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Review Article

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Recent advancements in polyoxometalate-functionalized fiber materials: A review

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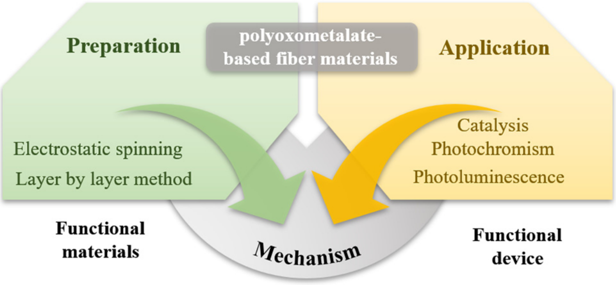
Abstract: The development of advanced composite materials based on polyoxometalates (POMs) and fibers has attracted significant attention due to their combination of the unique chemical reactivity of POMs and the flexible wearable properties of fiber materials. The exceptional properties exhibited by those resultant composites have been widely employed in catalysis and optical sensors. In this article, we aim to provide an overview of progress on POMs functionalized fiber materials involving the preparation methods, namely, electrostatic spinning and layer-by-layer self-assembly methods, as well as the developments in the fields of catalysis, photochromism, and photoluminescence. Current applications are critically assessed and promising future target systems are discussed.

Keywords: polyoxometalate, fiber, application



Graphical abstract: In this review, polyoxometalate-based fiber materials, including preparation and application, are introduced, showing promising performances in catalysis and optical property.

1 Introduction

A recent trend in molecular and material sciences is the development of multi-functional materials that meet societal needs in catalysis, material science, energy-related sciences, and magnetism [1–3]. It has been widely recognized that functional fibers offer additional value through effective enhancement. As such, fiber in the new era should not only meet the fundamental needs of consumers but also possess muti-functionals, such as photochromic property, anti-UV, and anti-bacterial [4,5]. Generally speaking, these significant functions are achieved by incorporating functional molecules on or within fibers or embedding relevant components. Among the suitable and tunable components considered by researchers, the resort to structurally defined inorganic building blocks appears as a convenient and feasible route to better control their dispersion in the hybrid system.

Polyoxometalates (POMs) are a class of discrete anionic molecular metal oxides of early transition metals (*e.g.*, V, Mo, W, Nb, Ta), usually constructed *via* the condensation of metal oxide polyhedrons in a corner-, edge-, and even face-sharing manner [6]. POM family that structurally and compositionally can be broken into two subcategories according to whether they contain heteroatoms, namely, isopolyanions and heteropolyanions. Currently, POMs have six basic structures: Keggin, Dawson, Anderson, Lindqvist, Waugh, and Silverton (Figure 1). POMs continue to attract the attention of research groups due to their intriguing chemical and physical features, allowing them to be employed in various research fields such as catalysis, and molecular electronics [7,8]. Several excellent reviews describe the state-of-the-art cluster designing and redox behavior characterization of POM for redox flow batteries [9], application of POMs in chemiresistive gas sensors [10], discussing synthetic methodologies of POM-based inorganic-organic hybrids for heterogeneous catalysts [11], and so on. Nevertheless, study on fiber as organic polymers and vehicle is limited. In particular, Carraro and Gross have described in their review paper that the hybrid materials are based on the embedding of organically modified transition metal oxoclusters or POMs into polymers for functional

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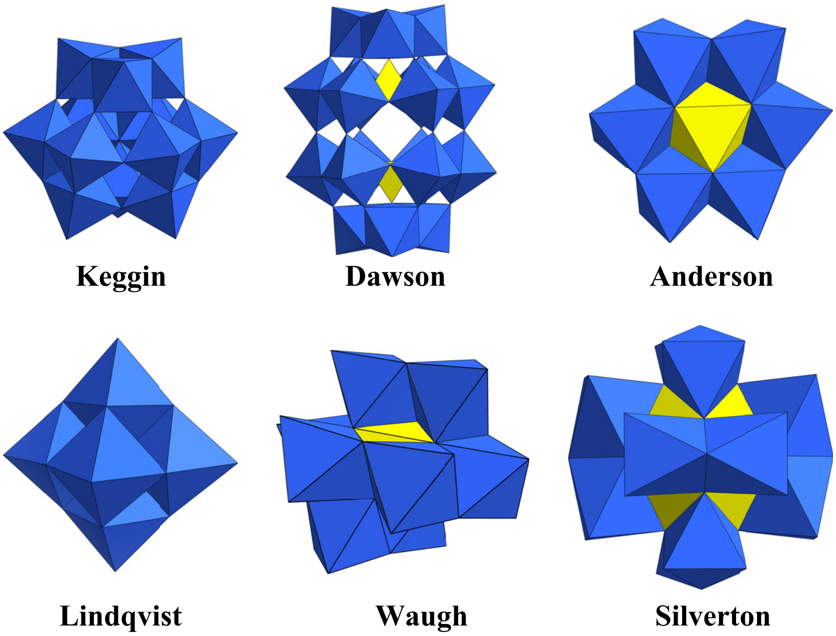

Figure 1: Polyhedral representation of six kinds of POM architectures.

applications [12]. Snider and Hill detailed the emerging field of functionalized reactive polymers for the elimination of CWAs including POMs as catalytic components [13].

Here, we will develop the discussion on composite materials combining POMs and fiber, focusing on the rational design and properties of hybrids achieved through two classical methods. These hybrids are further discussed in the light of multi-functional assemblies and materials; in particular those displaying encouraging results in catalysis and optical property, in the light of current challenges, such as multi-functional and stable material. Two main pathways for the preparation of the POM/fiber composites can be identified; their main advantages and disadvantages together with potential future directions are described. In the first part, we focus on the formation of hybrids through electrostatic spinning with different polymers: polyacrylamide (PAM), polyvinylpyrrolidone (PVP), polyacrylonitrile (PAN), polyvinyl alcohol (PVA), and polylactic acid (PLA). In the second part, we consider hybrids synthesized by layer-by-layer (LBL) self-assembly. In fact, there are differences, and relation as well, between them. Besides, the properties and applications of these systems are further highlighted in sole section, and their potential in future developments, within this emerging area at the interface of material and molecular sciences, are put into perspective.

2 Synthetic strategy

With the continuous advancement of science and technology, the research on the application of POM-based composites is experiencing rapid growth. Fiber, due to its morphology, structure, and properties, emerges as one of the most promising carriers for constructing functionalized fiber materials with POMs. The current preparation methods for this type of composite materials are primarily categorized into two approaches: electrostatic spinning method and LBL self-assembly method.

2.1 Electrostatic spinning method

The electrospinning technique is regarded as one of the most promising methods for nanofiber preparation due to its inherent advantages, including a simple and efficient process, high production yield, and rapid repetition rate [14]. Driven by the research on inorganic functional fibers and inorganic–organic hybrid fiber materials, pure POM nanofibers or POM-based nanocomposite fibers are synthesized using electrostatic spinning technology to showcase the role of POMs through fiber morphology. The current practice involves the utilization of organic polymers, with the specific preparation process outlined as follows (Figure 2): POMs are

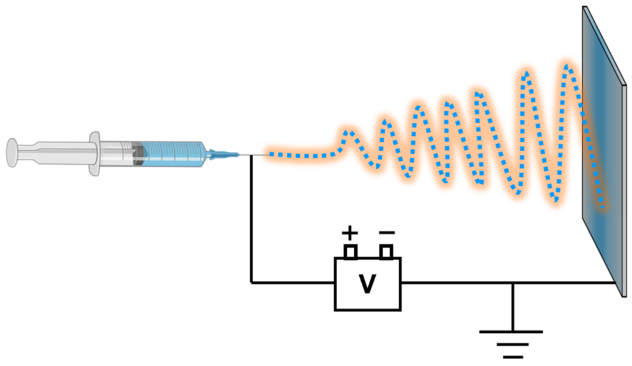

Figure 2: Diagram schematic of electrospinning device.

blended with a polymer to create an electrospinning solution, which is subsequently loaded into a syringe equipped with a copper needle. The copper needle and the aluminum foil receiving device are connected to the positive and negative terminals of a high-voltage power source, respectively. Under a specific voltage, the electrospinning solution is ejected from the copper needle and deposited on receiving device at an appropriate distance from the needle tip, resulting in the formation of nanofibers. The distance must be sufficient to allow for solidification and subsequent collection on the receiving device during the fine-flow injection process.

The common polymers used as POM carriers include PAM, PVP, PAN, PVA, PLA, *etc.* (Figure 3). Among them, PVA is applied most in many studies. In 2004 and 2007, Gong *et al.* reported PW_{12}/PVA, $SiW_{11}V$/PVA, SiW_9V_3/PVA, and $P_2W_{17}V$/PVA (the abbreviations are shown in Table S1) composite fibers furnished from spinning solution including different POMs and PVA, respectively. The results indicated that POMs are helpful in the crosslinking and in decreasing the swelling degree of PVA [15,16]. Later, $EuPW_{11}$ and $EuPW_{10}$-1 were dissolved in PVA to weave different fibers, which exhibited excellent photoluminescence [17]. Taking into account the ability to store and release electrons of POM-based materials under specific conditions, POMs are regarded as excellent candidates for the design of composite hybrid materials which exhibit interesting cooperative effects for behaving as electrode. Subsequently, Gong *et al.* reported POM-based composite nanofiber-modified electrode. At first, P_2W_{18}-1 was dissolved in PVA solution resulting in electrospinning solution. Then, the spun fibers were collected on the aluminum foil covered on the surface of ITO electrode. The formation of modified electrode was achieved by removing the aluminum foil [18]. Additionally, such a nitrite sensor was developed since P_2W_{18}-1 had the performance of electrocatalytic reduction of NO_{2-}.

