FACULTY OF TEXTILE ENGINEERING TUL

PREPARATION, CHARACTERIZATION AND APPLICATION OF CELLULOSE MATRIX COMPOSITES

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SUMMARY OF THE THESIS

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Form of study:	**Full time**
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Liberec, 2024

Abstract

In recent advancements within the realm of electronic components and devices, significant strides have been made towards creating light-weight, durable, and environmentally friendly conductive materials suitable for a wide range of applications. This thesis highlights innovative approaches towards the development of such materials, emphasizing their potential in revolutionizing future electronic devices with multifunctional capabilities.

The first part of this work delineates the creation of a cellulose/graphene oxide (GO) hybrid membrane via an eco-friendly silane crosslinking process, marked by simplicity and a minimal environmental footprint. This membrane showcases exceptional characteristics, a hydrophobic nature, enabling self-cleaning capabilities. This optimized sample also achieves a substantial reduction in surface resistivity, bringing it down to 720.69 Ω. The hybrid membrane's rapid thermal response, capable of both heating and cooling within a mere 5 seconds, alongside its electrothermal stability, earmarks it for applications in dynamic environments like smart textiles and electric heating devices.

The second part of this work focuses on the modification of viscose nonwovens with 3-Mercaptopropyltrimethoxysilane (3-MT) to facilitate an enhanced copper plating process. This innovative approach leads to the introduction of SH groups on the viscose surface, significantly improving its affinity for copper ions. The modified material showcases an improved corrosion resistance, with a reduction in corrosion rate by 58% compared to its unmodified counterpart. Furthermore, its Joule heating response is notably swift, occurring within 10 seconds at a low applied voltage of 1 V, and it demonstrates exceptional electromagnetic interference (EMI) shielding effectiveness, with a value exceeding 50 dB. It makes the material as a versatile candidate for smart clothing, EMI shielding barriers, and sensors.

In summary, this work provides promising insights into the future direction of electronic device development, focusing on sustainability, efficiency, and the integration of novel materials for enhanced performance and functionality.

Keywords: Cellulose; Conductive materials; Silane crosslinking; Joule heating performance; Electromagnetic interference (EMI) shielding; Characterization of materials.

Abstrakt

V současné době byly učiněny významné pokroky ve vývoji elektronických komponent a zařízení umožňující vytváření lehkých, odolných a ekologicky šetrných vodivých materiálů vhodných pro širokou škálu aplikací. Tato práce je zaměřena na inovativní přístupy k vývoji takových materiálů, se zdůrazněním jejich potenciálních multifunkčních projevů.

První část práce je zaměřena na vytvoření hybridní membrány celulóza/oxid grafénu (GO) prostřednictvím procesu ekologického síťování silanu, který se vyznačuje jednoduchostí a minimální ekologickou stopou. Tato membrána se vyznačuje výjimečnými vlastnostmi, hydrofobní povahou, podporující samočistící schopnosti. Tato optimalizovaná hybridní membrána také dosahuje podstatného snížení povrchového odporu na hodnotu 720,69 Ω. Rychlá tepelná odezva hybridní membrány, která se je schopna zahřát i zchladit během pouhých 5 sekund, spolu s její elektrotepelnou stabilitou, ji předurčuje pro aplikace v dynamických prostředích, jako jsou inteligentní textilie a elektrická topná zařízení.

Druhá část práce se zaměřuje na modifikaci viskózových netkaných textilií pomocí 3-merkaptopropyltrimethoxysilanu (3-MT), pro usnadnění procesu pokovování částicemi mědi. Tento inovativní přístup vede k zavedení skupin SH na povrch viskózy, což výrazně zlepšuje její afinitu k iontům mědi. Modifikovaný materiál vykazuje zlepšenou odolnost proti korozi se snížením rychlosti koroze o 58 % ve srovnání s jeho nemodifikovaným protějškem. Navíc jeho odezva zahřívání Joule je pozoruhodně rychlá, nastává během 10 sekund při nízkém použitém napětí 1 V a vykazuje výjimečnou účinnost stínění proti elektromagnetickému rušení (EMI) s hodnotou přesahující 50 dB. Díky tomu je materiál vhodným kandidátem pro chytré oblečení, stínící bariéry EMI a senzory.

Získané výsledky jsou důležité pro budoucí směr vývoje elektronických zařízení, se zaměřením na udržitelnost, efektivitu a integraci nových materiálů pro zlepšenou výkonnost a funkcionalitu.

Klíčová slova: Celulóza; Vodivé materiály; Zesítění silanizací; Joulův ohřev; Stínění elektromagnetického rušení (EMI); Charakterizace materiálů.

摘要

在目前关于电子组件和设备领域的最新进展中，轻质、耐用且环保的导电材料受到广泛关注并取得了一定的进展，这些新型材料具有广泛的应用。本文主要采用环境友好且价格低廉的纤维素作为主要材料，通过化学改性的方法赋予或改善纤维素基复合材料导电性。本文介绍了两种创新的改性方法，通过表征展示了其在未来具有多功能电子设备中的潜力。

本工作的第一部分详述了通过环保的硅烷交联过程创建纤维素/氧化石墨烯（GO）杂化膜的过程，这一过程简单且环境影响小。这种膜展示了极其出色的特性，如较低的电阻，疏水性和自清洁功能。这一方法还实现了表面电阻的大幅降低，降至 720.69 Ω。此外，杂化膜还展现出快速的焦耳响应能力，能在短短 5 秒内完成加热和冷却，以及其出色的电热稳定性，使其适用于智能纺织品和电加热设备等动态环境。

本工作的第二部分集中于使用 3-巯基丙基三甲氧基硅烷（3-MT）对粘胶非织造布进行改性，以促进更高效的镀铜过程。这种创新方法使粘胶表面引入了 SH 基团，显著提高了其对铜离子的亲和力。改性材料展示了改进的抗腐蚀性，与未改性材料相比，腐蚀速率降低了 58%。此外，其焦耳热响应方面表现的极为迅速，在 1V 的低电压下 10 秒内即可达到平台温度，并且展示出超过 50 dB 的卓越电磁干扰（EMI）屏蔽效能。这使得该材料成为智能服装、EMI 屏蔽障碍和传感器的多功能候选材料。

总而言之，这项工作为开发未来的绿色环保，高效，新型多功能电子设备提供了新的制备策略和参考。

关键词：纤维素；导电材料；硅烷交联；焦耳加热性能；电磁屏蔽；材料表征

Content

1 Introduction

It is well known that cellulose has many features such as stable, non-toxic, biodegradation, renewable, low cost, high strength, and extensive sources [1]. Cellulose is a linear polymer formed by repeating cellobiose units through β-(1→4)–D-glucose bonds [2,3]. Meanwhile, its macromolecules are regular structures, so high crystallinity is always obtained for better mechanical property [4]. Cellulose fiber consists of a well-organized crystallinity region that contributes to the strength and high stiffness, and amorphous region, which makes fiber more flexible and softer [5]. As a natural polymer material with great properties, it has been applied in many fields, such as building materials, biomedicine, coating, films, membranes, surface modification, and foodstuffs [6,7] (see in **Fig. 1.1**). In this work, we mainly focus on surface modification of cellulose-based materials and imparting conductive properties to them.

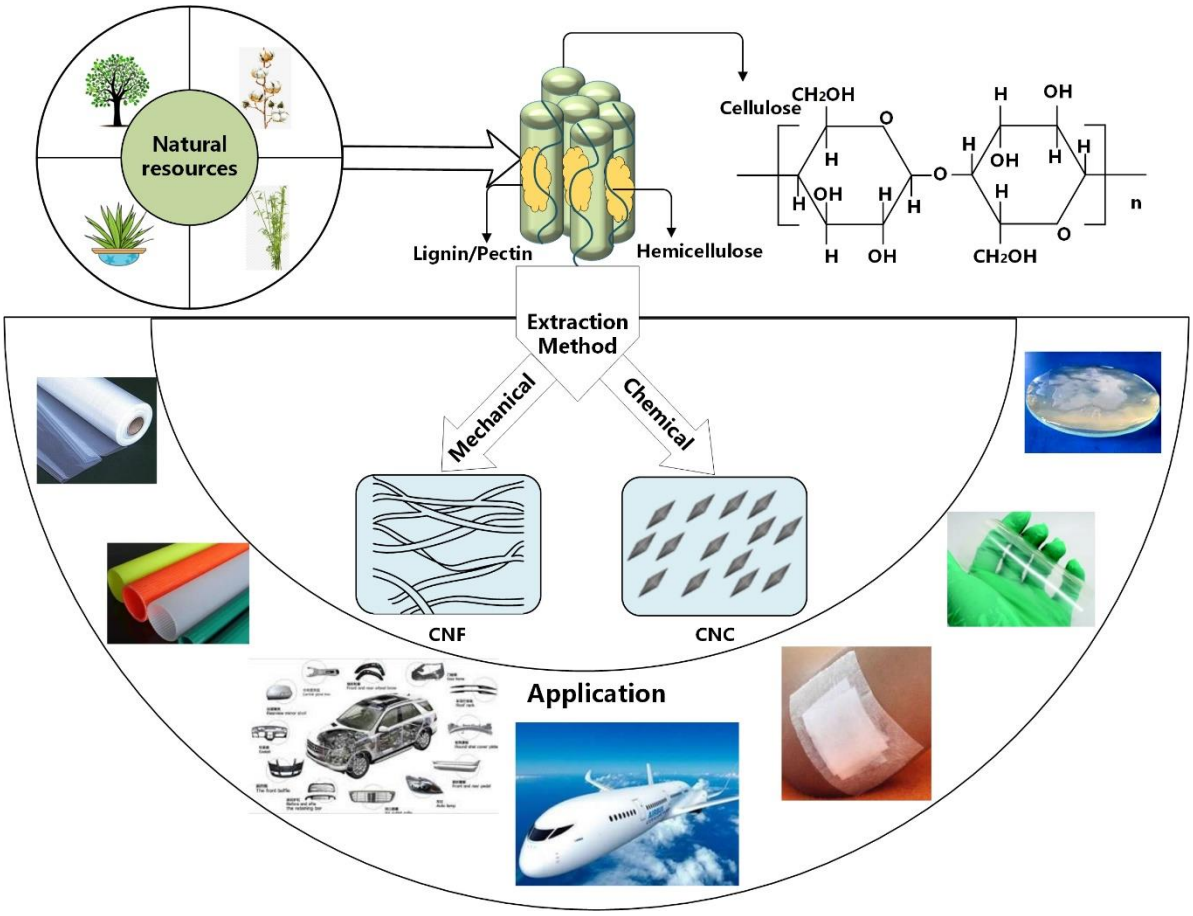


Figure 1.1 Extraction and application of nanocellulose from lignin biomasses [8].

Many approaches have been attempted to impart conductivity to cellulose-based materials, such as surface coating, doping, interfacial assembly/encapsulation [9–11]. Wang et al. sandwiched silver nanowires between regenerated cellulose membranes (as a flexible substrate) and

poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) and successfully prepared flexible conductors [12]. It has good performance as a strain sensor [11]. However, as far as we know, 3,4-Ethylenedioxythiophene has acute cytotoxicity, so there are risks in its preparation and use. Han et al. developed cellulose-based Ni-decorated graphene magnetic film [13]. However, this work needs to be carried out under high pressure for over 12 hours and the process is complicated, thus limiting its development.

In addition, physical blending[14,15], layer-by-layer stacking[16,17], vacuum filtration[18], etc. are popular method to prepare conductive hybrids of cellulose and graphene and its derivatives by many studies. But, due to the weak van der Waals forces such as π-π bond and hydrogen bond between such carbon material powders, it is difficult to disperse them uniformly. Many attempts have been done to solve those problems. Ghulam Yasin et al. used surfactants to enhance the electrostatic repulsion of graphene and hinder the agglomeration. However, the introduction of new impurities led to a decrease in the interfacial bonding force between graphene and the polymer, which weakened the performance of the coating [19]. Gaojie Han et al. successfully developed cellulose-based Ni-decorated graphene magnetic film [13]. Firstly, they subjected $Ni(OH)_2$ nanoribbon to hydrothermal reaction under high pressure for 12 h, followed by in-situ thermal reduction with GO suspension for 12 h, and finally vacuum filtration. It takes advantage of good dispersion of GO, but this work is time-consuming and complex.

In the field of textile material science, linking chemical modification with imparting conductivity to cellulose is a relatively new endeavor, with few studies combining these two concepts. Cellulose, being one of the most abundant natural polymers on Earth, is typically considered an insulator. However, combining cellulose-based materials with conductive materials through chemical modification not only expands the application range of cellulose but also offers new strategies for preparing conductive bio-based materials. This innovative exploration leverages the natural advantages of cellulose, such as renewability, biodegradability, and good mechanical properties, while introducing or enhancing its conductivity through chemical modification, breaking the traditional limitations on the functionality of cellulose.

2 State of the Art

2.1 Conductive cellulose-based composites

Cellulose stands out as an ideal candidate for crafting cutting-edge, flexible energy devices and sensors, thanks to its abundant functional groups, distinctive network and pore architecture, high flexibility, and minimal thermal expansion [20]. Yet, to meet the specific demands of energy and sensor applications, cellulose must undergo carbonization or be combined with conductive agents. The integration of cellulose or nanocellulose with conductive materials imparts electrical conductivity, marking a critical advancement in leveraging their outstanding

characteristics for applications in energy storage and sensing technologies [21]. While bulk cellulose can be directly shaped and then carbonized or blended with conductive elements to create conductive frameworks, nanocellulose requires pre-shaping before these enhancements. The strategic incorporation of certain polymers in designing composite structures can facilitate the molding and stabilization of both carbonized cellulose and its conductive composites.

When it comes to the development of Conductive Materials Based on Cellulose, the approaches can be categorized into three main strategies: forming cellulose composite carbon materials and incorporating cellulose with metallic nanoparticles. The primary role of cellulose in these strategies is to serve as a dispersion medium for nano-conductive materials [22]. Polymers, including cellulose itself, act as a stabilizing foundation, while the addition of conductive components not only aids in shaping the materials but also establishes conductive channels. Often, these approaches are combined to optimize the performance and application potential of cellulose-based conductive materials.

2.1.1 Cellulose composite carbon materials

Carbon materials, especially low-dimensional ones like graphene and carbon nanotubes (CNTs), are at the forefront of research due to their superior electrical and thermal conductivities and their capacity to exhibit various quantum effects [23]. Cellulose composite carbon materials merge the outstanding qualities of carbon materials with the versatility of cellulose, overcoming the challenges of engineering applications with low-dimensional carbon materials alone. These composites are ideal for developing flexible and portable devices for energy storage and sensing applications [20].

For instance, Pinto and colleagues crafted a multifunctional Bacteria cellulose (BC)/ GO aerogel, enhancing its porous structure through lyophilization [24]. The aerogel's stability and conductivity, reaching up to 8.7×10^{-1} S/m, were further improved by crosslinking nanophases via ammonia heat treatment (**Fig. 2.1a**). These BC/GO aerogels, with their high thermal stability, find applications in packaging, environmental treatment, and energy sectors.

Zhou and team fabricated a graphene/polyvinyl alcohol (PVA)/CNF composite aerogel through directional freezing and carbonization, achieving a remarkably low density and high porosity [25] (**Fig. 2.1b**). This anisotropic, hydrophobic, and lipophilic cellulose carbon aerogel boasts a layered, three-dimensional porous structure, excellent compression recovery, and thermal stability, making it highly effective for adsorption and recyclable uses.

