaolin and talc. Chemical neutralisation involves the conversion of CWAs into innocuous products through chemical reactions under ambient conditions. Physical adsorption is easy to operate but with the risk of secondary emitters, while chemical degradation mainly involves hydrolysis, microbial enzymatic degradation, oxidation, and photolysis (Munro et al. 1999). However, the chemical degradation of CWAs under natural conditions takes several days or more. Therefore, catalytic degradation of CWAs is a more efficient method to complete detoxification CWAs within a short period of time. Due to the high toxicity of CWAs, diverse alternative simulants with similar structures are chosen to study the degradation kinetics of CWAs by catalysts (Bartelt-Hunt et al. 2008). Among them, dimethyl 4-nitrophenyl phosphate (DMNP) of the organophosphorus and 2-chloroethyl ethyl sulfide (CEES) of the organosulphur compounds (as shown in

Figure 7B) are the two most common CWA simulants.

Catalytic degradation of CWAs mainly consists of hydrolysis and photocatalysis (Jabbour et al. 2021). Hydrolysis is the primary detoxification pathway for most cases. For example, organophosphorus nerve agents can be degraded through the unstable P-F, P-S bond. Organosulfides can be hydrolyzed through the C-Cl bond, but organosulfides generally have less solubility in water and the formation of intermediates will inhibit subsequent hydrolysis. In contrast, photocatalysis is a more indiscriminate degradation method. There are two main working approaches of photocatalytic degradation of CWAs. One is the generation of ROS by the photocatalyst under light irradiation, which directly oxidizes the CWAs. Another one is photothermal enhanced hydrolysis that increases the rate of hydrolysis of CWAs associated with photothermal conversion catalytic systems. For example, the hydrolysis half-life of HD at 0.6 °C is 158 minutes, while the hydrolysis half-life at 40 °C is 1.5 minutes (Munro et al. 1999), so the hydrolysis rate is temperature-dependent. Therefore, embedding photothermal materials in the photocatalytic component will indirectly accelerate the hydrolysis of the CWAs with the light-induced increase of temperature. Zuo et al. demonstrated that CWAs such as soman, sarin, sulfur mustard, cyanogen chloride and perfluoro isobutylene could be eliminated by TiO₂ through photolysis or photocatalysis under UV light irradiation (Zuo et al. 2007). Yao reported a solar photothermal-driven detoxification of DMNP simulants by polydopamine-mediated Zr-MOF (UiO-66-NH₂)-coated fabrics, the degradation half-time of DMNP on the PA-6@PDA@UiO-66-NH₂ nanofibers was only 0.5 min (Yao Aonan et al. 2020). In another work by Song (Song et al. 2020) that the photothermal material graphene was combined with UiO-66-NH₂ to fabricate nonwoven GF@UiO-66-NH₂ fabrics, the GF@UiO-66-NH₂ fabrics exhibited ultrafast photothermal catalytic degradation of DMNP and the half-time of the decontamination reaction reduced from 3.4 to 1.6 min under light irradiation.

In addition, many fabrics have been developed for the detoxification of CWAs. For example, Maya et al. integrated UiO-66 on the silk surface (López - Maya et al. 2015). Zhao et al. modified polyamide-6 nanofibers with UiO-66, UiO-66-NH₂, and UiO-67 (Zhao et al. 2016). Lee et al. assembled UiO-66-NH₂ onto polypropylene fabrics, and these fabrics showed ultra-fast degradation of CWA simulants (Lee et al. 2017). However, few studies about cotton fabric-based materials for the degradation

of CWAs have been reported.

In 2008, Grandcolas et al. was the first to report the use of WO₃/titanate nanotubes (WO₃/TiNT) photocatalysts for the degradation of diethylsulfide (DES, a simulant of yperite blistering agent). The WO₃/TiNT photocatalysts were further assembled onto the cotton fabric by layer-by-layer deposition(Grandcolas et al. 2009). The catalytic properties of these WO₃/TiNT-cotton fabrics were evaluated by the detoxification of the organophosphonate simulant, dimethyl-methylphosphonate (DMMP), the cotton textiles with WO₃/TiNT efficiently eliminated DMMP within 5 mins under 25W light illumination. With the idea of combining Cu-BTC MOF and oxidized graphitic carbon nitride (g-C₃N₄-ox), Giannakoudakis et al. deposited the obtained MOFgCNox nanocomposite onto cotton textiles(Giannakoudakis et al. 2017). The hybrid textile displayed supreme adsorption and detoxification ability toward the organophosphate nerve agents like dimethyl chlorophosphite. The as-prepared fabrics adsorbed about 7 g of dimethyl chlorophosphite/its degradation products per gram of copper. The detoxification mechanisms mainly include hydrolysis and photocatalytic degradation to methanol and phosphoric acid.