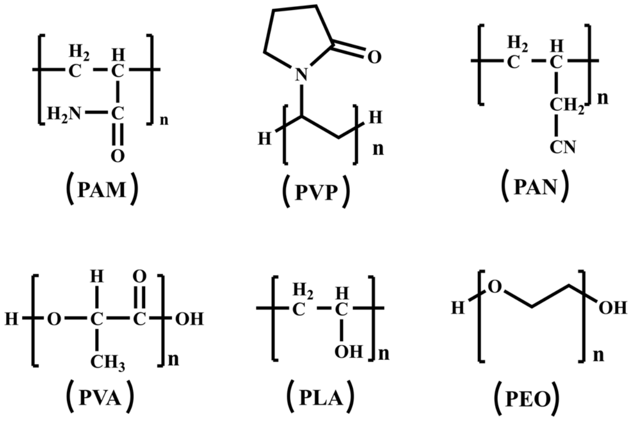

Figure 3: Polymer structure formula commonly used for POMs carriers.

In 2006, Peng *et al.* obtained PVA/$SiW_{11}Co$-P_2O_7 composite fiber, and the fiber underwent calcine to form thin fiber with 250 nm and maintained intact Keggin structure. Interestingly, the fiber showed thermal stability and color change performance [19]. Based on this, other polymers were used to prepare POM-based fiber materials with various properties. For example, Song *et al.* reported soft EuW_{10}-2/PAN composite film by blending EuW_{10}-2 and PAN [20] (Figure 4), while Qi *et al.* obtained hydrophobic PLA nanofibers blended with P_2W_{18}-1, OXA and PLA [21]. Furthermore, combined with hydrophilic PAN nanofibers containing PSP, double-layer Janus nanofiber was prepared with the help of hydrophobic PLA. Owing to the difference in wettability between them, excess exudate could be drained around the wound.

The loading of POMs onto the polymer by electrostatic spinning technology can prevent the POMs from changing into heterogeneous microphase and mass aggregation, which is an effective and simple method to avoid the phase separation of POMs in the polymer matrix. In 2006, Zhang *et al.* prepared PVA/EuW_{10}-3 composite fibers by electrostatic spinning. TEM showed that EuW_{10}-3 particles with diameters of several nanometers to tens of nanometers were dispersed in the composite fibers [22]. These monodisperse nanoparticles prevented the phase separation of EuW_{10}-3 from PVA matrix, making the inorganic component and polymer component good compatibility. In addition, POMs can be loaded on SiO_2 or other organic microporous polymers. In 2019, Wu *et al.* reported $Ni(CH_3COO)_2$ and Keggin-type SiW_{12} in PVA solution for electrospinning [23]. The product was carbonized in N_2, resulting in modified carbon nanofibers (SiWNi-CNFs) after decomposition and recombination. Besides, SiWNi-CNFs showed excellent electrocatalytic hydrogen evolution performance. In 2021, the PMo_{12}, TiO_2 (100 nm), and SiO_2 (12 nm) were dispersed in PVA solution to form electrospinning solution for further electrostatic spinning [24]. $PMo_{12}/TiO_2/SiO_2$ nanofibers were obtained by calcination, which were further

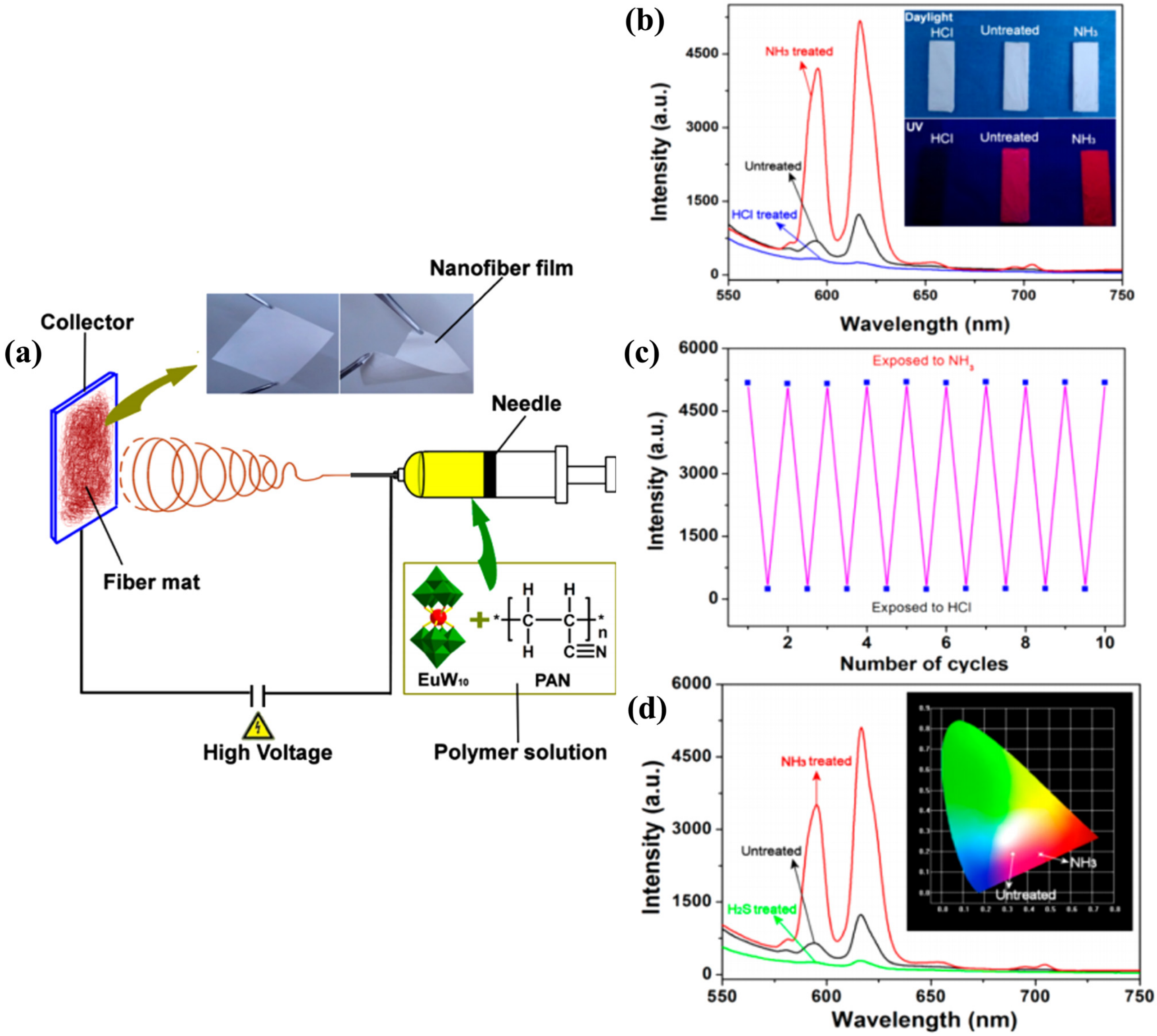

Figure 4: (a) Electrospinning process of the EuW_{10}/PAN nanocomposite films. (b) 23% EuW_{10}/PAN nanocomposite film exposed to HCl/NH_3. (c) Luminescent intensity at 616 nm of the nanocomposite film as a function of exposure cycles. (d) Luminescent intensity exposed to H_2S/NH_3. Reproduced from ref. [20].

mixed into polyvinylidene fluoride to obtain a film with excellent photocatalytic properties. In 2022, Farha *et al.* prepared functional microporous polymer PIM-1-AO with carboxylic acid and amide oxime groups, and then acetonitrile suspension of PW_{12}, PIM-1-AO, and DMF were mixed to make electrospinning solution for the formation of PIM-POM porous fiber pad through electrostatic spinning [25]. Additionally, PIM-POM had catalytic oxidation effect on CEES in the presence of H_2O_2. In 2020, Semnani *et al.* reported solvent-free nanofiber electrolyte, which was prepared using polyethylene oxide (PEO) as polymer matrix, lithium perchlorate as salt, ethyl carbonate as plasticizer, and Keggin-type POMs (Cu-POM@Ru-rGO, Ni-POM@Ru-rGO, CoPOM@Ru-rGO) as filler [26]. Compared with polymer electrolytes obtained by melting and solution spinning, electrospinning electrolytes had excellent ionic conductivity and were good candidates for solvo-free electrolytes for lithium-ion batteries (Figure 5).

Although electrostatic spinning technology is a very classical and practical method to yield nanofibers, it requires some special equipment and rigorous operating conditions, such as air humidity and spinning voltage, which affect the spinning effect. Consequently, inadequate control of operational conditions can lead to the emergence of issues.

2.2 LBL self-assembly method

LBL self-assembly method, known as chemical deposition technique, is that POMs or other materials are deposited on the fiber LBL, so that POMs can make full use of the fiber performance (Figure 6). Electrostatic interaction is the main driving force for deposition alternately. The details are as follows: first, the substrate with charge (negative charge as an example) is immersed in the solution with opposite charge. Owing to the electrostatic action, the particles with opposite charge will be adsorbed on the surface of substrate, making the substrate with positive charge. The materials were washed to remove the physical adsorption particles. Then, the substrate is dipped into a solution with negatively charged particles to assemble another layer of negatively charged particles on the surface of the substrate. By repeating the above process, the multilayer film can be obtained by alternating deposition.