Shi and associates developed a CNF composite–reduced graphene oxide (RGO) anode for sodium-ion batteries using microwave heating, maintaining a capacity of 340 mAh/g after numerous cycles [26]. The addition of a small amount of RGO facilitated ultra-high heating

rates during carbonization, while chemically modified CNF served as the primary sodium ion carrier, collectively enhancing the battery's electrochemical performance (**Fig. 2.1c**).

Zhu's team prepared a CNF/CNT composite bilayer paper sensor through spraying, leveraging the cellulose fiber's structure for rapid environmental water molecule exchange and utilizing CNTs for transmitting electrical signals, showcasing a significant current response [27] (**Fig. 2.1d**).

Furthermore, Chen et al. introduced a graphite sheet/CNF foam created without lyophilization, using expandable Cu^{2+} ion crosslinking [28] (**Fig. 2.1e**). This environmentally friendly foam avoids petroleum-based materials, offers low thermal conductivity, and remains mechanically robust even when wet, in addition to being recyclable and degradable. These advancements highlight the synergy between cellulose and carbon materials, paving the way for sustainable and efficient applications in various technological domains.

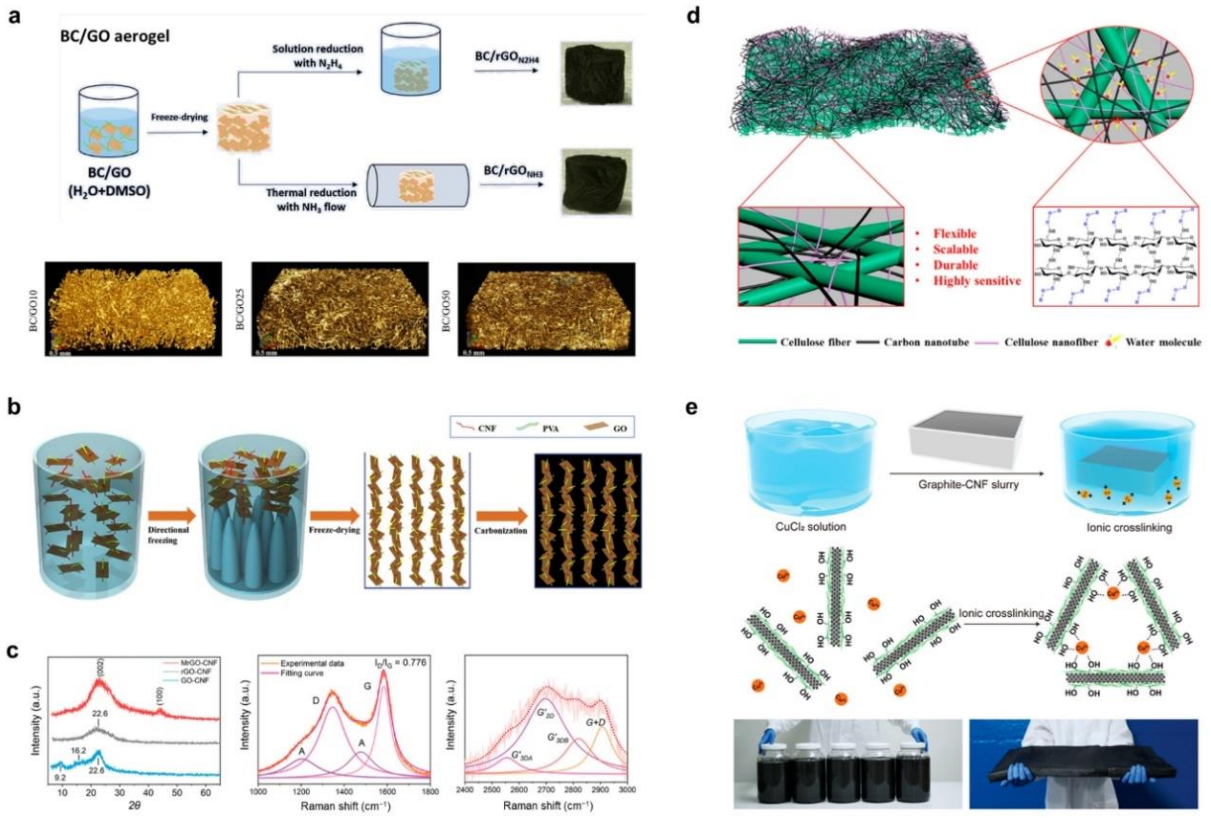


Figure 2.1 (a) Preparation of BC/ GO aerogels [24]; (b) Graphene/PVA/CNF composite aerogel [25]; (c) XRD and Raman spectra of CNF/graphene [26]; (d) CNF/CNT composite prepared using a spraying [27]; (e) Preparation of graphite/CNF foam crosslinked by Cu^{2+} ions [28].

2.1.2 Cellulose composite metal particles and inorganic compounds

The metal/inorganic compounds like metal particles, metal oxides, liquid metals, and MXene with cellulose is gaining increasing interest for its potential in creating effective conductive composite strategies. The appeal lies in achieving high conductivity, which translates to lower electrical resistance, minimizing power consumption and heat production in energy and sensing applications, and enhancing the efficiency of electrical signal transmission.

Zou and colleagues developed a self-supporting cellulose/RGO/silver (Ag) nanoparticle composite membrane by initially creating a slurry from cellulose filter paper, GO, and silver ammonia complexes [29]. The silver ammonia was reduced to Ag nanoparticles through heat treatment, and a thin film was formed via vacuum filtration. Subsequently, hot hydrazine vapors were employed to reduce GO to RGO, resulting in a vimentin/RGO/Ag nanoparticle composite film with a thickness of approximately 400 μm and exceptionally low electrical resistivity of 0.17 Ω/sq.

Fei and team utilized a metal–organic framework (MOF), specifically ZIF-67, anchored on CNF, which upon annealing yielded a cobalt/carbon@CNF aerogel [30]. This material demonstrated a remarkable electromagnetic shielding effect, with conductivity increased to 2.35 S/m and a specific shielding effectiveness of 20,172.4 dB cm^3/g after a 900 °C treatment for 3 hours in an argon atmosphere.

Garino and associates synthesized RGO/SnO_2 using a microwave method and combined it with micro-fibrillated cellulose to create a nanocomposite membrane characterized by excellent toughness and ductility [31]. This membrane exhibited superior capacitive behavior and catalytic redox reaction performance, achieving a maximum capacitance of 53 F/g at a scan rate of 10 mV/s.

Liao and team developed a composite of liquid metal and cellulose, producing self-supported liquid metal/CNF composite films through processes including ball milling, dispersion, freeze-drying, and compression molding [32]. This method resulted in the disruption of the liquid metal's oxide shells and the formation of a continuous conductive pathway by CNF, showcasing impressive conductivity of 96,000 S/m and tensile strength exceeding 30 MPa.

Wang and collaborators prepared a BC-loaded ternary heterostructure nanoflower composite through hydrothermal reaction and high-temperature phosphatization, suitable for hydrogen evolution reactions across a broad pH range [33]. In testing, the optimal sample exhibited an initial overpotential of 27 mV in 1.0 M KOH and current densities of 10 mA/cm2 at various overpotentials in different solutions, demonstrating the effectiveness of a MoS_2/CoP/MoO_2 doped with carbon in an alkaline two-electrode setup, delivering 10 mA/cm^2 at a low potential of 1.51 V.

These advancements underline the dynamic potential of cellulose-based composites in conjunction with metal/inorganic compounds, paving the way for innovative applications in conductive materials and energy solutions.

2.2 Application of conductive cellulose based composites

Conductive cellulose composite materials combine the natural, renewable resource of cellulose with conductive substances. This union garners attention for cellulose's superior biocompatibility, degradability, and mechanical strengths. By integrating cellulose with conductive elements such as polymers, metallic nanoparticles, or carbon derivatives (e.g., carbon nanotubes, graphene), composites with tailored conductivity can be crafted. These materials are pivotal in several domains:

2.2.1 Functional electrothermal heaters

Electrothermal heating is a method of heating objects by using the heat generated when electric current pass through a conductor. This heating method is based on Joule's Law (Eq. 1), also known as the electric heating effect. Joule's Law describes how the heat produced in a resistive material by an electric current is directly proportional to the square of the current's strength, the size of the resistance, and the time the current passes through the conductor [34].

$$Q = \frac{U^2}{R} t \qquad (Eq. 1)$$

Where Q, U, R, and t are heat generated, applied voltage, sample resistance, and operating time, respectively. As electric current passes through the resistive layer, triggered by the applied voltage, it converts electrical energy into heat based on the principle of Joule heating (**Fig. 2.2a**). The transformation results in energy dissipation, primarily through convective heat exchange with the surrounding air and radiation. Consequently, to determine the temperature of the heating element, one must apply the principle of energy balance, which can be formulated as follows (Eq. 2).

$$mc\frac{dT}{dt} = \frac{U^2}{R} - hA(T - T_0) \qquad (Eq. 2)$$

Where m is the mass of heater; c is specific heat capacity; h is total heat transfer coefficient of convection and radiation; A is area of the heater; T_0 is ambient temperature; T is the temperature of heater at t time.

Fig. 2.2b illustrates the typical temperature variations observed in membrane-type heaters throughout the phases of heating and cooling. Upon applying voltage to the membrane (activating the heater), the temperature rises steadily until it reaches a plateau, where heat

generation and dissipation balance out. Following the removal of the applied voltage (deactivating the heater), the temperature declines in an exponential manner.

Fig. 2.2c and **2.2d** present the dynamic heating and cooling responses of electric heaters made from cellulose, subjected to different voltage settings. The data for heaters based on PPy-coated regenerated cellulose yarn and those incorporating a cellulose/multi-walled carbon nanotube (MWCNT) composite indicate a clear correlation with theoretical expectations, showcasing an increase in peak temperatures proportional to the increment in supplied voltage [35,36].

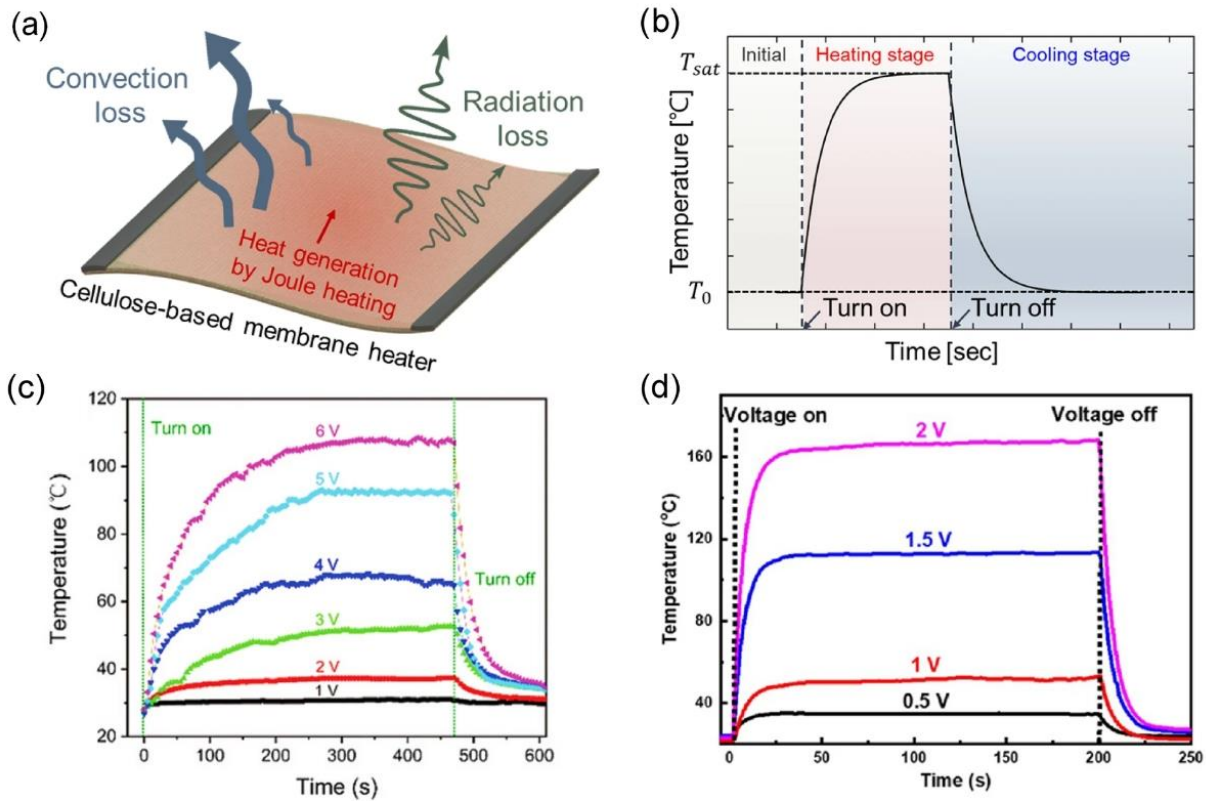


Figure 2.2 (a) Diagram illustrating the energy distribution via Joule heating [37]; (b) Overview of the heating and cooling patterns and (c), (d) Conceptual drawings representing the transient behavior of PPy and CNT-infused cellulose heaters [35,36].

Cellulose-based electrothermal heaters, merging a cellulose substrate with a heating element to convert electrical energy into heat through the Joule effect, stand out for their biodegradability, flexibility, affordability, and superior mechanical strength. With a rising demand for eco-friendly materials, clean energy solutions, and comfortable heating options, these heaters present an appealing solution.

To create these composites, electrical conductivity is introduced to readily available cellulose substrates like wood, textiles, and regenerated cellulose. Various electrode-coating techniques, including dip coating, filter coating, spray coating, alongside screen printing, stamping, and drawing, have been employed to achieve this conductivity. These methods facilitate the design of specific electrode configurations, broadening the scope for creating cellulose-based heating elements as depicted in **Fig. 2.3**.

Dip coating, illustrated in **Fig. 2.3a**, involves submerging the substrate into a conductive material solution, recognized for its simplicity, cost-effectiveness, and controllable electrical conductivity through successive dipping and drying, allowing for thicker conductive layers and adhesion control via molecular interactions between cellulose and conductive materials [38].

Vacuum-assisted filtration, shown in **Fig. 2.3b**, coats suspended conductive materials onto surfaces via vacuum filtering, following the preparation of a uniformly dispersed suspension [39]. This technique has been applied to fabricate cellulose composites with layered structures for metal nanowire deposition, significantly enhancing electrical conductivity for efficient Joule heating at lower voltages [40].

Spray coating, a quick method for covering large areas depicted in **Fig. 2.3c**, applies a low-viscosity suspension to surfaces, causing minimal mechanical damage and proving ideal for delicate materials like hydrogels [41]. This technique has been adapted for both hydrogels and commercial cellulose paper to produce conductive films through repeated application and drying.

Other methods like thermal evaporation and rod-coating, as shown in **Fig. 2.3d**, have been utilized to deposit thin metallic layers on cellulose films or apply conductive nanowires, enabling the creation of thin-film heaters with potential applications in smart windows due to their transparency and flexibility [42,43].

Screen printing and stamping, demonstrated in **Figs. 2.3e** and **2.3f**, offer rapid, cost-effective solutions for mass-producing conductive fabrics or patterning electrodes on paper [44,45]. The simplicity and efficiency of these methods support widespread production.

Drawing, a technique showcased in **Fig. 2.3g** by Kim et al., leverages traditional materials and conductive inks to pattern various electrode shapes easily, highlighting the method's versatility and straightforwardness in custom design [46]. Collectively, these innovative approaches underscore the potential of cellulose-based heaters in sustainable energy and heating applications, marrying traditional materials with modern technology for eco-friendly solutions.