Our group has also completed a series of works on the catalytic degradation of CWAs by HOF/MOF-cotton fiber composites. A “shape-matching” stacking strategy (Ma et al. 2020) was developed to synthesize hydrogen-bonded organic frameworks (HOF-100, HOF-101, and HOF-102), then we fabricated ultrastable HOF-102 onto cotton fiber surfaces. The photocatalytic degradation performance of HOF-102/cotton combining the pyrene-based chromophores was evaluated by using the CEES. When 1% of the catalyst is used, the HOF-102/cotton composite converted 100% of the CEES in 30 minutes, as shown in Figure 7D. Besides, we developed a series of Zirconium-based metal-organic framework (Zr-MOF)/hydrogel composites. Their catalytic hydrolysis properties toward DMNP and DEMP (O, S-diethyl methylphosphonothioate) of organophosphorus simulant were compared (Ma et al. 2021). The results showed that the MOF-808 and UiO-66-NH₂/BPEIH showed better catalytic activity for DMNP hydrolysis. To further improve the practicability of hydrogel components, we integrated MOF-808/BPEIH onto cotton fabrics, the as-prepared fabrics show uniform distribution in SEM images and catalytic stability under different treatment conditions. Moreover, the MOF-808 hydrogel-cotton fabrics rapidly detoxified CWA simulants as well as actual CWAs (as shown in Figure 7E). This work paves the way for further design of high- performance MOF-based cotton

protective textiles for the instantaneous detoxification of CWAs in practical conditions.

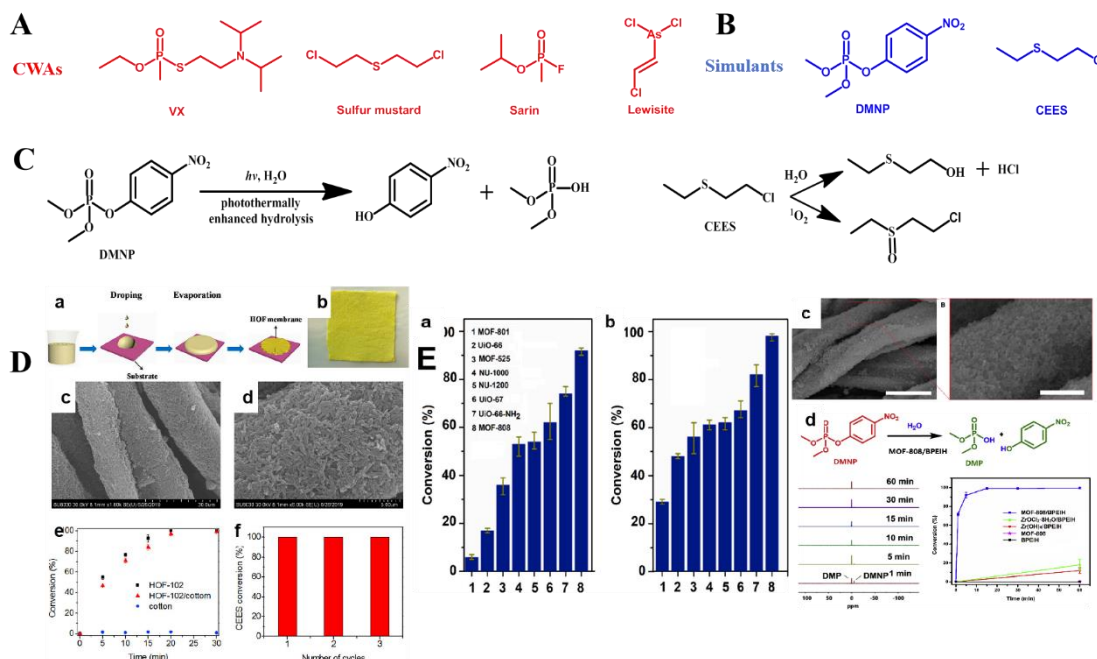


Fig. 7. (A) Chemical structures of the real CWAs: VX, Sulfur mustard, Sarin, and Lewisite. (B) Chemical structures of DMNP and CEES simulants. (C) Photocatalytic degradation mechanism of DMNP (Photothermal enhanced hydrolysis) and CEES (Hydrolysis and photooxidation). (D) HOF-102/cotton composite. (a) Preparation, (b-d) morphology and (e-f) photochemical catalysis (Ma et al. 2020). (E) Zr-MOF catalysts for catalytic hydrolysis of organophosphorus CWAs (Ma et al. 2021). (a-b) Comparison of DMNP hydrolysis using different Zr-MOF-based composites, (c) SEM images of MOF-808/BPEIH/fiber, (d) DMNP hydrolysis kinetics of MOF-808/BPEIH composite.

4. Conclusion and outlook

To conclude, this article reviews the recent developments in cotton fabric-based photocatalytic composites for the degradation of organic contaminants, specifically in the area of self-cleaning, degradation of gaseous contaminants, pathogenic bacteria or viruses, and chemical warfare agents. Some of the commonly used photocatalysts and its photocatalytic mechanisms in relation to their use on cotton fabrics were highlighted. Taking TiO_2 , the most important inorganic semiconductor photocatalyst, as an example, we summarise in detail its development in self-cleaning cotton and ways to improve its photocatalytic activity. Similarly, we present other photocatalysts such as complex metal oxides, conjugated polymers, and porous coordination polymers. Subsequent applications for the detoxification of gaseous pollutants and the

elimination of pathogenic bacteria/viruses, and chemical warfare agents are also described.

Despite these significant advances in cotton-based photocatalyst composites, challenges remain in the selection of photocatalysts and the way they are combined with cotton fabrics. First, excellent photocatalysts should be able to produce photocatalytic activity over a wide spectral range. Second, the actual loading of the fabric as well as the fast and sustained photocatalytic activity should be considered. Thirdly, the actual application should be able to resist repeated washing and cyclic stability. In addition, inorganic semiconductor materials are relatively well-established for photocatalysis in cotton fabrics. However, the study of metal-organic framework materials with excellent performance on cotton fabrics is still in the initial stage, so there is still a lot of work to be explored.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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