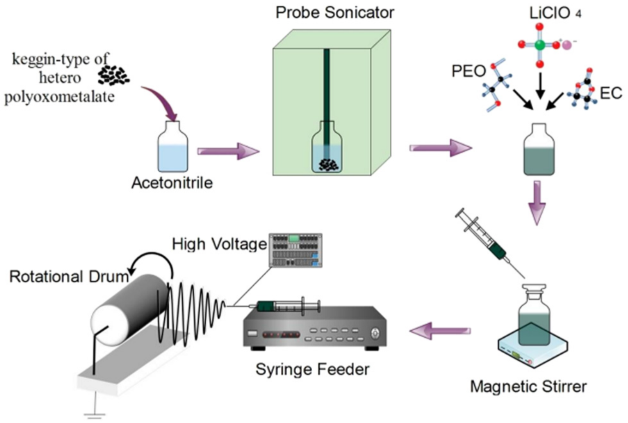

Figure 5: Electrospinning set-up. Reproduced from ref. [26].

In 2005, Ding *et al.* reported a composite cellulose acetate (CA) material by LBL self-assembly technology, employing positively charged polyacrylamide hydrochloride (PAH) and negatively charged SiW_{12} [27]. After high-temperature calcination, pure Keggin-type SiW_{12} nanotubes with wall thickness of about 50 nm were obtained (Figure 7). Furthermore, the investigation and application of fibers and nanotubes with nanostructured features have been in various fields including catalysis, conduction, photochromism, and electrochromism.

Additionally, the combination of electrospinning technology and LBL self-assembly technology is also an effective method to prepare POMs functionalized fiber materials. In 2006, Dong *et al.* successfully fabricated PVA nanofibers using electrospinning technology, which was applied on ITO electrode [28]. Then, PAH and P_2Mo_{18} with opposite charge were sequentially deposited on the composite electrode PVA/ITO, resulting in the formation of a multilayer film composed of P_2Mo_{18}/PAH. Interestingly, the electrospun PVA nanofiber can be used as a self-assembly platform because of its large surface area and the negative charge generated by the dissociation of $-CH_2OH$ in PVA. As mentioned above, Zhou *et al.* prepared negatively charged polyacrylic acid (PAA)/PVA/PW_{12} nanofibers by electrospinning, followed by the deposition of negatively charged PW_{12}, positively charged polyethylenimide (PEI) and Ag^+ using LBL self-assembly technology [29]. The electrostatic forces between the cationic compounds (such as PEI or Ag^+) and the PAA/PVA/PW_{12} substrate facilitate the attraction of negatively charged PW_{12} to form a double ultra-thin layer

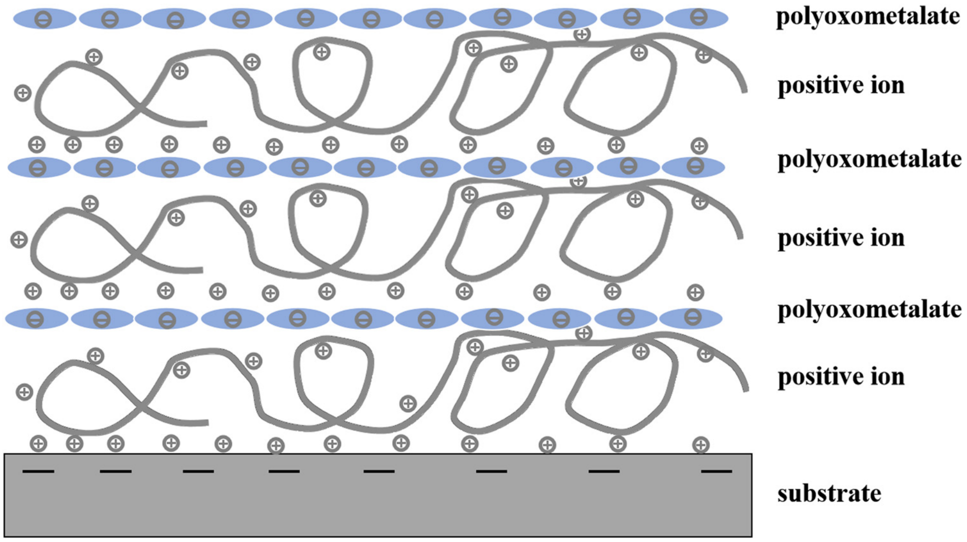

Figure 6: Diagram schematic of LBL self-assembly.

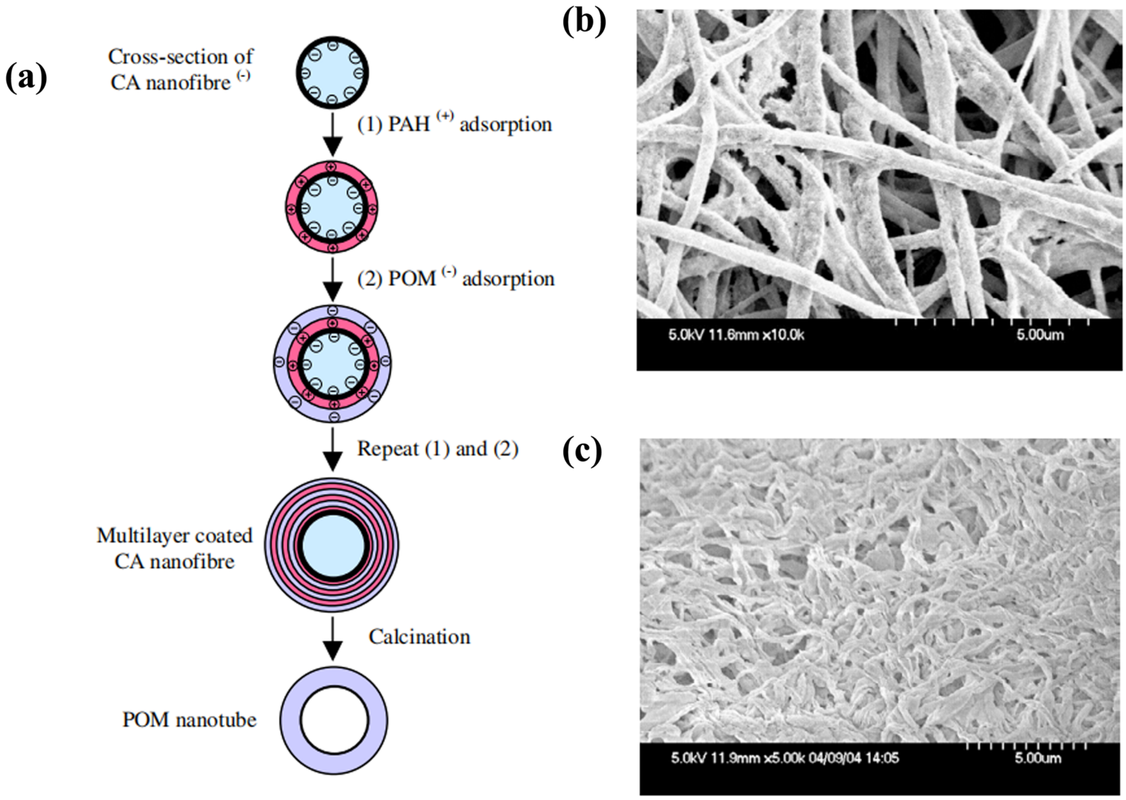

Figure 7: (a) Fabrication of POM nanotubes *via* LBL coating and thermal removal of the electrospun nanofiber. (b) SEM images of (PAH$_{2.5}$/H$_4$SiW$_{12}$O$_{40}$2.5)$_5$ film-coated fibers. (c) SEM images of (PAH$_{2.5}$/H$_4$SiW$_{12}$O$_{40}$2.5)$_5$ film-coated fibers calcined at 380°C. Reproduced from ref. [27].

or multilayer film on the substrate. Finally, NaBH$_4$ was employed to reduce Ag$^+$, resulting in Ag-NPs deposited on the multilayer film. Besides, the results demonstrated that the Ag-(PEI)$_n$(PW$_{12}$)$_n$ film exhibited remarkable photocatalytic activity toward MB (Figure 8). Moreover, the self-assembly of multilayer films can be achieved through hydrogen bonding as the driving force. In 2020, decatungstate (DTS) and PEI were deposited on linen fabric alternately, resulting in the formation of a multilayer film through repeated dipping [30]. Linen, being a cellulose fiber, possesses a large number of hydroxyl groups, which have the capability to establish hydrogen bonds with amino or imino groups on PEI. Meanwhile, the amino groups in PEI can also form hydrogen bonds with oxygen atoms in DTS (Figure 9). In the same year, the group employed a similar method to fabricate PAA and DTS multilayers on cotton fabrics [31].

In a word, LBL assembly technology offers straightforward equipment and operation, along with a wide range of driving forces (such as electrostatic force, hydrogen bond, coordination, covalent, and other secondary forces) for device formation. Besides, there is an abundant of substances available for film formation including POMs, carbon nanotubes [32,33], proteins [34], *etc.* Additionally, the size and shape of the substrate do not impose limitations on these formations; furthermore, precise control over composition and structure of the film at the nanometer level can be achieved. The resulting films exhibit stable mechanical and chemical properties. However, it should be noted that various factors affecting film stability need to be considered in LBL technology, such as solvent type, ionic strength, solution concentration, temperature, and pH value of the system, making it necessary to continuously improve and study this technique. In fact, there are other methods in this field, such as sol–gel method [35], dry-jet wet spinning [36], deposition method [37], blending method [38–40], and covalent binding method [41,42]. Among them, deposition method and blending method are applied in many fields.