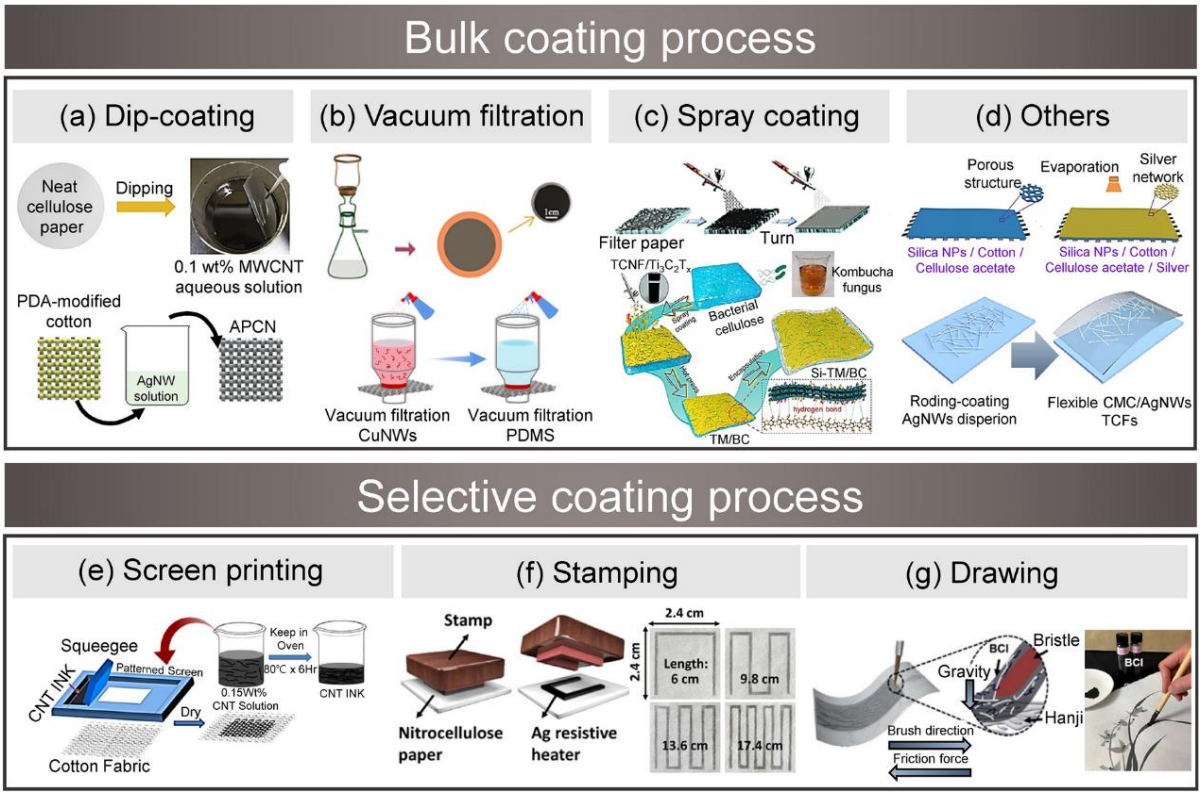


Figure 2.3 (a) dip-coating [38]; (b) vacuum filtration [40]; (c) spray coating [47]; (d) other processes [42]; (e) screen printing [44]; (f) stamping [45]; (g) drawing [46].

2.2.2 EMI shielding

EMI shielding operates on the principle of using materials that are either conductive or magnetic to deflect, soak up, and reroute electromagnetic waves. The effectiveness of EMI shielding is measured in terms of shielding effectiveness (SE), defined as the comparison between the energy of electromagnetic waves (EMW) that hit the shield and the energy that gets through, across a specified range of frequencies. Shielding effectiveness is quantified in decibels (dB) and can be calculated using this equation:

$$SE(dB) = 10log_{10}\frac{P_i}{P_t} = 20log_{10}\frac{E_i}{E_t} = 20log_{10}\frac{H_i}{H_t} \qquad (Eq.3)$$

Where P_i, E_i and H_i are the incident electric field, magnetic field, and power intensities, respectively. P_t, E_t and H_t are the transmitted electric, magnetic field, and power intensities, respectively. Generally, an increase in the SE value signifies improved shielding performance.

Based on Schelkunoff's theory of EMI shielding, **Fig. 2.4** demonstrates that when EMW encounter shielding materials, they simultaneously undergo reflection, absorption, multiple reflections, and transmission. Consequently, the overall effectiveness of EMI SE encompasses three components: the effectiveness of reflection shielding (SE_R), absorption shielding (SE_A),

and shielding effectiveness due to multiple internal reflections (SE_M), which can be expressed through a mathematical formula.

$$\mathrm{SE} = SE_R + SE_A + SE_M$$

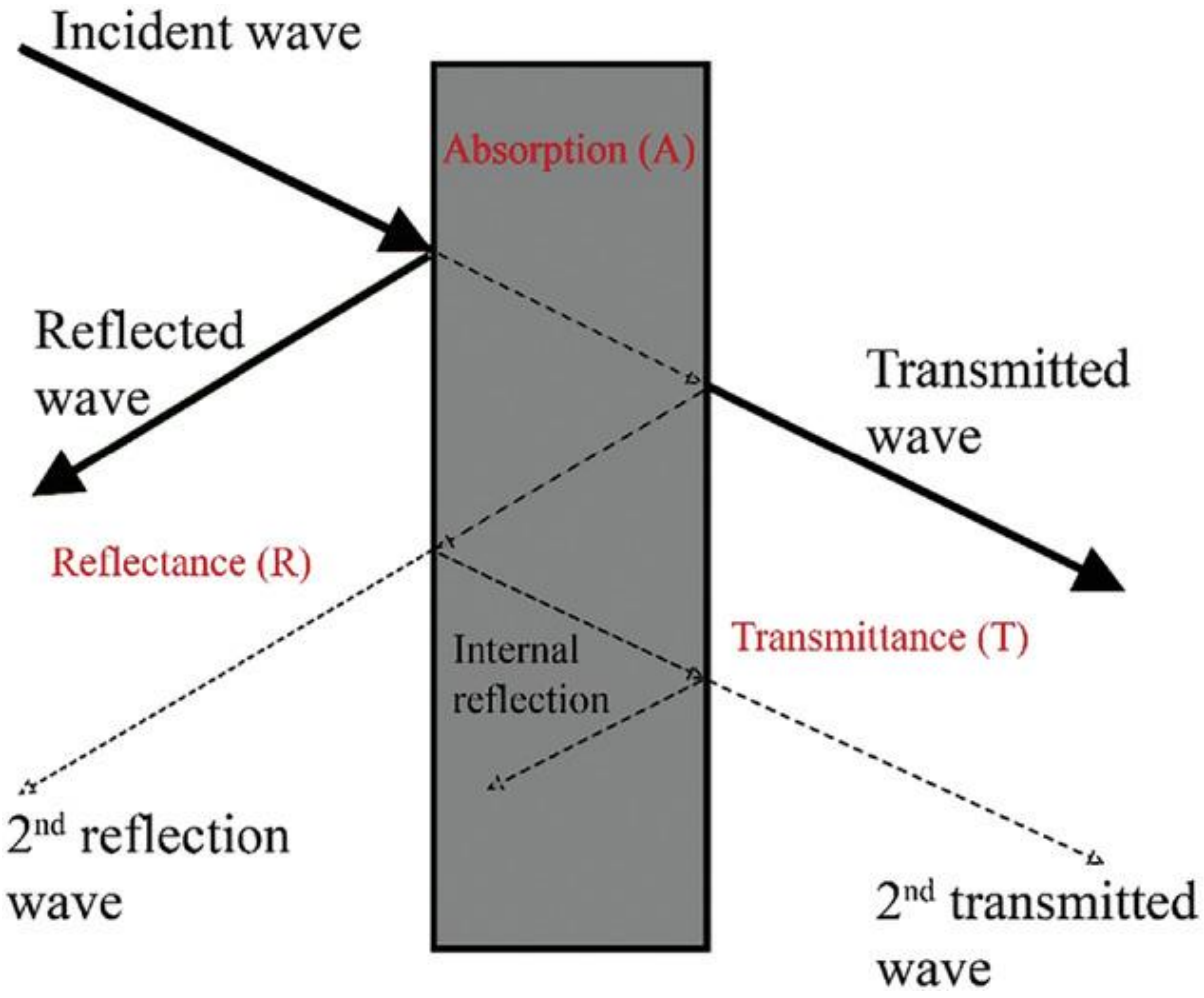


Figure 2.4 Mechanisms of EMI shielding [48].

With the advancement of electronic information technology, electromagnetic waves have become a key medium for information transmission, finding applications across numerous fields. However, the proliferation of electronic devices, while convenient, has also led to a complex electromagnetic environment. This environment can disrupt the functioning of sensitive precision instruments and may pose health risks to humans [48]. Consequently, there's a pressing need to develop highly efficient EMI shielding materials. These materials are increasingly demanded to meet the evolving technological landscape, necessitating features like high absorption capacity to mitigate electromagnetic pollution, lightweight for ease of integration, broad operational frequency range to cover various electronic devices, and excellent thermal and mechanical stability to ensure durability under different environmental conditions.

This development is crucial not only for enhancing the performance and reliability of electronic systems but also for safeguarding human health and sensitive equipment against the adverse effects of electromagnetic pollution [49].

Yang et al. explored the development of ultrathin and flexible composite films made from CNFs and RGO through a conventional vacuum filtration technique (**Fig. 2.5a**) [50]. In this composite, CNFs serve as the polymer matrix, where their one-dimensional nanofiber structure minimizes insulating contacts among conductive layers. This unique architecture results in RGO/CNFs composite films with a dense, layered structure (**Fig. 2.5b**). Within these layers, RGO sheets are oriented to lie flat, maximizing the interface between conductive sheets and facilitating smoother transitions for both phonons and electrons.

These engineered films demonstrate remarkable EMI SE, achieving an impressive SE of approximately 26.2 dB (**Fig. 2.5c**). It's noted that the EMI shielding capabilities of the films improve as the RGO content increases. The study further illustrates the mechanisms of EMW transfer within the material, providing a clear schematic representation of how these waves interact with the composite structure (**Fig. 2.5d**). This research not only underscores the potential of RGO/CNFs composite films as efficient EMI shielding materials but also highlights the critical role of material composition and structure in achieving superior performance.

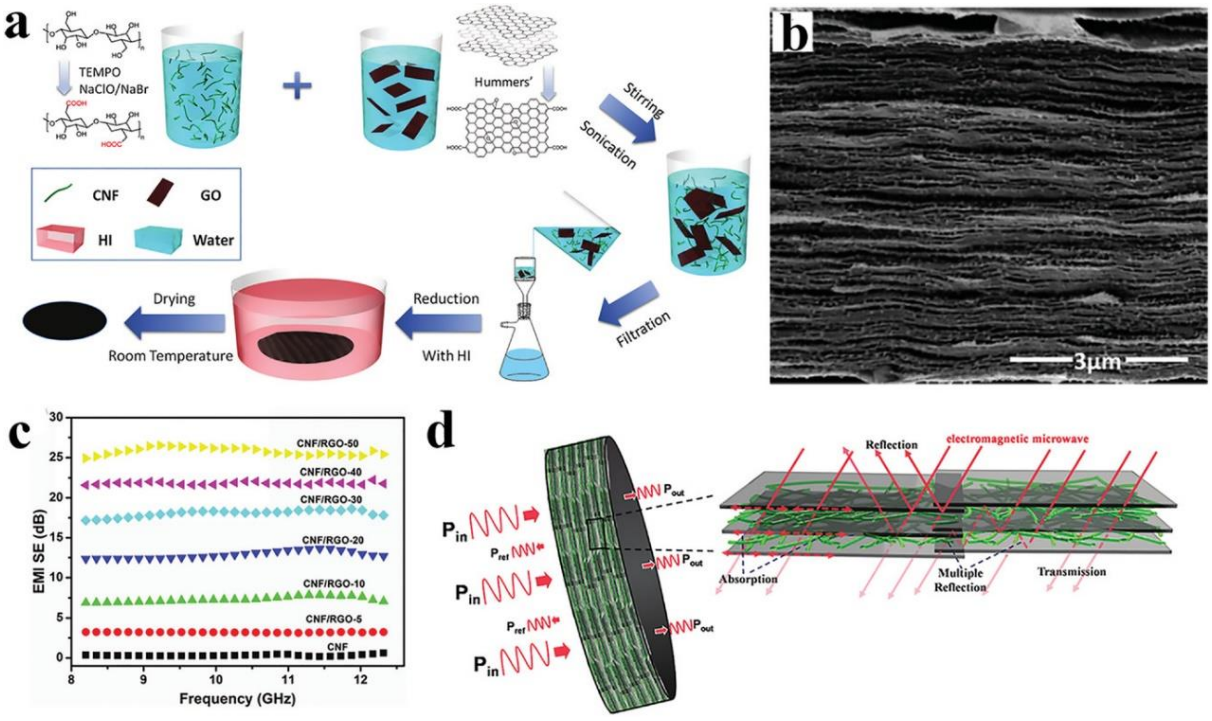


Figure 2.5 (a) Schematic diagram of the RGO/CNF films; (b) Cross-sectional images of RGO/CNF film; (c) EMI SE of the RGO/CNF films; (d) Schematic of the EMW transfer across the composite films [50].

Utilizing a vacuum-induced self-assembly technique, Zhang et al. produced nanocomposites combining CNF with PANI, yielding films characterized by a core-shell layout [51]. These films, measuring 0.28 mm in thickness, demonstrated an EMI SE spanning 20.4 to 25.2 dB. Notably, this represents an increase in shielding efficiency of 49.1 to 55.7% over pure PANI films of the same thickness, highlighting the composite's superior shielding capabilities.

Meanwhile, Marins et al. crafted composite films of PPy using BC as the substrate [52]. This process involved in situ chemical synthesis combined with the application of a polysiloxane solution. The best-performing composite films achieved an SE of up to 15 dB. These studies illustrate the benefits of combining cellulose with conductive polymers through advanced fabrication methods to enhance EMI shielding, showcasing the potential of these composites in addressing the needs of modern electronic and material science applications where effective EMI shielding is crucial.

Lee and colleagues investigated the EMI SE of cellulose papers coated with AgNWs through a dip-coating technique [53]. They observed that increasing the number of dip-coating cycles enhanced the SE value, a result linked to improved electrical conductivity. The AgNW-coated cellulose paper reached an optimal EMI SE of approximately 48.6 dB.

Chen et al. developed a novel paper made from CNF and AgNWs, employing a unique "blending-filtration-peeling" technique [54]. This paper exhibited a hierarchical structure, achieving a high EMI SE of 39.3 dB along with a tensile strength of 49.1 MPa.

Lv et al. explored BC/Cu nanocomposites, applying a sputter coating method [55]. They found that increasing the duration of the coating process significantly boosted the EMI SE of the nanocomposites, with the highest recorded SE reaching 55 dB. These studies collectively highlight the potential of using cellulose-based materials combined with metallic nanocomposites for creating highly effective EMI shielding solutions, demonstrating significant advancements in material science and engineering for addressing electromagnetic pollution.

3 Motivation and aim of the research

The advantages of chemical modification in improving or enhancing the conductivity of cellulose-based materials are significant.

(1) This approach allows for the control over the distribution and concentration of conductive substances within the cellulose matrix, thereby achieving regulation of the material's conductive properties.