3 Applications

3.1 Catalysis

Based on their inherent redox activity, POMs can be employed for a wide range of storage and transfer electrons. The remarkable stability of POMs, coupled with

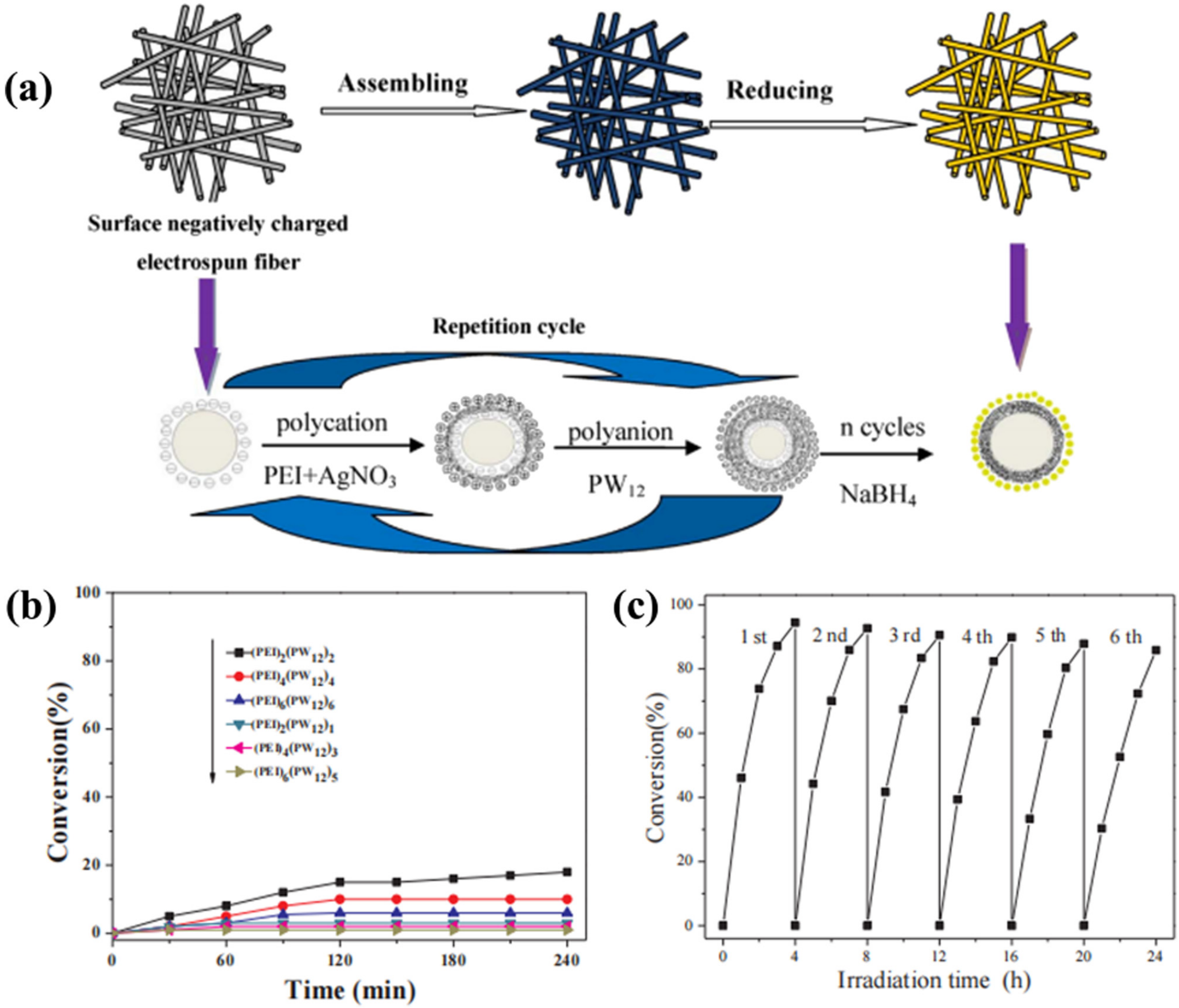

Figure 8: (a) LBL self-assembly process by depositing polycation and polyanion onto the PAA/PVA/PW_{12} fiber. (b) Photocatalytic degradation curves for different LBL films. (c) Cycle testing of photocatalytic activity of Ag-$(PEI)_2(PW_{12})_2$ film. Reproduced from ref. [29].

their versatile synthetic tunability, renders them highly attractive for investigating charge during light absorption. These general features of POMs, combined with alterable acid-base properties, make them valuable catalysts. Fiber materials have gained significant attention across various fields due to their unique nanosized structures with exceptional flexibility features. In recent years, researchers have begun exploiting the synergistic effects between POMs and fiber materials by developing a range of composite materials to address the pressing global energy challenges. Currently, research efforts focusing on POM-functionalized fiber materials primarily revolve around oxidation catalysis, photocatalysis, and electrocatalysis.

3.1.1 Oxidation catalysis

Oxidation is one of the most important chemical processes, often requiring catalysts. POMs are preponderant catalysts due to their noteworthy redox properties, strong persistence against oxidants, and environmental compatibility. Meanwhile, POM anions with high electron density can donate electrons to other acceptors, while accepting electrons into their vacant orbitals. Thus, POMs exhibit unique redox stability and reversibility. When reduced, POMs can be re-oxidized back to their original state by oxides such as O_2. In 2011, Cavaco-Paulo *et al.* found that the laccase-POM system (LMS) could effectively catalyze the oxidative polymerization of catechol for *in situ*

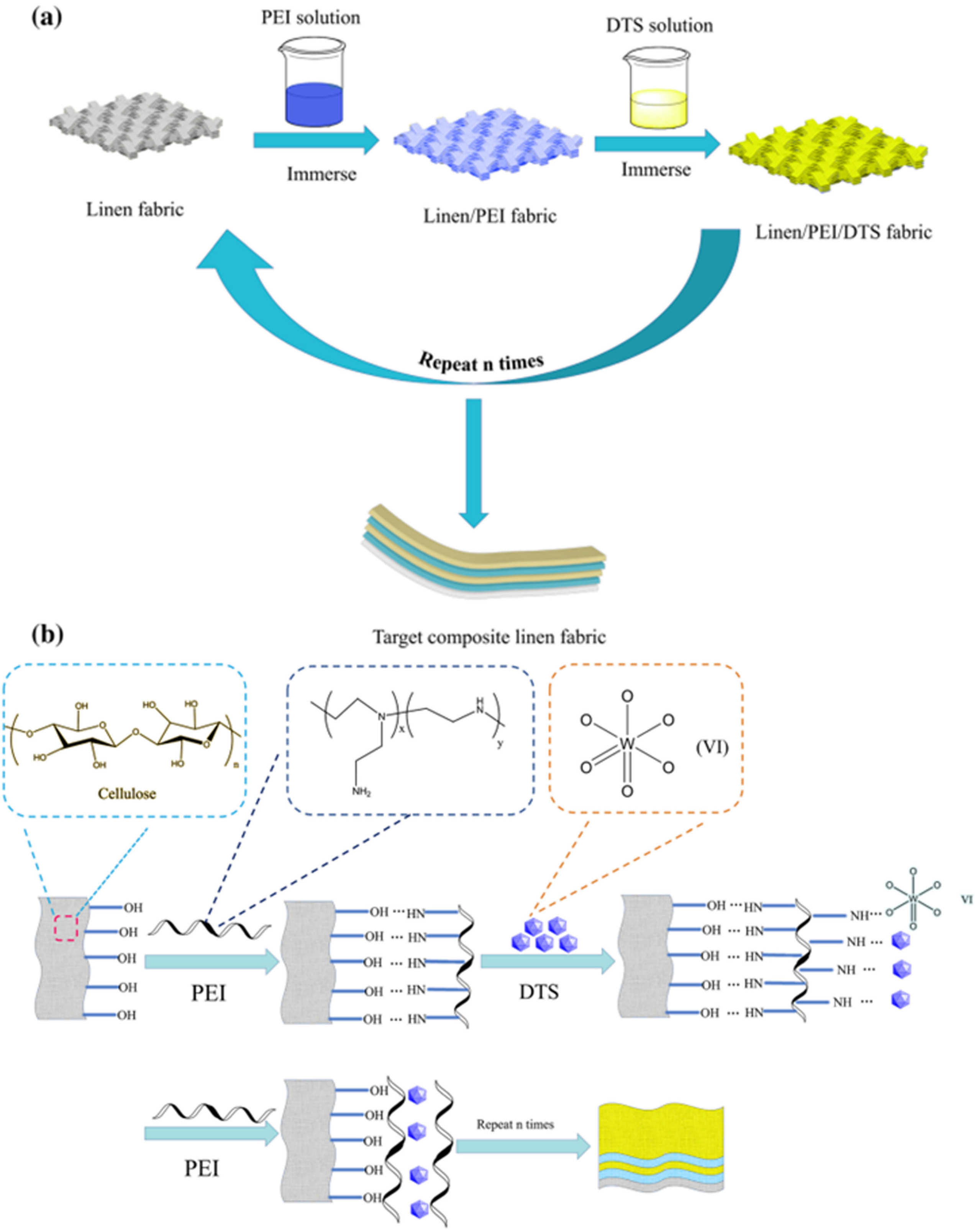

Figure 9: (a) LBL self-assembly preparation of composite fabric. (b) Mechanism scheme of LBL self-assembly to prepare composite fabric. Reproduced from ref. [30].