(2) By selecting appropriate chemical reactions and conditions, it's possible to achieve uniform loading and stable anchoring of conductive particles without damaging the natural structure of cellulose, ensuring the optimization of the material's conductivity and electrical performance.
(3) Chemical modification provides the possibility of compatibility with a variety of functional materials, such as metal nanoparticles, conductive polymers, and carbon-based materials, which is extremely valuable in the design and preparation of new types of composite functional materials.

Overall, imparting conductivity to cellulose-based materials through chemical modification not only opens new avenues for the functionalization and value enhancement of cellulose materials but also provides strong technical support for the development of new, environmentally friendly smart materials and electronic devices.

Therefore, in this thesis, we first attempted to modify cellulose-based materials with various types of silanes, exploring the changes in the chemical structure of cellulose-based materials due to chemical modification. Then, by combining them with different conductive particles, we endowed cellulose-based materials with conductivity and studied their conductivity and other electrical properties.

In details, we have chosen two methods to impart conductivity to different cellulose substrates:

- The first method involves chemically modifying cellulose films with vinyltrimethoxysilane (VTMS) and covalently bonding them with graphene oxide (GO, 15-20 sheets, 4-10 % edge-oxidized).
- The second method uses 3-Mercaptopropyltrimethoxysilane (3-MT) to first chemically modify viscose fabrics, grafting SH groups onto their surface, followed by copper plating. Herein, the copper plated 3MT modified viscose fabric was named 3MT@Cu@Viscose.

The specific objectives are as follows:

- Objective 1: To develop and characterize advanced cellulose-based materials enhanced with GO and metal nanoparticles for multifunctional applications.
  Employing innovative chemical modification techniques—such as silane crosslinking and thiol modification—to improve the electrical conductivity and other electrical properties of cellulose substrates. This will involve synthesizing a hydrophobic conductive membrane from cellulose and GO, and a flexible conductive viscose fabric through thiol modification followed by copper plating (**Figure 3.1**).
- Objective 2: To establish a foundational understanding of the interaction between cellulose substrates and conductive enhancements at the molecular level.

Utilizing techniques like Fourier-transform infrared spectroscopy (FTIR), wide-angle X-ray diffraction (WAXD), and scanning electron microscopy (SEM) to analyze the morphological and structural changes in cellulose after chemical modifications and metal plating. This analysis will help in understanding the binding efficiency and durability of conductive enhancements on the cellulose substrate.

- Objective 3: Characterization of the produced materials conductivity and other electrical properties.

  Testing the developed materials under various conditions to assess their electrical resistivity, corrosion resistance, Joule heating capabilities, and electromagnetic interference (EMI) shielding effectiveness. Determine the suitability of these materials for integration into smart textiles, sensors, and other electronic applications where flexibility and conductivity are crucial.

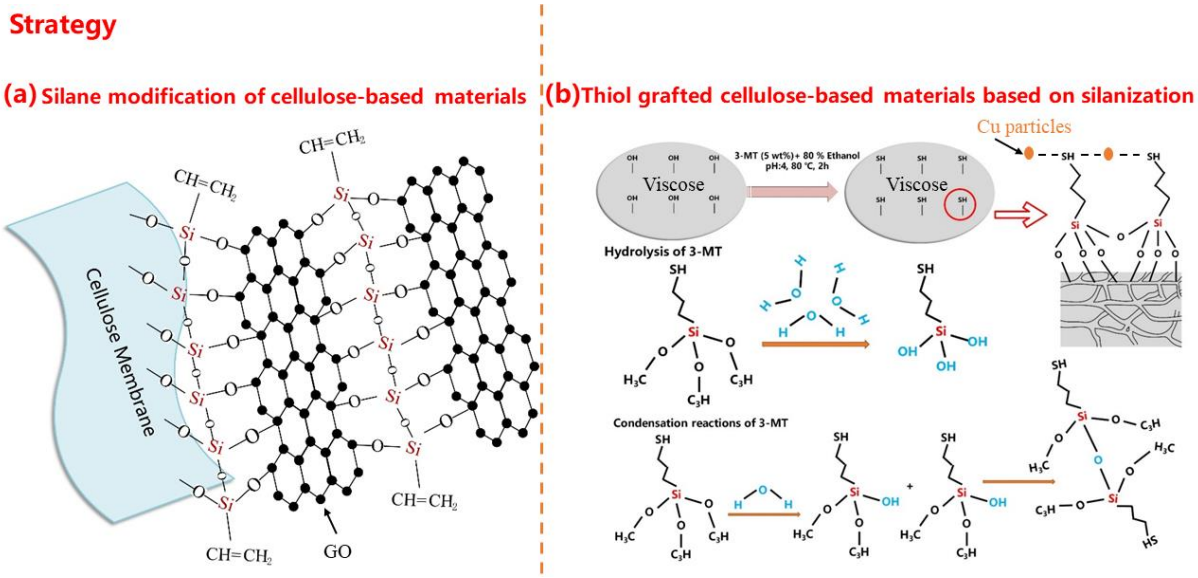


Figure 3.1 Possible reaction mechanisms of silane crosslinking and thiol-modified viscose and development strategy.

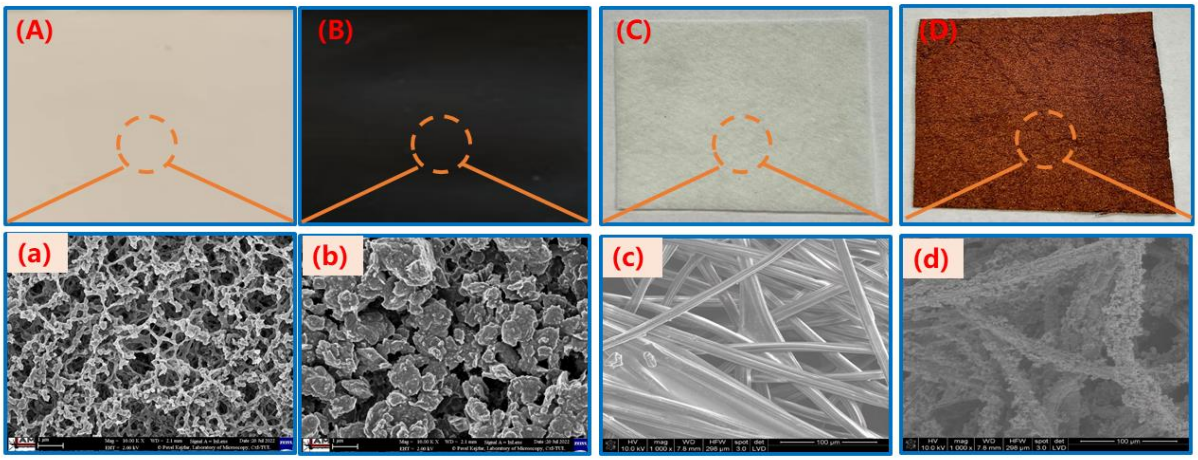


Figure 3.2 Surface morphology and structure of samples. (A), (B), (C) and (D) are macroscopical images of cellulose film, cellulose/GO hybrid film, viscose and 3MT@Cu@Viscose; (a), (b), (c) and (d) are SEM image of cellulose film, cellulose/GO hybrid film, viscose and 3MT@Cu@Viscose.

4 Construction of conductive cellulose based materials

Cellulose-based conductive composites have been successfully prepared through two different strategies. After examining their chemical structure and electrical properties, the prepared samples performed as expected. The first strategy involved a condensation reaction, where cellulose and GO were covalently bonded using VTMS (with GO being 4-10% edge-oxidized) to achieve the desired conductivity and other properties. The second strategy also utilized a condensation reaction to graft SH groups onto the surface of the cellulose base material, which was used to enhance its affinity with metal particles and improve its electrical performance.

4.1 Silane modification of cellulose-based materials

4.1.1 Characterization of chemical structure

Chemical structural changes in conductive cellulose-based composite materials were analyzed. As illustrated in **Figure 4.1**, the cellulose/GO hybrid film exhibits several new characteristic peaks after silane crosslinking. Notably, peaks at approximately 1645 cm^{-1} represent the C=C and C=O stretch vibrations in GO. At 1411 cm^{-1}, a peak is noted for the CH_2 stretch from VTMS, and at 1276 cm^{-1}, CH_3 vibrations are evident. A distinct peak characteristic of cellulose around 1050 cm^{-1} corresponds to the C-O-C stretch of the glycosidic ring, with an adjacent shoulder peak at 1008 cm-1 indicating Si-O presence. Peaks between 700 cm-1 and 850 cm^{-1} are assigned to Si-C bonds, confirming the complete hydrolysis of VTMS and effective cross-linking with cellulose/GO. Post-silanization, the OH stretch vibration in the cellulose/GO films appears diminished, likely due to VTMS hydrolysis and subsequent condensation with the

hydroxyl groups of GO and cellulose to form (Si-O)n chains. Characterization of GO powder can be found in SI.

Figure 4.2(a) presents Raman spectroscopy of the cellulose/GO hybrid membrane compared to GO powders. Distinct D, G, and 2D bands of GO are visible, affirming the successful grafting onto the cellulose membrane. The symmetrical and broad 2D peaks suggest effective GO dispersion during cross-linking on the cellulose membrane surface. Typically, the D band reflects in-plane sp^3 hybrid carbon irregularities, while the G band denotes in-plane vibrations of sp^2 hybrid carbon in the hexagonal lattice. Notably, the G band shifts to a lower wavelength after silanization, indicative of multilayer GO deposition on the cellulose film surface. Additionally, the emergence of the D* band around 1100 cm^{-1} points to a disordered graphite lattice, as supported by relevant literature [56].

The ratio of intensities between the D peak and G peak (I_D/I_G) was utilized to analyze defects in GO composites. According to **Figure 4.2(b)**, the I_D/I_G ratio for GO powder initially declined and then rose as the concentration of GO increased. This trend might reflect the successful covalent integration of GO with the silanol groups in VTMS at lower concentrations of GO, which avoids disrupting the carbon lattice during the condensation process. Additionally, there is a possibility that the silane treatment could have concealed existing defects on the GO surface [57,58], though further studies are needed to confirm this. Another possibility is that during the preparation process of the sample, a small amount of GO was thermally reduced, which was also the reason for the decrease in the ratio. However, there is no obvious evidence to prove this through XRD testing. This may be because the purity of GO used in this study is not high enough, resulting in insignificant experimental results. As the concentration of GO increases, an expansion and intensification of the 2D band are observed, indicating the formation of a multilayer GO coating. Simultaneously, an increase in the I_D/I_G ratio suggests an excessive accumulation of GO powders on the cellulose film surface. This excess, coupled with uneven silanization and random deposition, leads to inconsistent GO growth in different areas, creating more pronounced defects due to the lack of a uniform crystalline orientation.

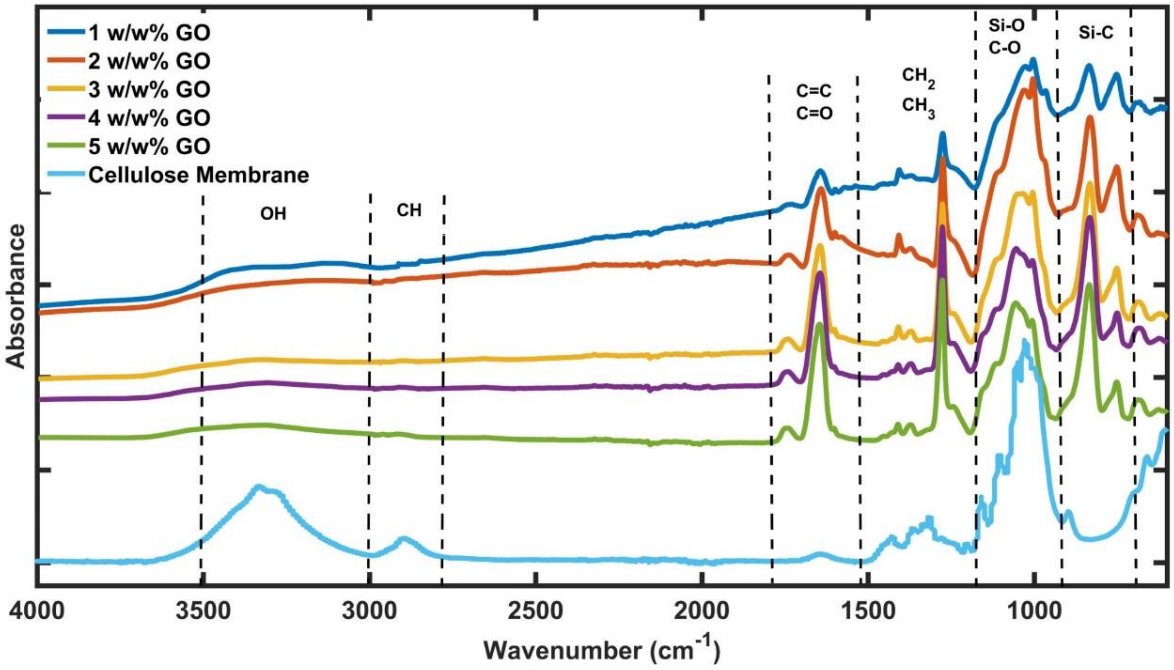


Figure 4.1 FTIR spectra of cellulose membrane and cellulose/GO hybrid membrane.

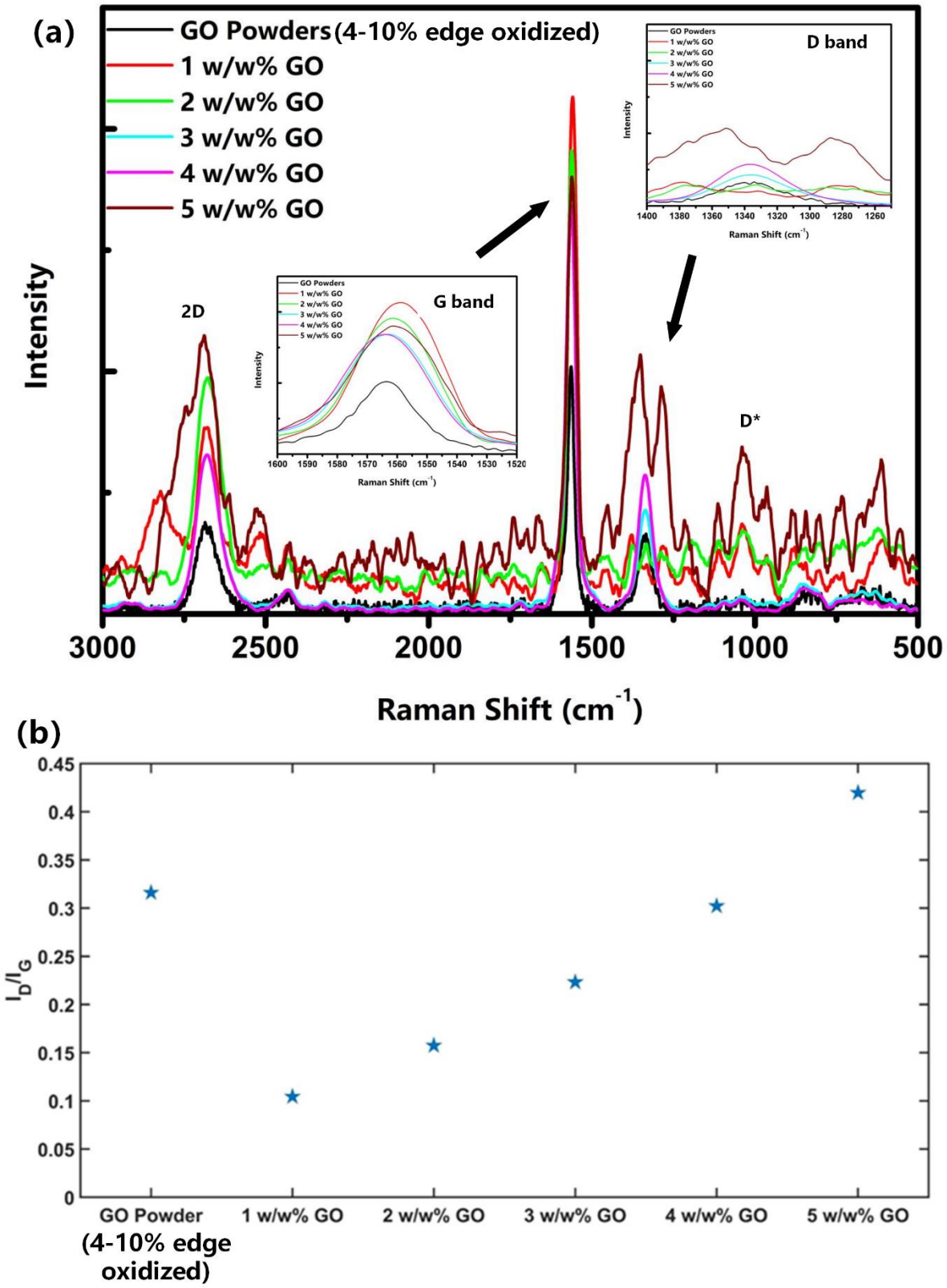


Figure 4.2 (a) Raman spectra of cellulose/GO hybrid membrane; (b) I_D/I_G of GO powder and different concentration of GO.