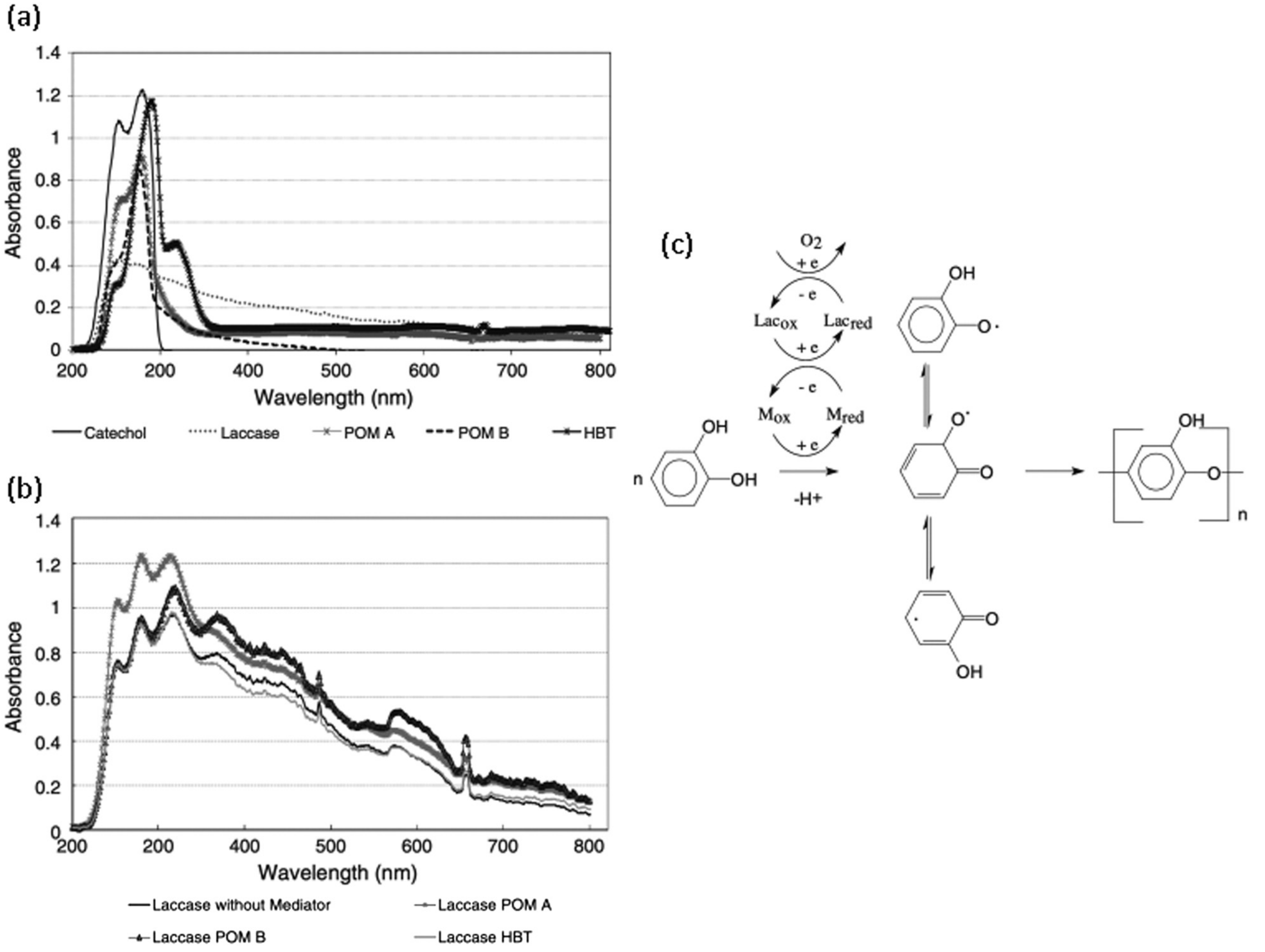

Figure 10: (a) UV–Vis spectra of single reaction solutions monitored with acetate buffer. (b) UV–Vis spectra of the oxidized solutions after incubation at 50°C for 2 h. (c) Mechanism of catechol polymerization in LMS. Reproduced from ref. [43].

dyeing of linen fabric with improved dyeing and washable properties [43] (Figure 10). Inspired by this work, our group reported the one-step one-bath method for *in situ* dyeing of cotton fabric using MnV_{13}-catalyzed catechol polymerization [44]. Through comprehensive analysis of various factors, it was found that the increase of POM concentration led to continuous enhancement in dyeing depth on treated cotton fabric while minimizing color loss during friction. The results indicated that POMs promoted the fixation level of the colorant.

In 2013, Dong *et al.* reported a new catalytic membrane composed of PV_2Mo_{10} attached to a PVDF hollow fiber membrane [36]. This membrane exhibited efficient oxidation and degradation of phenol in wastewater at room temperature using air as a green oxidant. Notably, the catalytic degradation efficiency was improved by reducing the air pressure above the water surface. In 2016, Allen *et al.* reported a CA/PEO (polyethylene oxide) nanofiber membrane grafted with PV_2Mo_{10} [45]. The grafted nanofiber membrane demonstrated remarkable capability for oxidizing and degrading organophosphorus or other toxic substances. The reduced POMs were oxidized to the original state by any oxides such as O_2 in the air. Therefore, the cellulose POM-grafted membrane exhibited the self-decontamination ability for many cycles.

As known, Ru-based compounds are considered promising oxidation catalysts due to their unique redox ability. POMs with more than one Ru atom generally have better catalytic oxidation performance than those with only one Ru atom, facilitating the formation of peroxy or oxygen complex and promoting selective oxidation. In 2016, Gamelas *et al.* reported a cellulose fiber/silica material loaded with Ru-POM for the decomposition of formaldehyde through its oxidation catalytic capacity of Ru-POM [46].

Compared to traditional hydrodesulfurization methods, oxidative desulfurization is particularly appealing due to its mild conditions, high desulfurization rate, and simple process. POMs are ideal candidates to address this challenge as their highly redox-active metals. In 2019, Zhao *et al.* synthesized Co^{2+}-PMo_{12}-based MOF-199 [47], which was then loaded on the CA fiber for oxidative desulfurization. Due to the large pore size of CA fiber, the specific surface area of POMs in polar reaction system can be increased while its solubility is reduced. Besides, the catalytic oxidation desulfurization effect was better than that of Co^{2+}-PMo_{12}/MOF. Subsequently, Zhao *et al.* synthesized a new type of inorganic-organic hybrid PMo_6W_6@MOF@CA fiber [48]. The oxidative desulfurization efficiency achieved 99.23% at 313 K with O_2 as oxidant. And the catalyst was easily recovered after drying at 323 K and reused more than 10 times.

3.1.2 Photocatalysis

POMs exhibit oxygen pπ to metal dπ, ligand to metal charge transfer (LMCT) transitions with absorbance maximum in the UV spectral region between 200 and 400 nm. Exciting into the LMCT, the resulting CT excited state consists of a reduced metal center and cation radical at the oxygen sites. In general, the reactivity of cation radicals is regarded to be the origin of the photocatalytic ability of the POMs. Specifically, there are two main mechanisms of POMs as a photocatalyst: (1) POMs have a band gap similar to the valence band and the conduction band in semiconductors. Under UV irradiation, the electrons on O 2p in POMs transferred to transition metal M 5d orbital transition, corresponding to photogenerated holes and photoelectrons. (2) Under light irradiation, POM LMCT excited states can result in photocatalysis of substrate through direct electron transfer or electron coupled atom transfer, thus leading to reduction of POM.

TiO_2, being the earliest semiconductor material in photocatalysis, imposes limitations on the utilization of visible light due to its inherent properties. The short lifetime, low mobility, and easy recombination of photogenerated carriers produced by TiO_2 necessitate a deeper understanding of sensitizer photophysics. POMs serve as excellent electron acceptors, effectively suppressing the recombination of photogenerated carriers and facilitating their separation and migration by capturing photogenerated electrons on the semiconductorduction band. Therefore, combining with POMs provides a feasible method to address the inherent limitations of TiO_2, thereby enhancing its overall photocatalytic performance. Due to the wide band gap of POMs and TiO_2, the POMs-TiO_2 system can only generate an optical response in the near ultraviolet region. For example, Guo *et al.* have designed a new type of photoreactor consisting of Ag/PW_{12}/TiO_2 film-coated optical fiber bundles [49]. The surface plasmon resonance effect of Ag nanoparticles was used to broaden the spectral absorption of TiO_2 and effectively inhibited the recombination of photogenerated electron-hole. Because of the synergetic photocatalysis effect between POMs and TiO_2 as well as the surface plasmon resonance effect of Ag, the photocatalytic effect of optical fiber-photocatalyst film was more excellent. The results showed that the combination of fiber and Ag/PW_{12}/TiO_2 film enhanced the photocatalytic degradation of RhB and 4-NP in aqueous solution under natural light irradiation (Figure 11). Wang *et al.* then prepared a new type of PMo_{12}-TiO_2 composite nanofiber loaded with Ag-NPs [50]. The photocatalytic experiment revealed that the PMo_{12}/TiO_2/Ag catalyst showed high efficiency and stable activity for the photodegradation of methyl orange under visible light ($\lambda > 420$ nm). In the process of photocatalysis, PMo_{12} was reduced to heteropoly blue undergoing light irradiation, which enhanced the visible light absorption of PMo_{12}/TiO_2/Ag composite material and significantly increased the density of photogenerated carriers. At the same time, the loaded Ag-NPs increased the photogenerated electron-hole separation, thus improving the photocatalytic activity of PMo_{12}/TiO_2/Ag composites. In 2021, Mahmoodi *et al.* reported a mixed matrix membrane formed by PMo_{12}/TiO_2/SiO_2 nanofibers and PVDF, showing excellent photocatalytic degradation activity for methylene blue and humic acid. In the report, PMo_{12} was used to eliminate photocatalytic defects in TiO_2 [24].

Driven by the HOMO-LUMO orbitals in POM, analogous to photogenerated electron–hole pairs, POMs are employed independently for photocatalysis. In 2014, Meng *et al.* have studied a new green catalytic membrane grafted polyionic liquid PVBMC onto polypropylene (PP) non-woven fabric and was further combined with PMo_{12} [51]. In such a light-driven system, the membrane exhibited excellent catalytic performance for acid orange 7 with a degradation rate of 95% under the irradiation of two 55 W fluorescent lamps. Besides, the catalyst showed good reusability and stability. In 2017, Zhou *et al.* reported multilayer catalytic films formed by PW_{12}, PEI, and Ag-NPs deposited onto PAA/PVA/PW_{12} nanofiber substrates [29]. Experiments have shown that the photocatalytic activity of negatively charged surface $(PEI)_n(PW_{12})_n$ on MB was higher than that of positively charged surface $(PEI)_n(PW_{12})_{n-1}$. Because negatively charged $(PEI)_n(PW_{12})_n$ films can not only absorb positively charged MB due to strong electrostatic attraction but also improve the degradation rate of MB solution owing to the top layer PW_{12} as a photocatalyst. PW_{12} was always covered by PEI as the number of layer (PEI-PW_{12} as a layer) increased, which reduced the photocatalytic activity of the catalyst. By comparison, $(PEI)_2(PW_{12})_2$ had the best catalytic effect. Nevertheless, the photocatalytic activity of $(PEI)_2(PW_{12})_2$ film was still not excellent. To further enhance electron transfer and

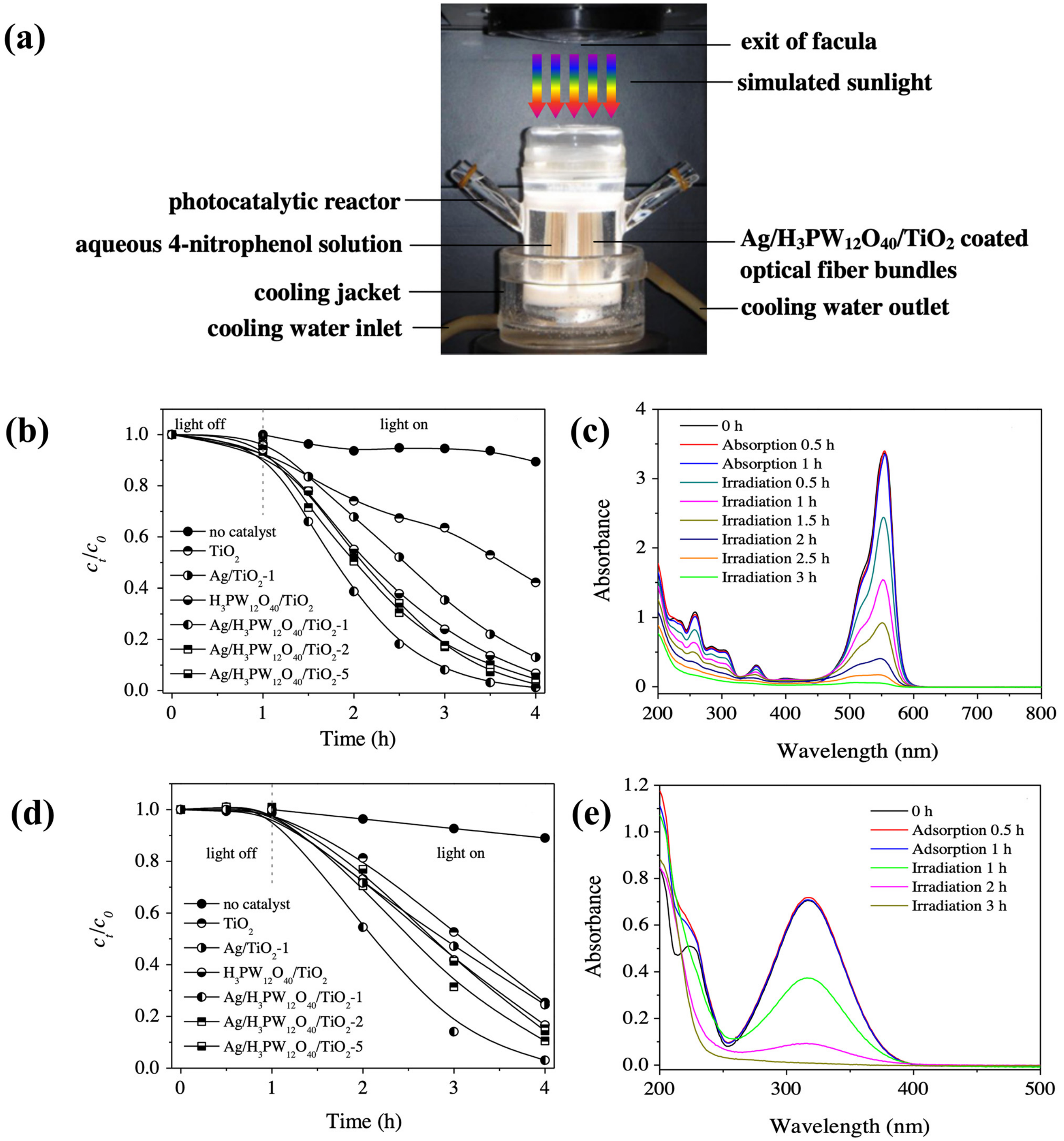

Figure 11: (a) $Ag/H_3PW_{12}O_{40}/TiO_2$-coated optical fiber photoreactor system. Photocatalytic activity of various fibers toward the degradation of RhB (b and c) and 4-NP (d and e). Reproduced from ref. [49].

improve MB degradation rate, Ag-NPs were deposited on $(PEI)_2(PW_{12})_2$. Apparently, this is a catalysis-promoting process and is advantageous to photocatalytic activity, because Ag-NPs can effectively capture photoelectrons, and the double-layer structure is helpful in interfacial charge transfer. Therefore, the photocatalytic activity of Ag-$(PEI)_n(PW_{12})_n$ film is much higher than that of $(PEI)_n(PW_{12})_n$ film.

In terms of composite material, the combination of POMs with fiber supports provides POMs with much larger surface areas, which may increase their catalytic activities by providing large contact areas between the catalysts and substrates for the surface-mediated electron-transfer reactions. For example, activated carbon fiber (ACF) as a photosensitizer can improve the light response of POMs in the visible light region. Besides, ACF exhibits high conductivity and facilitates efficient transmission of photogenerated electrons to prevent recombination with photogenerated holes. Additionally, its large surface area and exceptional absorption capabilities make it an ideal carrier for composite preparation. Due to the presence of a large number of active groups on ACF surface, stable composite materials can be formed with POMs. In 2015, Xu *et al.* prepared $ZnSiW_{11}NB$/ACF composite materials [40]. Contrast the photocatalytic activity of $ZnSiW_{11}NB$ with $ZnSiW_{11}NB$/ACF on the degradation of RhB in aqueous solution, it was found that excess ACF could promote the recombination of photo-generated electron–hole pairs and reduced the photocatalytic efficiency. When $ZnSiW_{11}NB$:ACF was 100:1, the photogenerated electron–hole pairs was separated effectively and had excellent catalytic activity for RhB degradation. The enhancement of photocatalytic activity was attributed to the synergistic effect between $ZnSiW_{11}NB$ and ACF (Figure 12).

3.1.3 Electrocatalysis

Owing to the high oxidation states of metal in metal-oxygen polyhedra of MO_x, POM anions undergo several rapid one- or two-electron reversible reductions, and even irreversible multi-electron reductions accompanied by decomposition. In 2012, Gong *et al.* reported an ITO electrode on which PVA/P_2W_{18} covered through electrospinning [18]. After thermal crosslinking, P_2W_{18} composite nanofibers would not dissolve in aqueous solution even after 24 h. It ensured the electrochemical stability of P_2W_{18} composite nanofibers modified ITO electrode and its good electrocatalytic activity for nitrite reduction in acidic solution.

However, the properties of POMs used for loading, such as electrical conductivity, also have a certain impact on the electrocatalytic performance of modified electrodes. In 2006, Dong *et al.* reported modified ITO electrodes, which were formed by depositing P_2Mo_{18}/PAH multilayer films on PVA nanofibers. However, the poor conductivity of PVA nanofibers resulted in a low peak current of P_2Mo_{18}, which limited the application of modified electrodes [28]. To increase the conductivity, subsequently, Gong *et al.* combined P_2W_{18} with chitosan nanofibers to modify the ITO electrode and the composite electrode, exhibiting excellent electrocatalytic reduction of NO_{2^-} [52]. As known, chitosan has a high positive charge density, providing support for the adsorption of P_2W_{18} ions. Notice that chitosan is stable in the common potential range, and the complex formed with chitosan can ensure high proton conductivity. Thus, the electrocatalytic activity of cationic polyelectrolyte chitosan nanofibers is better than that of the modified electrode. In addition, in 2018, Anderson-type $CoMo_6$ had been applied to produce vertically arranged oxidation CoS_2-MoS_2 (CoMoS) hetero-film on conductive and flexible carbon fiber cloth [53]. Besides, the O-CoMoS hetero-film was used as anode and cathode for the electrocatalyse water decomposition. Under 10 mA current density, only 1.6 V of low voltage was needed for 10 h catalysis, with high electrocatalytic decomposition water activity (Figure 13).

POMs can also improve the reaction performance of hydrogen evolution and oxygen evolution of electrolytic water. In 2019, Wu *et al.* prepared carbon nanofibers (SiWNi-CNFs) modified by $SiO_2/WO_3/NiWO_4$ composites. The experimental results showed that SiWNi-CNFs haved more efficient electrocatalytic hydrogen evolution (HER) performance [23]. Because the $SiO_2/WO_3/NiWO_4$ composites modified on the surface of carbon nanofibers can produce a large number of active centers through the synergistic action of each component. Meanwhile, the close combination of ternary oxides and carbon nanofibers can accelerate the electron transfer of active components in carbonization and improve the stability of active components to prevent them from gathering. In 2022, Haider *et al.* loaded Co containing POMs Co_4POM onto carbon nanofiber tubes (CNTFs) generating Co_4POM@CNTF, which could be used for electrocatalytic oxygen evolution reaction [39]. CNTF is an excellent electronic medium and highly conductive carrier with efficient electron transfer and high electrochemical activity. Co_4POM can be used as the catalytic site of OER through self-activation to produce cobalt oxide or hydroxide in alkaline medium.