4.1.2 Electrical and joule heating properties

In this study, we investigate the electrical conductivity and Joule heating characteristics of cellulose/GO hybrid films. **Figure 4.3(a)** illustrates that the hybrid film achieved the lowest surface resistivity (720.69 Ω) at a GO concentration of 3 w/w%, demonstrating its excellent conductivity. At lower GO concentrations, the GO is sparsely and unevenly distributed across the film surface, resulting in a suboptimal conductive network. As the concentration of GO increases, however, a more continuous network forms, enhancing electron mobility. Whatsmore, we also checked the resistivity of the GO powder we purchased (1.38±0.000135 kΩ). It can be observed that the resistivity of the sample we prepared is slightly lower than that of the powder, which may be that a small part of GO is thermally reduced during the preparation process. However, since our GO is not pure GO, there is no obvious change in the XRD results. Therefore, in future work, we will purchase higher purity GO and verify the hypothesis whether it has been reduced.

The film's high electrical conductivity provides it with superior Joule heating capabilities. **Figure 4.3(b)** details the Joule heating performance at varying levels of GO, where, according to Joule's law ($Q = \frac{U^2}{R}t$, where Q is heat generated, U is applied voltage, R is sample resistance, and t is operating time), films with lower surface resistivity exhibit significantly better Joule heating effects. The hybrid film also allows for temperature control by varying the applied voltage (ranging from 0.01A to 0.05A). Demonstrated in **Figure 4.3(c)**, the heating temperature increases with rising voltage, achieving up to 182 ℃ at a safe voltage of 15 V. Furthermore, the film heats up and cools down rapidly, reaching high temperatures within just 5 seconds and cooling down equally quickly when the power is shut off, thus showing exceptional thermal response and control.

For evaluating the stability of the Joule heating performance, the voltage was alternated every 10 seconds, and the corresponding heating and cooling temperatures were recorded. **Figure 4.3(d)** shows minimal fluctuations in heating temperature through these power cycles, indicating reliable and stable electrical heating performance. These findings suggest that the cellulose/GO hybrid films' robust electrical conductivity and effective Joule heating capacity hold significant promise for applications in electrothermal clothing, wearable technology, and sensor systems.

In terms of performance comparison [59–65], the cellulose/GO hybrid membrane exhibits a remarkable advantage in rapid response, with a response time of only 5 seconds across a voltage range of 3-15V and a test temperature range of 38-182°C (**Fig. 4.4**). Compared to other research findings, such as rGO-CNR-CDs (Carbonized CNC nanorods-Carbon nanodots) films,

CP/PU/PPy composite aerogels, AgNW/cellulose films, CNF/MXene films, carbon fibers/cellulose composites, Ag/cellulose/CNT membranes, and MXene/Ppy coated cellulose, our material not only shows a clear advantage in response time but also demonstrates better adaptability in terms of working voltage and temperature range. For instance, although the rGO-CNR-CDs film is stable at higher temperatures, its response time reaches 100 seconds; other materials like CP/PU/PFC composite aerogels and AgNW/cellulose films, despite their shorter response times, have narrower voltage and/or temperature ranges, limiting their potential in broader application scenarios.

In summary, the cellulose/graphene oxide hybrid membrane prepared through silane cross-linking technology showcases excellent electrical properties and quick response characteristics in the domain of electric heating, that is better than most wearable heaters reported in literature. Its broad working temperature and voltage range, along with rapid response time, make it highly suitable for a wide array of applications including sensors, energy storage, and electronic devices, presenting extensive prospects for future research and development.

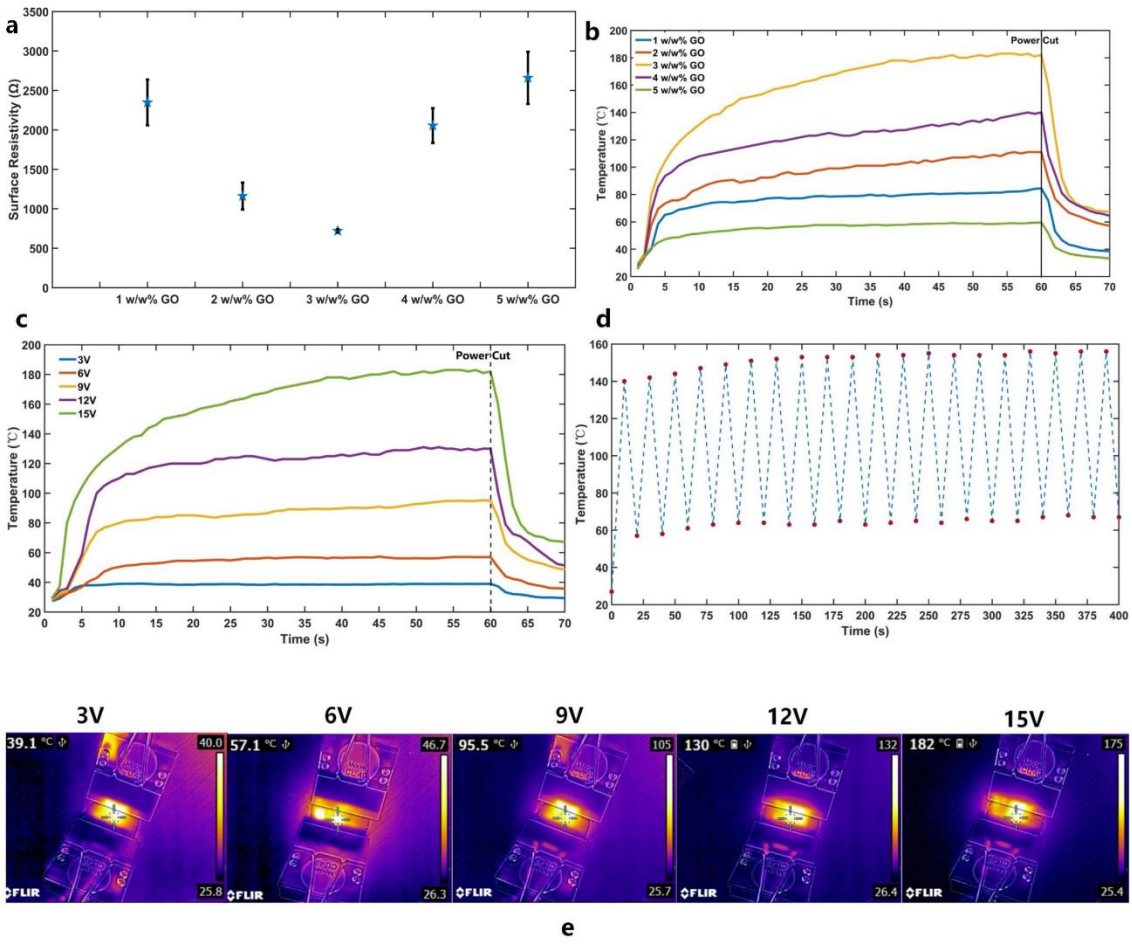


Figure 4.3 a: Surface resistivity of cellulose/GO membrane; b: Joule heating curve of different GO concentration; c: Joule heating curve in different voltage; d: Repeat the switching thermal response at 15 V; e: Thermal imaging at different voltages.

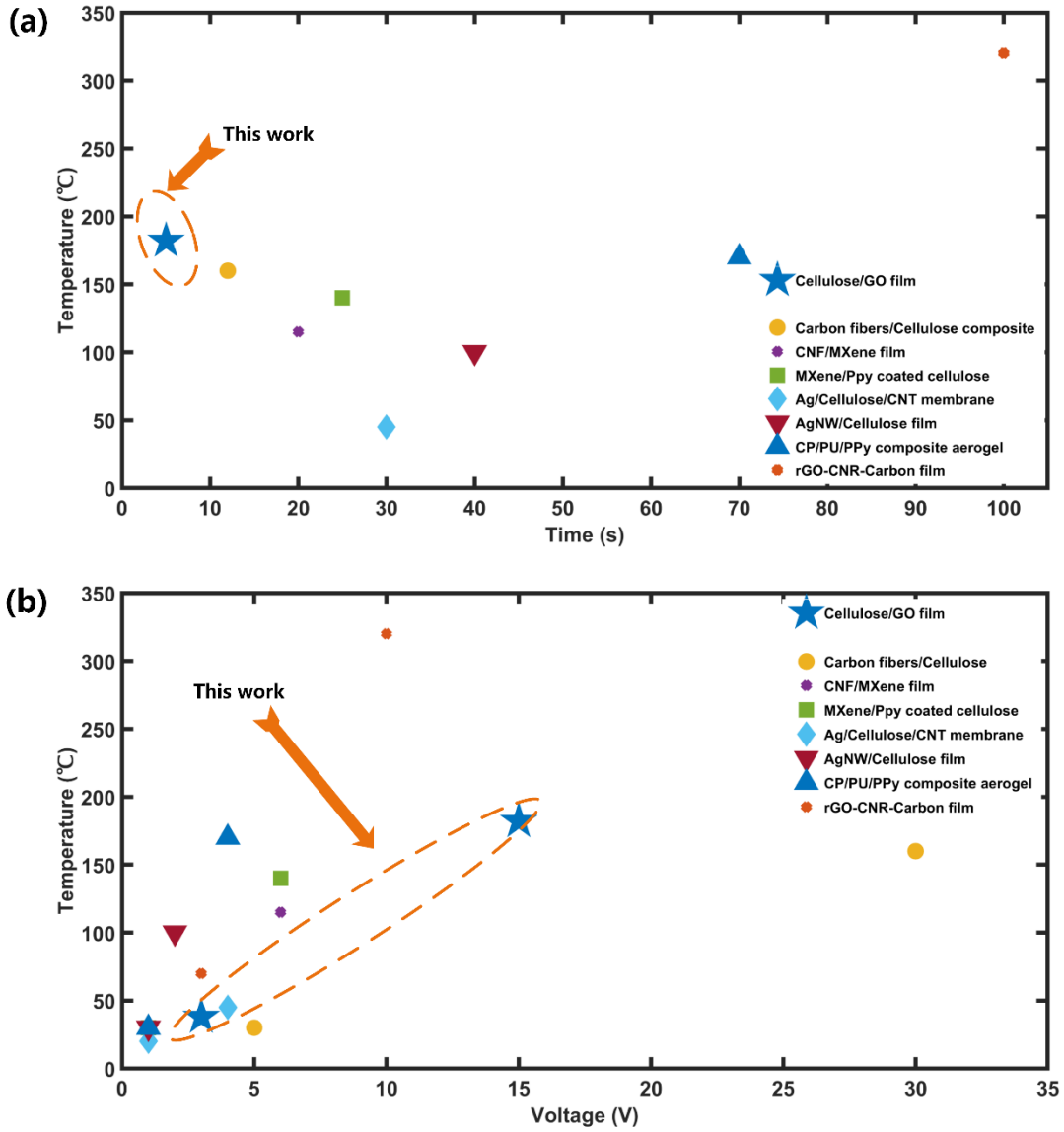


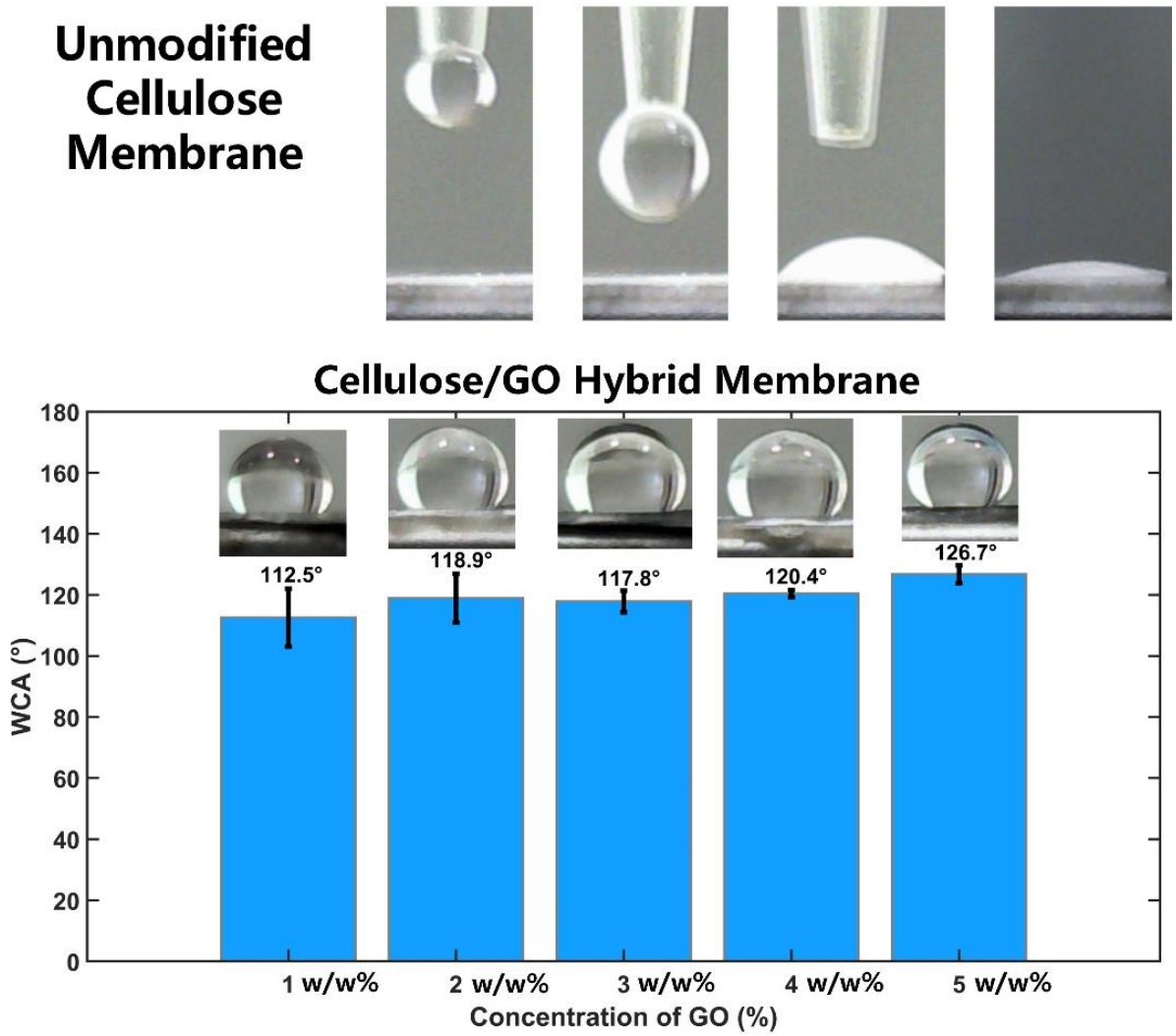
Figure 4.4 (a) and (b) comparison of this work to other products for Joule heating performance.

4.1.3 Surface wettability and self-cleaning of cellulose/GO hybrid membrane

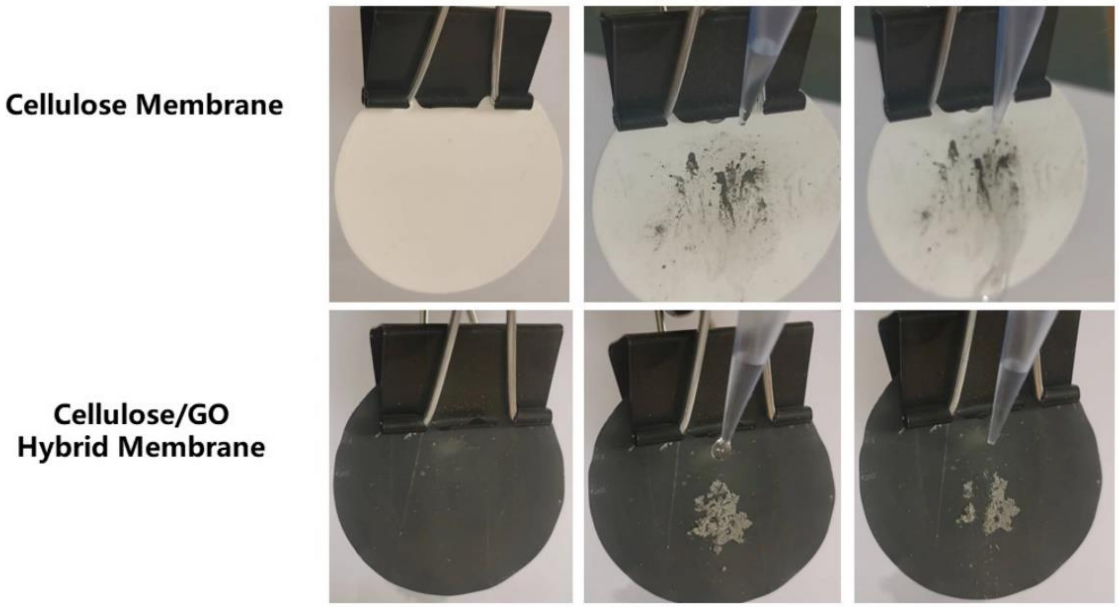
The surface wettability of cellulose/GO hybrid membranes was assessed using WCA measurements. **Figure 4.5** shows that unmodified cellulose films absorbed water droplets instantly, exhibiting no measurable WCA, which indicates very high surface hydrophilicity. On the other hand, silane-crosslinked cellulose/GO films displayed high WCAs ranging from 112.5° to 126.7°, classifying them as hydrophobic materials.

This hydrophobicity is likely due to the reaction between oxygen-containing functional groups in cellulose and GO with hydrophobic VTMS, which forms covalent bonds. Additionally, the silane creates a protective layer on the surface, enhancing the material's water resistance. The increased roughness of the membrane surface also contributes to this hydrophobic effect.

To evaluate the self-cleaning properties of these films, the surfaces were smeared with soot and then exposed to water droplets. As illustrated in **Figure 4.5(b)**, unlike the pristine cellulose membrane which retained soot, the soot on the cellulose/GO hybrid membrane was readily washed away, leaving behind a clean surface. This cleaning effect is attributed to the hydrophobic layer formed by silane crosslinking, which significantly reduces the surface energy and prevents impurities from adhering, allowing them to be easily lifted and removed by water.



(a)



(b)

Figure 4.5 (a) Surface hydrophobicity of cellulose/GO membrane; (b) Self-cleaning performance of cellulose/GO membrane.

4.2 Thiol grafted cellulose-based materials based on silanization

4.2.1 Characterization of thiol modified viscose

Figure 4.6(a) presents the FTIR spectra comparison between original viscose and 3MT@Viscose. Initial observations reveal characteristic bands at 3350 cm^{-1} and 2920 cm^{-1} for the O-H and C-H stretching vibrations respectively, associated with the hydrogen bonds in cellulose molecules within viscose. A band at 1700 cm^{-1} likely arises from O-H bending vibrations in water molecules. Post-modification, 3MT@Viscose displays several new bands, including one at 1260 cm^{-1} linked to CH_3 vibrations from 3MT. The cellulose’s typical band at 1060 cm^{-1}, related to the C-O-C stretching of the glycoside ring, shifts to 1020 cm^{-1} in 3MT@Viscose, suggesting the formation of a Si-O-Si chain. Furthermore, bands near 800 cm^{-1} indicative of Si-C bonds confirm the complete hydrolysis and successful modification with 3MT.

XRD analysis in **Figure 4.6(b)** shows two prominent peaks at approximately 20.0° and 22°, aligning with the (1 1 0) and (0 2 0) lattice planes of regenerative cellulose II. The use of 3MT slightly reduces the crystallinity, potentially affecting the cellulose structure. Conversely, copper plating causes no significant alterations to the supramolecular structure of the substrates, demonstrating the suitability of the chosen modification technique for viscose. Following

copper plating, the presence of crystalline copper is evidenced by sharp peaks around 43° and 50.6°, which correspond to the (1 1 1) and (2 0 0) copper lattice planes respectively, confirming a successful copper ion coating without the formation of unwanted oxide byproducts.

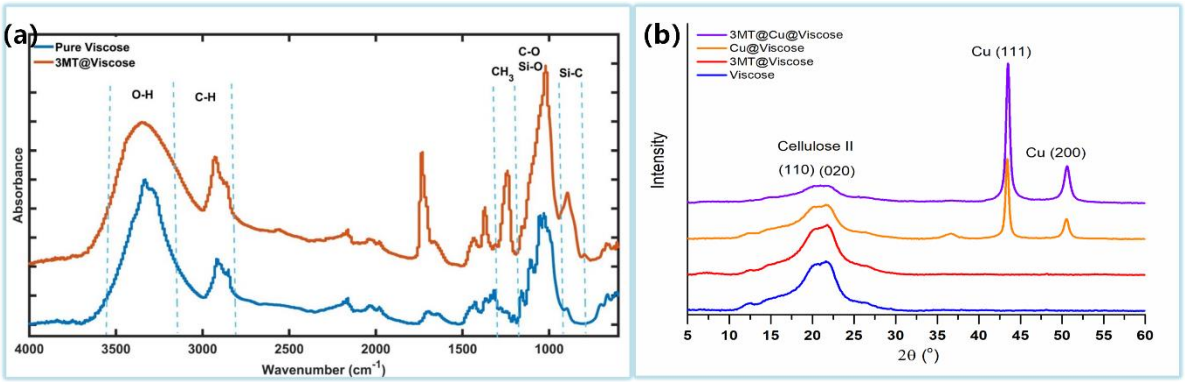


Figure 4.6 Chemical structure analasis of samples. (a) FTIR spectra of original viscose and 3MT@Viscose; (b) XRD of original viscose, 3MT@Viscose, Cu@Viscose and 3MT@Cu@Viscose.

4.2.2 High performance in Joule heating

In this study, we explore the Joule heating properties 3MT@Cu@Viscose materials. The 3MT@Cu@Viscose material shows impressive heating capabilities, reaching 114°C at a minimal voltage of 1V, well below the safe threshold for human contact, as shown in **Figure 4.7(a)**. This material too reaches a high temperature swiftly, within 10 seconds, and cools down rapidly post power-off, underscoring its effective thermal management.

Further experiments, as illustrated in **Figure 4.7(b)**, reveal that the Joule heating performance of 3MT@Cu@Viscose remains robust even when the material is bent or twisted. This durability is likely due to the thiol groups enhancing the copper ion deposition during the plating process, which ensures a dense accumulation of copper particles on the viscose substrate. This maintains the conductivity even under mechanical stress.

Compared to other works [59,60,66–70], 3MT@Cu@Viscose boasts an unrivaled response speed, quickly reaching a stable temperature of 114°C while operating at a low voltage of just 1V (**Fig 4.8**). This not only ensures human safety but also allows wearable heater textiles to be powered by portable batteries or even wearable capacitors.

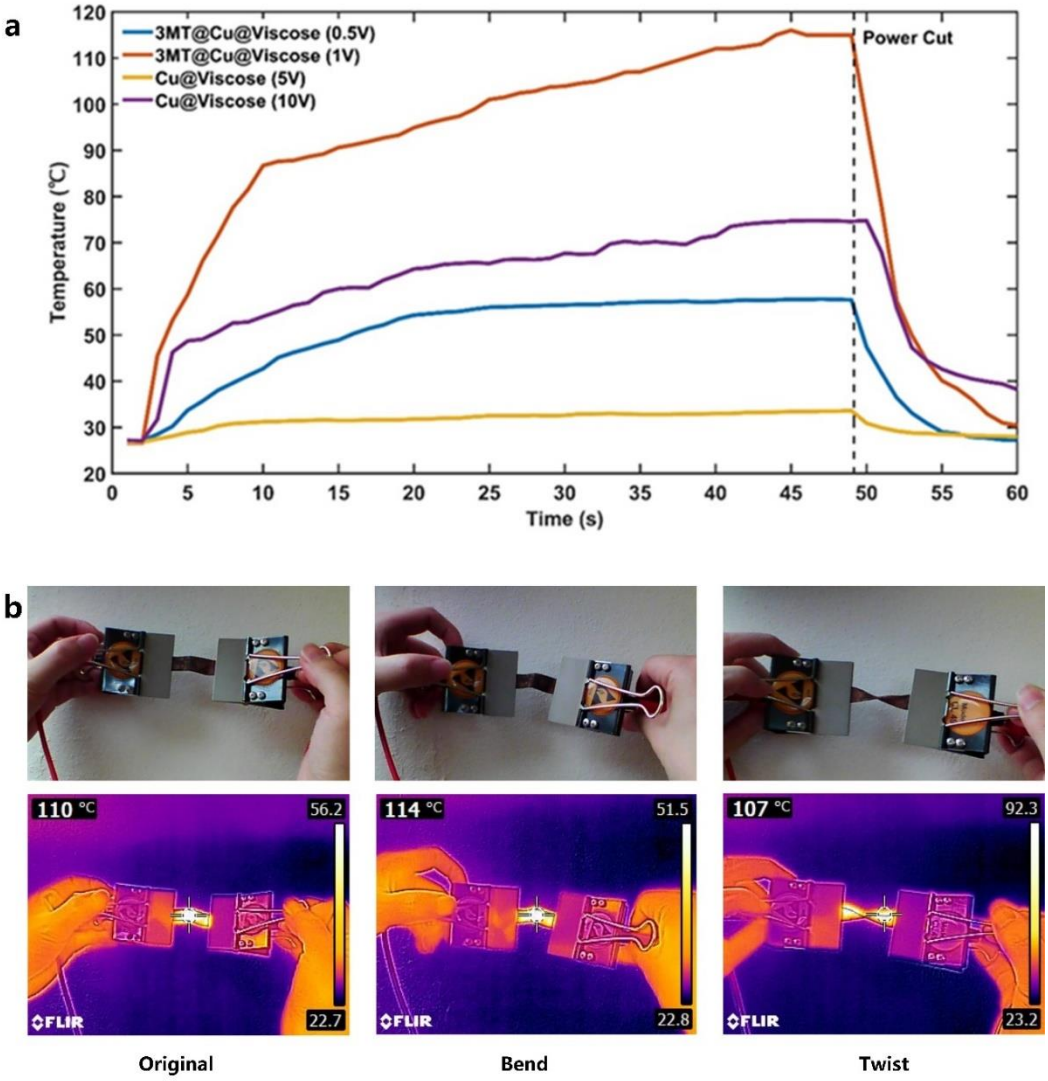


Figure 4.7 (a) Joule heating performance of Cu@Viscose and 3MT@Cu@Viscose in different voltage; (b) Joule heating performance of 3MT@Cu@Viscose in bent and twisted states under 1 V.

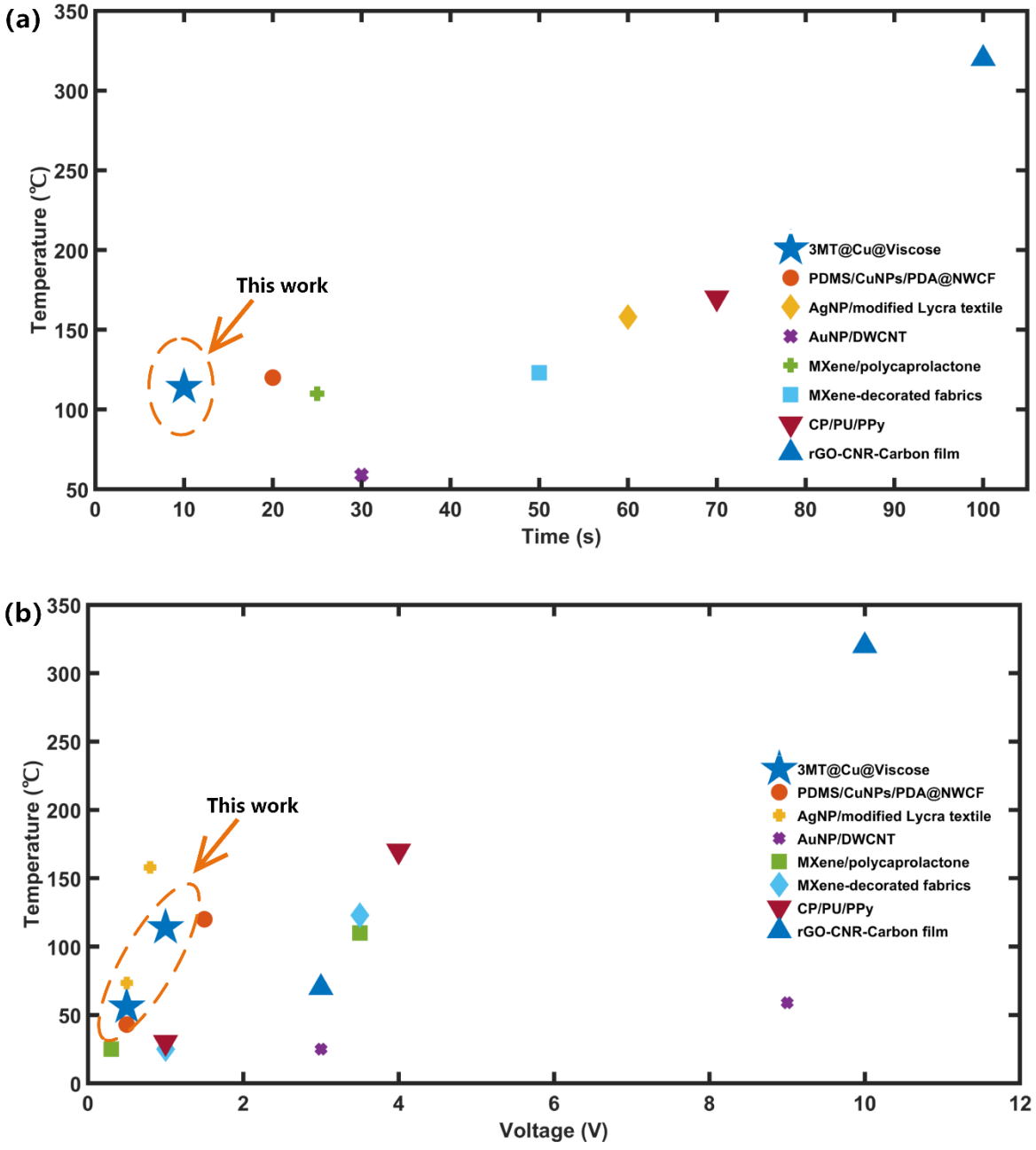


Figure 4.8 (a) and (b) comparison of this work to other products for Joule heating performance.