3.2 Photochromism

Photochromism refers to the change of molecular structure under the irradiation of visible light, ultraviolet light, infrared light, *etc.*, leading to the corresponding color change. Besides, most of these changes are obvious, rapid, and generally reversible. In general, photochromic materials can be classified into two categories, inorganic and organic photochromic materials. The synthesis of organic photochromic materials is typically challenging, expensive, high toxicity, and poor light fatigue resistance. In contrast, inorganic photochromic materials such as POMs can address the limitations associated with organic counterparts by virtue of their reversible redox-based photochromic mechanism. The photochromic mechanism of POMs is as follows. Due to the photoexcitation, LMCT results in the

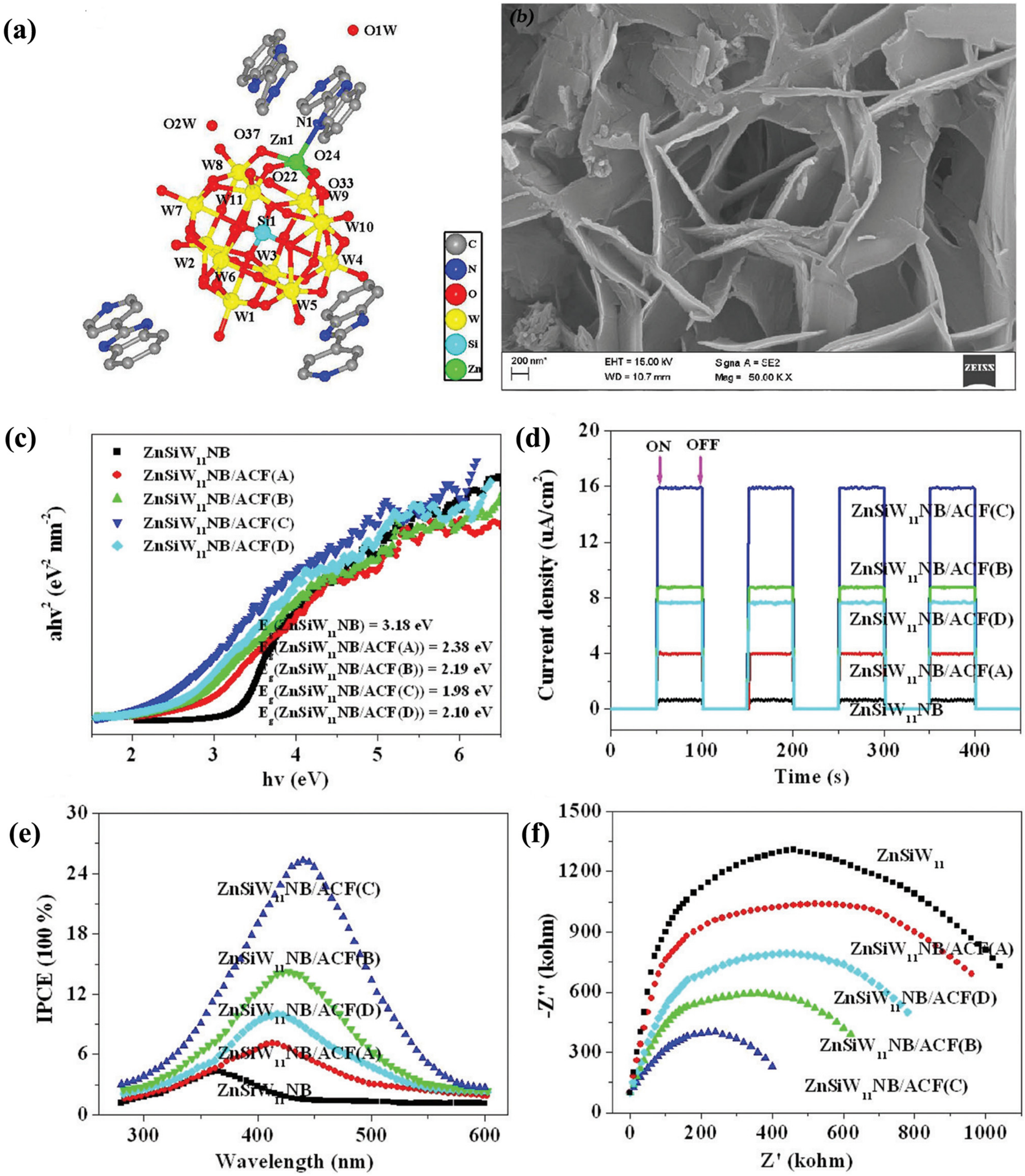

Figure 12: (a) Ball-and-stick of $ZnSiW_{11}$. (b) SEM of $ZnSiW_{11}$. (c) Tauc plots of $ZnSiW_{11}NB/ACF$. (d) photocurrent spectra of $ZnSiW_{11}NB$ and $ZnSiW_{11}NB/ACF$ under visible light. (e) IPCE of $ZnSiW_{11}NB$ and $ZnSiW_{11}NB/ACF$; (f) EIS of $ZnSiW_{11}NB$ and $ZnSiW_{11}NB/ACF$. Reproduced from ref. [40].

transfer of a hydrogen proton from the nitrogen of the ligand to the bridge oxygen atom of POMs. Meanwhile, interaction between O → W LMCT transfer and nonbond electrons on the nitrogen site forms a charge transfer complex (N → O), leaving a hole at the oxygen site. Owing to the transfer of hydrogen protons, the hexavalent W or Mo is reduced to pentavalent. The bands in the visible or near-infrared regions are mainly derived from the intervalence

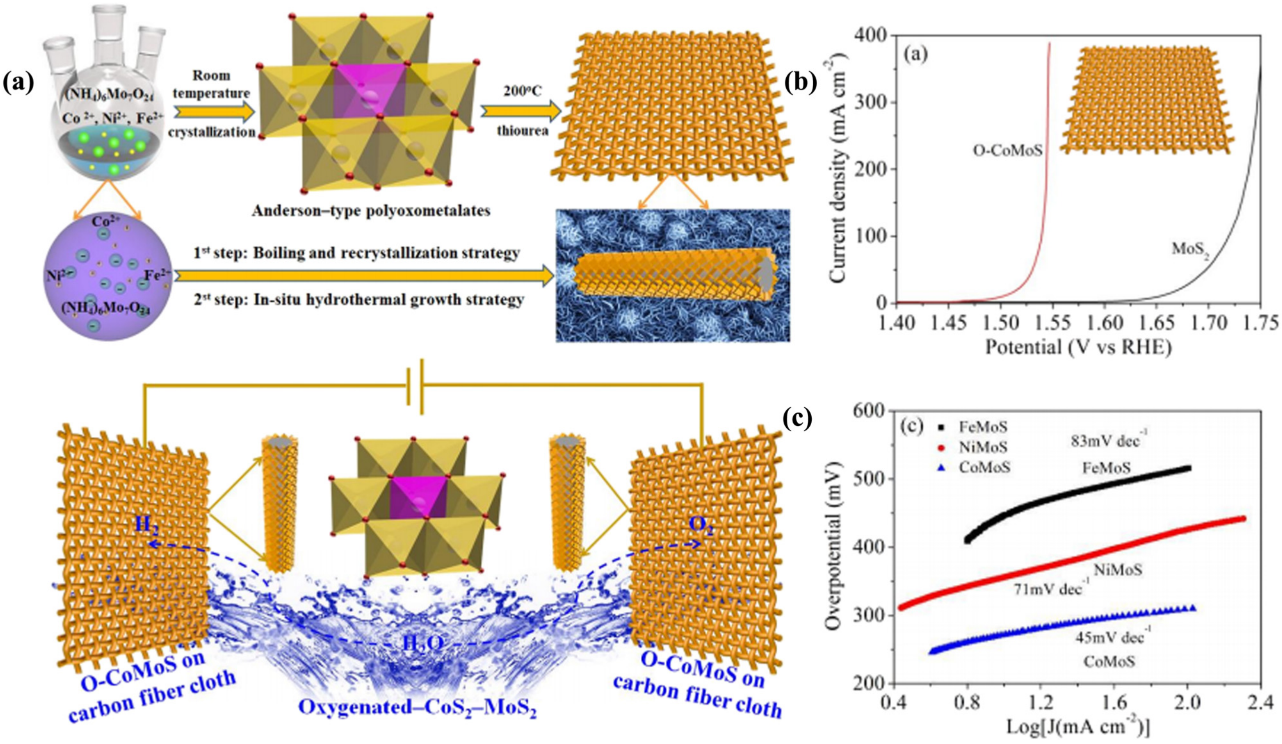

Figure 13: (a) Synthesis of as-prepared heteronanosheets arrays grown on carbon fiber cloth and overall water splitting. (b) HER polarization curves of metal sulfides nanosheet arrays. (c) Tafel slopes of O-CoMoS, O-NiMoS, and O-FeMoS arrays. Reproduced from ref. [53].

charge transfer transition filled 5 d1 electrons and d–d transitions. Meanwhile, there may be occurrence of delocalized electron on N···O bond or radical on amine molecule along with an unpaired electron on metal atom. Moreover, fading of colored POMs is caused by the reverse reaction.