4.3 High performance in EMI sheilding

With the growing prevalence of electronic and electrical products and technologies, there is a corresponding increase in EMI, which can negatively impact surrounding devices and living organisms. Consequently, it is essential to advance the development of shielding materials that

can efficiently absorb or reflect this radiation, thereby mitigating or neutralizing the effects of EMI.

In our research, we assessed the electromagnetic interference (EMI) shielding effectiveness of various materials across a frequency range from 30 MHz to 3 GHz. This range is significant as it includes frequencies used in many civilian technologies like radio broadcasting, mobile communications, television, wireless LAN, radar, GPS, and others. According to the data in **Figure 4.9**, the EMI shielding effectiveness (SE) of the 3MT@Cu@Viscose sample was consistently between 55-60 dB at each frequency, with an average of 56.6 dB. This suggests that the sample reflected or absorbed at least 99.9% of the electromagnetic waves. In contrast, the Cu@Viscose sample showed a much lower shielding effectiveness, under 10 dB, indicating only 70-90% of the electromagnetic waves were mitigated. Further analysis revealed that the predominant shielding mechanism for both materials was reflection. This is typical for many metal surfaces, where electromagnetic waves are primarily bounced back upon contact with the conductive fabric due to the impedance mismatch caused by the high concentration of free electrons in the metal network [71]. Any remaining waves then penetrate and interact with the copper lattices, where their high electron density induces ohmic losses and interfacial polarization losses, resulting in a reduction in wave energy [72].

In addition, we also compared a range of cellulose-based samples used for EMI shielding in recent years. As can be seen in **Figure 4.9**, the 3MT@Cu@Viscose material exhibits significant EMI SE, achieving 56.6 dB, outperforming most of its counterparts. This success is largely attributed to the modified process involving the grafting of thiol groups onto the surface of viscose fibers, followed by chemical copper plating. Compared to other high-performance EMI shielding materials on the market, such as $Ti_3C_2T_x$ MXene, 3MT@Cu@Viscose offers a significant cost advantage. For instance, $Ti_3C_2T_x$ MXene is prohibitively expensive due to its complex production process and the scarcity of raw materials, with costs exceeding 500 euros for just 0.5 g, limiting its application on a commercial and industrial scale. In contrast, viscose fibers, widely used in textiles, are readily available and inexpensive. The methods employed for chemical modification and copper plating are also cost-effective, making 3MT@Cu@Viscose not only exceptional in performance but also suitable for mass production. Compared to other studies, our samples show significantly higher EMI efficiency. Hence, the material developed in this study not only achieves high-efficiency EMI shielding but also considers economic viability and industrial scalability, providing a viable solution for commercialization.

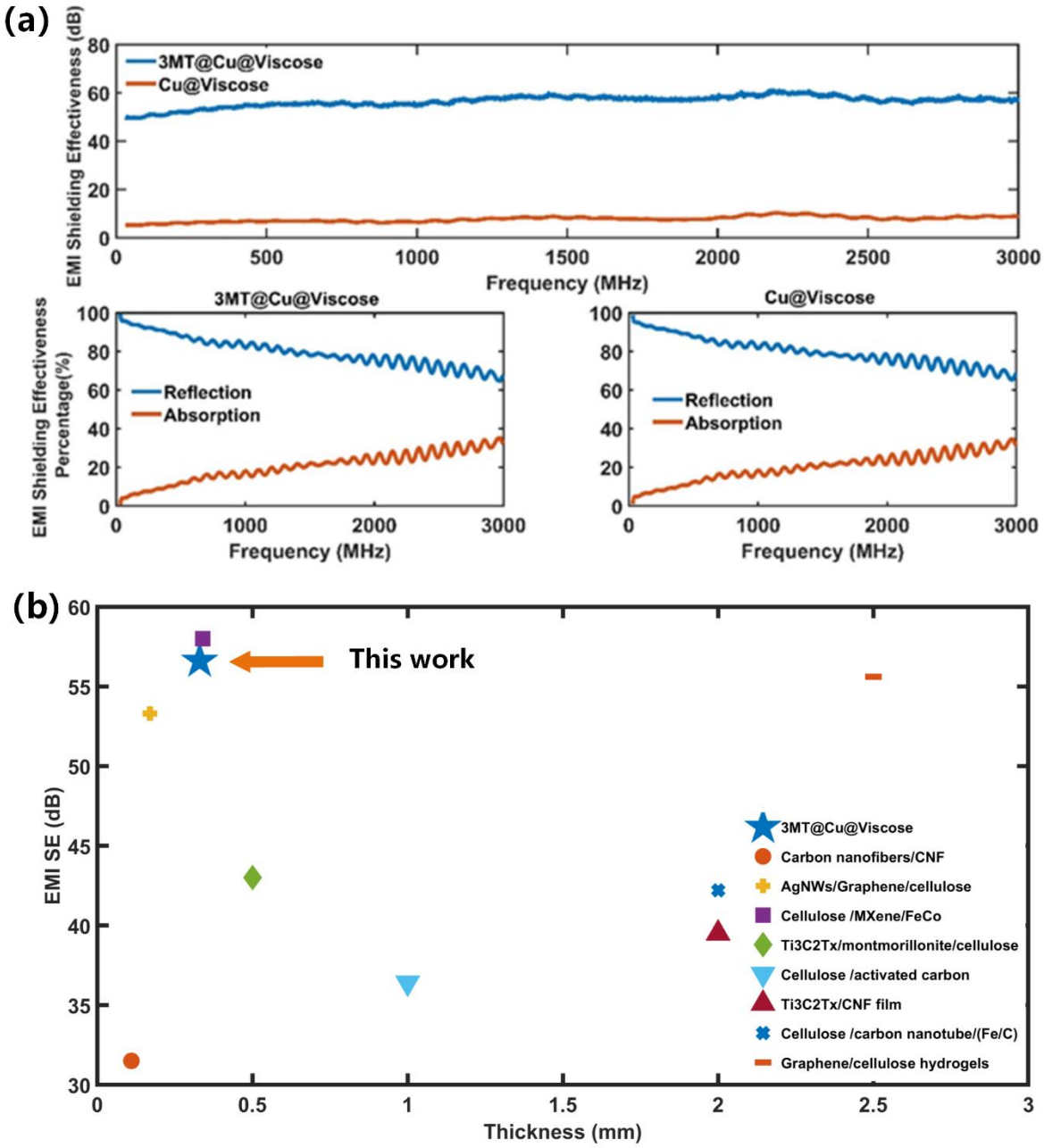


Figure 4.9(a) EMI shielding effectiveness of samples in the 30 MHz–3 GHz band; (b) Comparison to other works.

4.4 Good performance in anti-corrosion properties

Over the past several decades, there has been heightened interest from researchers in understanding corrosion because of its extensive economic, social, and environmental impacts. This interest has largely been driven by the substantial damage corrosion causes to numerous metal structures. During the 1970s and 1980s, studies investigating the economic costs of corrosion demonstrated that it could account for up to 3% of a nation's GDP [73]. Copper and

its alloys are extensively employed in numerous industrial sectors due to their exceptional thermal and electrical conductivity, alongside other notable mechanical properties. They are also crucial in marine applications. However, despite their generally excellent resistance to corrosion, these materials are particularly vulnerable to severe corrosion in marine environments, where large quantities of aggressive chloride ions are present. Therefore, understanding and managing the corrosion of copper and its alloys is critically important in the industry.

By scanning potentiodynamic polarization, we observed a positive shift in the potential of 3MT@Cu@Viscose, while the polarization current for both the cathode and anode showed a slight increase, as displayed in **Figure 4.10**. This indicates that 3MT@Cu@Viscose has enhanced corrosion resistance compared to the standard copper-coated viscose. To derive more precise conclusions, we utilized Tafel analysis to calculate the anode and cathode Tafel slopes (βa and βc), corrosion potential (E_{corr}), corrosion current density (I_{corr}), and the corrosion rate (r_{corr}), presented in **Table 4.1**. The Tafel curve analysis revealed a 72 mV increase in the corrosion potential of 3MT@Cu@Viscose, a reduction in corrosion current by approximately 5.2 $\mu A/cm^2$, and a significantly lower corrosion rate—about 58% less than that of the unmodified copper-plated adhesive. According to the corrosion rate classification for metals in the international standard ISO-9223, the corrosion resistance of copper can be categorized into five levels. The corrosivity range from least to most severe as follows: C1 (very low, $r_{corr} \leq 0.01$ μm/y), C2 (low, 0.01 μm/y $< r_{corr} \leq 0.6$ μm/y), C3 (medium, 0.6 μm/y $< r_{corr} \leq 1.3$ μm/y), C4 (high, 1.3 μm/y $< r_{corr} \leq 2.8$ μm/y), and C5 (very high, 2.8 μm/y $< r_{corr}$). In this study, the 3MT@Cu@Viscose is classified at the C3 level, whileas the unmodified sample is classified at the C4 level, which means it is more susceptible to corrosion in the atmosphere or electrolyte. These improvements are likely due to the structure of copper particles deposited on the viscose surface. The surface of the modified copper-plated viscose fibers is densely covered with compact copper particles, which create more intricate pathways that hinder Cl^- ions in the electrolyte from penetrating and diffusing copper ions, thereby reducing the corrosion rate. Furthermore, FTIR analysis confirmed the formation of a Si-O-Si network in the modified copper-coated viscose. This modification could decrease the fabric's hydrophilicity, lessen the contact area between the electrolyte and the copper surface, and consequently enhance the corrosion resistance [58].

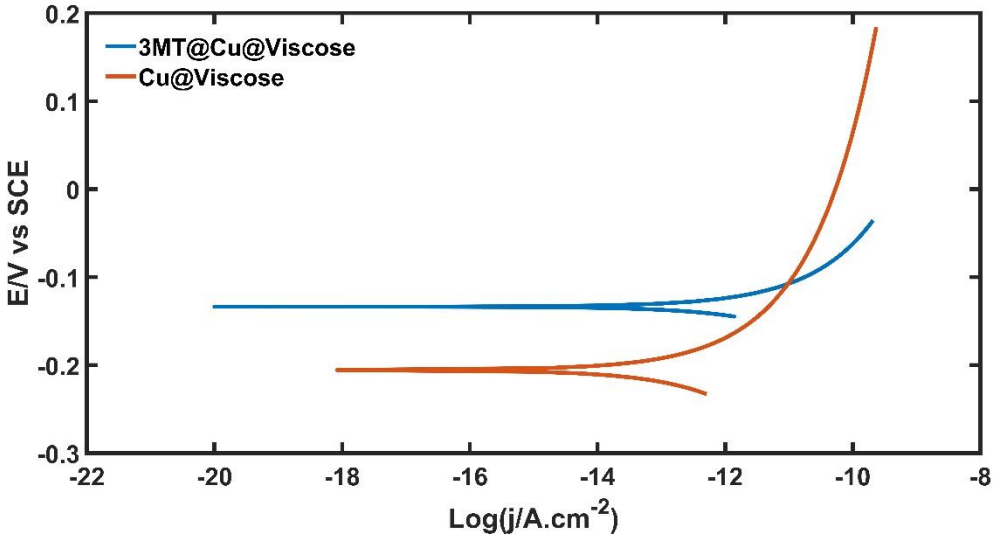


Figure 4.10 Potentiodynamic polarization curves of Cu@Viscose and 3MT@Cu@Viscose.

Table 4.1 Tafel`s analysis.

Sample	β_a (mV)	β_c (mV)	E_{corr} (mV)	I_{corr} ($\mu A/cm^2$)	r_{corr} ($\mu m/y$)
3MT@Cu@Viscose	70.253	17.646	-133.61	3.809	1.143
Cu@Viscose	284.17	210.41	-205.66	9.012	2.692

5 Conclusion

5.1 Silane modification of cellulose-based materials

In this research, cellulose/GO multifunctional hybrid membranes were successfully fabricated through silane cross-linking. The FTIR results indicated that the oxygen-containing groups on the surface of cellulose and GO underwent condensation with VTMS, forming covalent bonds. Raman spectroscopy revealed the unique G and D bands of GO, suggesting that silane cross-linking effectively reduced the defects observed on the surface of GO. Owing to VTMS being a hydrophobic silane, the samples exhibited excellent hydrophobicity and self-cleaning properties, with surface dust easily removed by water droplets. At a 3 w/w% GO concentration, the membranes demonstrated a low surface resistivity of 720.69 Ω. Furthermore, they exhibited exceptional performance in Joule heating, with controllable electric heating temperatures at various voltages, an extremely fast thermal response speed (within 5 s), and stable electrical

performance through repeated power cycling. In summary, this multifunctional membrane, endowed with hydrophobicity, self-cleaning, and outstanding electrical properties, stands as a potent candidate for the next generation of electronic components.

5.2 Thiol grafted cellulose-based materials based on silanization

In this work, we successfully developed a conductive modified viscose fabric with multiple functionalities. FTIR analysis confirmed the grafting of SH groups onto the surface of the prepared samples. XRD tests indicated that 3MT modification does not alter the supramolecular structure of cellulose, making it a suitable modification approach. Tafel analysis confirmed that the corrosion rate of 3MT@Cu@Viscose is about 58% lower than that of unmodified Cu@Viscose, greatly enhancing the composite's stability and durability. Due to its excellent electrical conductivity, 3MT@Cu@Viscose achieved Joule heating performance with a fast thermal response (10 s) and high temperature (114°C) at an extremely low voltage (1 V). The sample maintained its electric heating capability even when bent and twisted, showing high potential in the field of electric heating. Additionally, we examined its performance in EMI shielding. Results showed that between 30 MHz and 3 GHz, the average EMI SE reached 56.6 dB, indicating it could reflect or absorb at least 99.9% of electromagnetic waves. Compared to other related studies, this work offers significant cost advantages and excellent EMI shielding effectiveness.

6 Proposed further activities

1. High-purity GO will be selected for silane bonding with cellulose materials. By comparing the changes in the oxidation peaks in XRD, the hypothesis of whether GO was reduced during the experiment will be verified.
2. Continue to study the applications of cellulose-based conformal materials in other aspects, such as mechanical enhancement, environmental remediation, food packaging, etc.
3. Investigate the performance of silane and thiol modifications in different cellulose-based materials.
4. Study the effects of the structure of different cellulose-based materials on surface modification and coating.

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8 List of publications

Journal of articles

1. **Tan, X.,** Peng, Q., Yang, K., Yang, T., Saskova, J., Wiener, J., ... & Xu, J. (2022). Preparation and characterization of corn husk nanocellulose coating on electrospun polyamide 6. ***Alexandria Engineering Journal***, *61*(6), 4529-4540. https://doi.org/10.1016/j.aej.2021.10.011. **(Q1, IF: 6.628)**
2. **Tan, X.,** Peng, Q., Subrova, T., Saskova, J., Wiener, J., Venkataraman, M., ... & Lammer, H. (2023). Characterization of Cellulose/Polyvinyl Alcohol/Expanded Graphite 3D Porous Foam and Adsorption of Methylene Blue. ***Journal of Natural Fibers***, 20(1), 2190189. 10.1080/15440478.2023.2190189 **(Q1, IF: 3.507)**
3. **Tan, X.,** Jiang, Y., Peng, Q., Subrova, T., Saskova, J., Wiener, J., ... & Xiong, W. (2023). Development and characterization of silane crosslinked cellulose/graphene oxide conductive hydrophobic membrane. ***Cellulose***, 1-14. 10.1007/s10570-023-05079-x **(Q1, IF: 6.123)**
4. **Tan, X.,** Jiang, Y., Puchalski, M., Peng, Q., Hu, S., Xiong, W., ... & Militky, J. (2024). The multifunctional flexible conductive viscose fabric prepared by thiol modification followed by copper plating. ***Cellulose***, 1-16. 10.1007/s10570-024-05764-5 **(Q1, IF: 6.123)**
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6. Yi, C., **Tan, X.,** Bie, B., Ma, H., & Yi, H. (2020). Practical and environment-friendly indirect electrochemical reduction of indigo and dyeing. ***Scientific Reports***, 10(1), 4927. 10.1038/s41598-020-61795-5 **(Q1, IF: 4.996)**
7. Peng, Q., **Tan, X.,** Venkataraman, M., Militky, J., Xiong, W., Mahendran, A. R., ... & Kejzlar, P. (2022). Effects of ultrasonic-assisted nickel pretreatment method on electroless copper plating over graphene. ***Scientific Reports***, 12(1), 21159.

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9. Peng, Q., Yang, K., Venkataraman, M., **Tan, X.,** Xiong, X., Novotna, J., ... & Militky, J. (2022). Preparation of electrosprayed composite coated microporous filter for particulate matter capture. ***Nano Select***, 3(3), 555-566. 10.1002/nano.202100186 (**Cited in Scopus**)
10. Yang, K., Zhang, X., Venkataraman, M., Wiener, J., Palanisamy, S., Sozcu, S., **Tan, X.,** ... & Militky, J. (2023). Structural Analysis of Phase Change Materials (PCMs)/Expanded Graphite (EG) Composites and Their Thermal Behavior under Hot and Humid Conditions. ***ChemPlusChem***, e202300081. 10.1002/cplu.202300081 **(Q2, IF: 3.21)**
11. Yang, T., Hu, L., Chen, A., Tunák, M., Zhang, S., Yu, D., **Tan, X.,** ... & Palanisamy, S. (2022). AFDeter: A MATLAB-based tool for simple and rapid determination of the structural parameters and the airflow-related properties of fibrous materials. ***SoftwareX***, 20, 101213. 10.1016/j.softx.2022.101213 **(Q2, IF: 2.868)**
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Conference papers

1. **Tan X.-D.,** Peng Q.-Y., Subrova T., Saskova J., Wiener J., Venkataraman M., Militky J., Mahendran A.R., Lammer H. Preparation of Cellulose-based Foam Composites and Their Application in Dye Adsorption. ***TBIS 2022.***
2. K. Yang, Q. Peng, M. Venkataraman, J. Novotna, X. Xiong, J. Wiener, Y. Wang, **X. Tan,** G. Zhu, J. Yao, J. Militky, Hydrophobic Breathable Fabric via Electrospraying Technology. **Autex Conference 2021**.

3. **Tan X.-D.,** Peng Q.-Y., Yang K., Wang Y.-F., Yang T., Wang D., Hu S., Xiong X.-M., Saskova J., Wiener J., Venkataraman M., Militky J. The effect of electrode materials and ultrasound on electrochemical reduction. ***TBIS 2020.***
4. Wang Y.-F., Baheti V., Yang K., Hu S., Wang D., **Tan X.-D.,** Yang T., Militký J. Electrical heating properties of various carbonized textile structures. ***TBIS 2020.***
5. Hu S., Wang D., Yang K., Wang Y.-F., Yang T., Peng Q.-Y., **Tan X.-D.,** Kremenakova D., Militky J., Venkataraman M., Periyasamy A.P. Copper coated textiles for inhibition of virus spread. ***TBIS 2020.***
6. Peng Q.-Y., Xiao S.-L., **Tan X.-D.,** Yang K., Wang Y.-F., Yang T., Wang D., Hu S., Xiong X.-M., Venkataraman M., Militky J. Dendrimer-grafted PLGA nanofibrous matrix-mediated gene delivery systems. ***TBIS 2020.***
7. **Tan X.-D.,** Peng Q.-Y., Yang K., Saskova J., Periyasamy A.P., Militky J., Wiener J. Influence of UV light and ozonization on microbes. ***TBIS 2020.***
8. **Tan X.,** Xiong W., Zhang J., Xu J., Yi C. Indirect electrochemical reduction of indigo and dyeing. ***Key Engineering Materials 2018***.

Book Chapters

1. **Tan, X.,** Peng, Q., Yang, K., Saskova, J., Periyasamy, A. P., Militký, J., & Wiener, J. (2021). Influence of UV Light and Ozonization on Microbes State. In ***Textiles and Their Use in Microbial Protection*** (pp. 155-170). CRC Press. 10.1201/9781003140436-8

Curriculum Vitae

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Project handled

1. Student Grant Competition of Technical University of Liberec no. 2023-6374 granted by Ministry of Education Youth and Sports of Czech Republic as team leader.
2. Participating Student Grant Competition of Technical University of Liberec No. 2022-6069, No. 2020-6031and No. 2024-6449 granted by Ministry of Education Youth and Sports of Czech Republic as team member.

9 Reccomendation of the supervisor

FAKULTA TEXTILNÍ TUL

Supervisor's thesis's evaluation for the PhD thesis of Mr. Tan Xiaodong M.Sc.

Title of thesis

Preparation, Characterization and Application of Cellulose Matrix Composites

The presented work is aimed on composites with a cellulose matrix. The aim of the research was to improve or enhance of conductivity of cellulose-based materials. Two methods to impart conductivity to different cellulose substrates was chosen

- First involves chemically modifying cellulose films with vinyltrimethoxysilane and covalently bonding them with graphene oxide. Prepared multifunctional membrane, endowed with hydrophobicity, self-cleaning, and outstanding electrical properties, as like as rapid thermal response, capable of both heating and cooling within a mere 5 seconds, alongside its electrothermal stability, earmarks it for applications in dynamic environments like smart textiles and electric heating devices.
- The second method uses 3-Mercaptopropyltrimethoxysilane to first chemically modify viscose fabrics, grafting SH groups onto their surface, followed by copper plating. The modified material shows an improved corrosion resistance, its Joule heating response is notably swift, and it demonstrates exceptional electromagnetic interference (EMI) shielding effectiveness. It makes the material as a versatile candidate for smart clothing, EMI shielding barriers, and sensors.

In summary, this work provides provide interesting results for future development of electronic device, based on sustainability, efficiency, and using novel materials for higher performance and functionality.

The thesis contain a description of the two methods mentioned above and 4 full texts of articles, publisehd in journals (Q1) during the study period, whose content corresponds to the described topic.

In the research work, candidate has done all work systematically on required scientific level, results are presented logical and understable, and conclusions of thesis are interesting and novel. This is supported, as already mentioned, by the high level of publication activity - alongside the articles reprinted in the dissertation, is the candidate the author of 1 book chapter, co-author of 8 other articles and also has 8 conference papers.

I recommend the thesis for final defense

Liberec 7/11/2024

Ing. Jana Šašková Ph.D

(Supervizor)

10 Opponent's reviews

Opponent review of PhD Thesis

Opponent: Ing. Karel Kupka, PhD.

DissertationThesis:
Preparation, Characterization and Application of Cellulose Matrix Composites
Author: **Xiaodong Tan,M.Eng.**, Department of material engineering, TUL Liberec

Overall Evaluation

The PhD thesis presents a comprehensive and innovative exploration into the modification of cellulose-based materials with the goal of imparting electrical conductivity, electromagnetic interference (EMI) shielding, and corrosion resistance. Through chemical modifications, specifically using silane and thiol grafting techniques, the candidate successfully develops novel functional materials with potential applications in wearable electronics, sensors, and environmental protection. The research demonstrates originality, particularly in combining cellulose—a natural, biodegradable material—with modern conductive materials like graphene oxide (GO) and copper. Overall, the thesis is well-structured, with clear experimental methodologies and in-depth analysis of results, making it a significant contribution to the field of material science.

Key Contributions and Novelty

The main novelty of this thesis lies in its innovative approach to modifying cellulose-based materials using silane crosslinking and thiol grafting. The combination of these modifications with conductive elements, such as graphene oxide (GO) and copper, introduces several advanced functionalities to cellulose-based substrates. Key novelties include:

- The development of multifunctional cellulose-based materials that demonstrate both electrical conductivity and hydrophobicity, achieved through silane crosslinking with GO.
- The novel use of thiol-grafted copper plating on cellulose to achieve high EMI shielding effectiveness (up to 56.6 dB), a significant result for a cost-effective and biodegradable material.
- The introduction of corrosion resistance properties in cellulose materials through thiol modification, leading to a 58% reduction in corrosion rate compared to unmodified materials.

The work is novel in its effort to integrate sustainable materials into fields traditionally dominated by synthetic polymers or metals. The thesis opens new possibilities for the application of cellulose-based materials in areas such as wearable electronics, flexible energy devices, and environmentally friendly packaging.

Results and Potential Applications

The results presented in the thesis are of high significance and showcase the practicality of these modified cellulose-based materials. The materials developed exhibit:

- High electrical conductivity, especially in the cellulose/GO hybrid materials, making them suitable for electronic and sensor applications.
- Excellent EMI shielding performance, making the thiol-grafted copper-plated cellulose a strong candidate for use in electronic devices to prevent electromagnetic interference.
- Strong corrosion resistance, which suggests potential for applications in environments where material durability is crucial, such as in marine or industrial settings.
- Joule heating properties, particularly in thiol-modified viscose fabrics, enabling their use in wearable heating applications, such as smart textiles.

These results demonstrate the versatility and effectiveness of the modified cellulose-based materials, with applications ranging from electronic textiles to environmental protection, energy storage, and packaging solutions.

Weaknesses and Omissions

Despite the strengths and novelties of the thesis, there are some weaknesses and omissions that should be addressed in future work:

- **Scalability and Industrial Feasibility**: The complexity of the silane crosslinking and thiol grafting processes may present challenges for large-scale production. Further work is needed to simplify these procedures or explore alternative methods that can be easily scaled for industrial applications.
- **Long-term Durability**: The thesis does not thoroughly investigate the long-term durability of the materials, particularly under harsh environmental conditions such as high humidity, mechanical stress, or extreme temperatures. Future studies should focus on testing the material's stability and performance over prolonged exposure.
- **Environmental Impact**: While the thesis emphasizes the use of biodegradable cellulose-based materials, the environmental impact of the chemical modifications and the disposal of these materials after use has not been fully explored. Future research should include life-cycle assessments and sustainability evaluations of the modified materials.

Future Directions

The research presented in this thesis opens many avenues for future work. Key directions include:

- **Exploring Other Conductive Additives**: While the thesis focuses on GO and copper, other conductive additives, such as reduced graphene oxide (rGO), silver nanowires, or carbon nanotubes, could be investigated to further enhance the conductivity and functionality of cellulose-based materials.
- **Improving Scalability**: Simplifying the chemical modification processes or developing alternative methods that are more feasible for mass production would enhance the industrial applicability of the findings.
- **Testing in Real-World Applications**: The materials should be tested in real-world applications, such as wearable electronics or packaging, to validate their performance in practical settings.
- **Further Environmental Assessments**: A deeper investigation into the environmental impact of the materials and processes used in this research would be beneficial for promoting the sustainable development of cellulose-based technologies.

Recommendation for Defense

In conclusion, this PhD thesis presents a significant contribution to the field of cellulose-based material science and its potential applications in electronics, environmental protection, and beyond. The candidate has demonstrated technical proficiency in both experimental methodologies and data analysis, and the research outcomes including five high-impact journal articles in last 1 year offer practical insights for future developments in the industry. Despite some areas that require further exploration, the thesis is of a high standard and worthy of recommendation for defense. I strongly recommend the candidate be allowed to defend their thesis.

Reviewer: Ing. Karel Kupka, PhD. & PhD.
Pardubice, 15.9. 2024

Review to dissertation titled "Preparation, Characterization and Application of Cellulose Matrix Composites"

This dissertation is focusing on the development of cellulose matrix composites with multi-functions by combining graphene oxide and copper particles with cellulose-based materials. It aims to improve and regulate the conductivity and electrical performance of cellulose matrix composites which can be applied as smart materials and applied in smart textiles. This work is significant in textile material science and engineering area.

The application of functional particles onto cellulose-based materials is mainly facing the problems of agglomeration and weak interface bonding strength. This dissertation work proposed to use silane and 3-Mercaptopropyltrimethoxysilane in a chemical reaction system to solve the above problems. And then, the graphene oxide and copper particles were well bonded with cellulose-based materials. Additionally, properties of cellulose matrix composites, including electrical conductivity, electrical and joule heating, surface wettability and self-cleaning, EMI shielding, anti-corrosion properties, were also evaluated and discussed. This dissertation work presented its innovation in chemical modification on cellulose-based materials and improved the properties of cellulose matrix composites mentioned above.

In the state of the art section, the literature review demonstrated a concise and clear summary about conductive cellulose based composites and their applications with some specific functions, which provide detailed information for reader to understand the current focus in this area, and also provide a solid theoretical foundation for the dissertation work.

In the experimental (construction of conductive cellulose-based materials) section, the experimental process and testing methods were presented clearly. Since the dissertation is in the form of combining publications of the candidate. Therefore, the experimental work, results and discussions are also well described in the Appendix. The experimental results are presented clearly and discussed appropriately. The conclusions are concise and supported by experimental results.

During the Ph.D. study, the candidate has published 4 papers in journals with high impact factor, 4 international conference papers, 1 book chapter, which indicates that the candidate has

contributed a good research work to his dissertation area and got the recognition by peer review. Therefore, I recommend the Ph.D. dissertation for defence.

Apart from the above comments, there are some questions to be addressed,

1. The detailed discussions in FTIR spectra are helpful to confirm the covalent modification for both cellulose film and viscose. In addition, the presence of SH groups and Cu particles on viscose surface should be confirmed.

2. In Section 4.1.1, ID\IG values initially declined and then rose as increasing GO concentration. It mentions that "This trend might reflect the successful covalent integration of GO with the silanol groups in VTMS at lower concentrations of GO, which avoids disrupting the carbon lattice during the condensation process". The reason should be explained.

3. In Section 4.1.2, the resistivity of cellulose/GO hybrid films with 3 w/w% of GO is lower than pure GO. The candidate mentioned that a small part of GO is thermally reduced during the preparation process. However, the resistivity of other samples (like 1%, 4%, 5% of GO) is higher than that of pure GO. Can the candidate explain the variation and verify the thermal reduction?

Reviewer:

Prof. Lin Liu

School of Materials Science and Engineering

Zhejiang Sci-Tech University