The photochromic property of POMs enables them to be used as photoresponsive switches. Especially, the research and development of photoresponsive intelligent textiles is expected to develop low-cost and practical photochromic textiles. In 2005, Gong *et al.* prepared PVA/SiW_{12} microfine composite fiber [54]. Under ultraviolet light, the electron transfer occured between PVA and SiW_{12}. SiW_{12} was reduced through single-electron reaction while PVA was oxidized. The color of the fiber changed from white to blue, and the color faded without light. In 2006, Dong *et al.* made photochromic films by depositing P_2Mo_{18}/PAH on PVA nanofibers [28]. In the presence of UV light, P_2Mo_{18} was reduced, that is, Mo(VI) was reduced to Mo(V), and charge transfer complex was formed between PAH and P_2Mo_{18}, producing the color of nanofibers gradually changing from light yellow to dark blue.

In 2018, Freire *et al.* introduced the prepared SiO_2@C_{18}-PMo_{12}-NPs hybrid nanomaterials into PP fiber to prepare a new type of photoresponsive PP fiber. Under UV light, Mo(VI) was reduced to Mo(V), and the corresponding fiber color changed from the initial yellow-green to blue after 30 min irradiation. After oxygen bleaching, Mo(V) was oxidized to Mo(VI) again, and the color was changed from blue to yellow-green [55]. In 2020, Yu *et al.* obtained a composite fabric by loading $(DTS/PEI)_n$ onto linen fabric through hydrogen bond [30]. Under UV irradiation, the electron on the amino group of PEI was transferred to W^{6+} through hydrogen bond. Correspondingly, colorless W^{6+} was reduced to blue W^{5+}. The composite fabric showed rapid and obvious color changes in 5 min, and it would be oxidized and faded exposure without UV light for 5 h. Meanwhile, the composite fabric showed excellent stability. After 15 times of reduction–oxidation process, the color proportion of the material had only decreased by about 10%, indicating good resistance to optical fatigue of composite fabric. In the same year, an analog with cotton fabric was reported by them [30]. With the enhancement of UV irradiation, the conversion rate of W^{6+} increased, so did the photochromic speed of the fabric. Therefore, the composite fabric could be used for visual and rapid detection of different UV intensity. Likewise, the blue composite fabric could be oxidized and faded in the air for 2 h. In 2022, our group obtained the composite fabric with DTS and cationic-modified cotton fabric [56]. Under low-power UV light (5 W) irradiation, the composite fabric would produce color difference changes (white gradually turns to

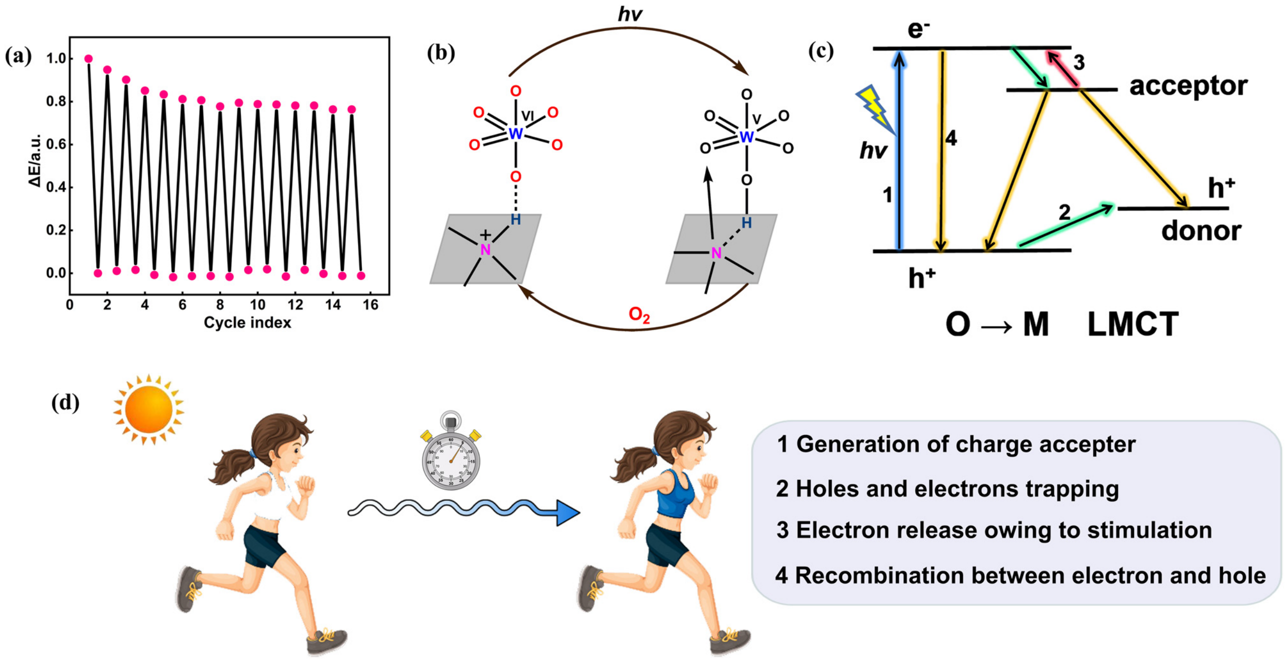

Figure 14: (a) Cyclability of the composite fabric. (b) Mechanism of photochromism. (c) Simple model showing the electronic transitions in the POMs containing electron donor and acceptor. (d) Schematic diagram of the color change of the composite fabric. Reproduced from ref. [56].

blue) within 5 s, showing fast light response. When the UV light was removed, the blue color could fade. Besides, as the increase of temperature, the fading time was shortened. In addition, the composite fabric after chemical modification still maintained its original moisture absorption and mechanical properties (Figure 14).

3.3 Photoluminescence

Photoluminescence, is the phenomenon of emitting energy in the form of light radiation after absorbing energy, and is commonly. The property makes it suitable for applications in light-emitting sensors. At present, extensive research has been conducted on photoluminescence properties of lanthanide-based POMs. Therefore, combining lanthanide POMs with the fibers enables the development of flexible composite materials with fluorescence properties.

In 2009, Gong *et al.* prepared $EuPW_{11}$/PVA and EuW_{10}/PVA photoluminescent composite microfiber pads [17]. They found that different polyoxotungstate ligands exhibited different luminescence behaviors in composite microfibers. In 2013, Song *et al.* developed EuW_{10}/PAN nanofiber composite membranes [20]. Upon light stimulation, the nanofiber films showed strong Eu^{3+} red light emission and demonstrated sensitivity toward acidic and alkaline gases. In the presence of HCl and H_2S acid gas, $-C\equiv N-H\ldots O-W$ could be formed between the −CN of PAN and the O atom of WO_6 in EuW_{10}/PAN nanofiber membrane. The hydrogen bonding prevented the energy transfer of the intramolecular luminescence resonance between WO_6 and Eu^{3+} ions, therefore hindering sufficient energy release to activate photoluminescence in acid gas environments. Under SO_2 atmosphere, SO_2 reacted with H_2O to produce weak electrolyte H_2SO_3, which ionized into H^+ and HSO^{3-}, thus resulting in the protonation of −CN in PAN and hindering the energy transfer mentioned above. Therefore, photochromism did not occur. However, when the EuW_{10}/PAN nanofiber membrane was exposed to alkaline gas such as NH_3 again after exposure to acid gas, the photoluminescence phenomenon was restored because of complete deprotonation of −CN groups. Besides, the relative luminescence intensity was even stronger than that of the original membrane. Therefore, owing to its high sensitivity and adjustable luminescence signal, EuW_{10}/PAN nanofiber membrane could be used as a pH-responsive luminescence switch.

Additionally, owing to the strong absorption in the range of 200–400 nm, POMs endow a new functionality on fiber. Recently, we reported an anti-UV blocker compatible with cotton fabric by simple covalent bond self-assembly [57]. The as-designed composite fabric showed excellent UV blocking property with a UPF value of 397.19, superior to original cotton (7.09).

4 Conclusion and outlook

To summarize, the design, synthesis, and reactivity of novel POM/fiber composite materials based on two methods, namely, electrostatic spinning method and LBL self-assembly, have been discussed in detail. Apparently, the structure and performance of composite materials are improved by combining the superiority between POMs and fibers. Furthermore, this study highlights various applications such as catalysts, luminous sensors, and health monitoring. Fiber materials based on POMs possess several unique advantages: first, POMs with diverse architectures facilitate the structural regulation of composite materials for achieving different characteristics; second, the excellent coordination ability of POMs enables the combination with other functional molecules; and third, POMs are of great importance in enhancing the analysis of catalytic mechanism and photoelectric property theory.

There is no doubt that POM/fiber composite materials exhibit remarkable diversity and their unique properties led to new discoveries. Although there has been considerable progress in POMs functionalized fiber materials, there remain several crucial challenges that need to be addressed, and the following points may need to be focused on: 1) overcoming the limitations of POMs with stable structures and exceptional performance by developing new POMs with simplified synthesis processes, cost-effectiveness, and superior properties. Similarly, the synthesis and design of fibers with specialized characteristics contribute to the preparation of functional devices; 2) in terms of composite material, electrostatic spinning method, and LBL are employed. Electrostatic spinning needs some special equipment, and operating conditions, such as humidity of the air, spinning voltage, and solvents, which can affect the effect of spinning and stability of POMs. The LBL self-assembly method mainly relies on electrostatic interaction; therefore, it is necessary to enhance the durability of constructed functional fiber materials while also exploring novel theories and solutions. Therefore, it is necessary to comprehensively consider the use of functional fiber materials and to select the appropriate POMs and fabric type. Besides, it is important to solve the problem of combining POMs with the base material, so as to ensure the robustness and persistence of materials; 3) fiber or textiles possess softness and breathability as inherent characteristics which may be affected during the process of functionalization. Therefore, when developing POM-functionalized fiber materials, how to maintain the original flexibility and air permeability of fiber under the premise of ensuring excellent performance? Or whether other processes such as dyeing and functionalization of fibers interacting with each other should be considered.

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