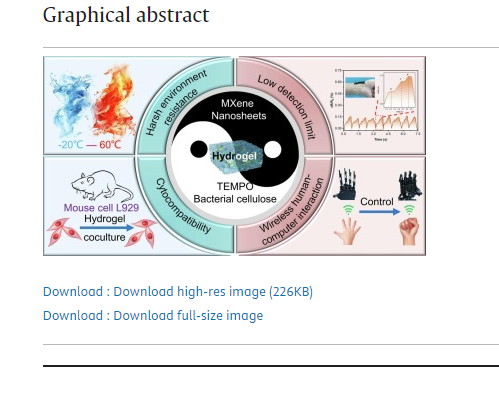
TEMPO bacterial cellulose and MXene nanosheets synergistically promote tough hydrogels for intelligent wearable human-machine interaction

## **Abstract**

Conductive hydrogels have received increasing attention in the field of wearable electronics, but they also face many challenges such as temperature tolerance, biocompatibility, and stability of mechanical properties. In this paper, a [double network hydrogel](https://www.sciencedirect.com/topics/chemistry/double-network-hydrogel) of MXene/TEMPO bacterial [cellulose](https://www.sciencedirect.com/topics/chemistry/cellulose) (TOBC) system is proposed. Through solvent replacement, the hydrogel exhibits wide temperature tolerance (−20–60 °C) and stable mechanical properties. A large number of [hydrogen bonds](https://www.sciencedirect.com/topics/chemistry/hydrogen-bond), MXene/TOBC dynamic three-dimensional network system, and micellar interactions endow the hydrogel with excellent mechanical properties (elongation at break ~2800 %, strength at break ~420 kPa) and self-healing ability. The introduction of [tannic acid](https://www.sciencedirect.com/topics/chemistry/tannic-acid) prevents the [oxidation](https://www.sciencedirect.com/topics/biochemistry-genetics-and-molecular-biology/alpha-oxidation) of MXene and the loss of electrical properties of the hydrogel. In addition, the sensor can also quickly (74 ms) and sensitive (gauge factor = 15.65) wirelessly monitor human motion, and the biocompatibility can well avoid the stimulation when it comes into contact with the human body. This series of research work reveals the fabrication of MXene-like flexible wearable electronic devices based on self-healing, good cell compatibility, high sensitivity, wide temperature tolerance and durability, which can be used in smart wearable, wireless monitoring, human-machine Interaction and other aspects show great application potential.



## **Introduction**

In recent years, hydrogels (G. Li, Li, et al., 2022; Yao et al., 2019; L. Zhang et al., 2023) owing to their commendable flexibility, wearability, biocompatibility (Zhou et al., 2023), and precision in information capture, have emerged as promising materials for applications in intelligent wearable electronic devices and human-machine interaction. Yet, the integration of hydrogels into flexible wearable electronics brings forth stringent requirements: Their electrochemical stability, extensive temperature tolerance, specific water retention, and robust mechanical performance must collectively enable stable electrical signal transmission across varied environmental conditions (Cheng et al., 2023; Liu et al., 2023; Yuan et al., 2022; Zheng et al., 2023). In particular, conductive hydrogels, found in flexible electronic devices, can detect and translate external physical signals into recordable electrical outputs. This has led to potential applications in flexible touch screens, (Cao et al., 2019) human-machine interfaces, (Hang et al., 2020) biomimetic electronic skins (H. Zhang, Guo, et al., 2021), health monitoring (H. Lei et al., 2021), and robotic applications (M. Li, Zhang, et al., 2022). Elastomeric polymers, typified by extensibility, high transparency, and relative stability, are utilized widely in stretchable electronic sensors, including polyacrylamide, polyacrylic acid, and polydimethylsiloxane. Yet, limitations such as low mechanical strength, inadequate sensitivity, and subpar conductivity restrict their application in flexible electronic devices. Conventional hydrogels also suffer from the inability to withstand freezing at sub-zero temperatures and a tendency to dehydrate at room or elevated temperatures. Taking inspiration from natural anti-freezing behaviors, researchers have developed temperature-resistant hydrogels by incorporating salts, alcohols, and ionic liquids (Dong, Yu, & Liu, 2023; Ou et al., 2022; K. Wang et al., 2019; D. Zhang, Liu, et al., 2021). Nevertheless, achieving precise monitoring of human signals (e.g., pulse, respiration) and detection ranges (e.g., from frowning to elbow bending), while maintaining response time and stability, remains challenging (Y. Dong, Xu, et al., 2023; Y. Dong, Yu, et al., 2023; Ge et al., 2023).

MXene (Ti2C3Tx), a noteworthy member of the two-dimensional nanomaterials family, offers diverse surface terminal groups, hydrophilic surface terminals, and high conductivity. This has led to its wide use in the fabrication of hydrogel flexible electronic devices (Shang et al., 2019; Y.-Z. Zhang et al., 2020; Y. Zhang, Gong, & Wan, 2021). Existing MXene-based devices are usually constructed by integrating MXene as fillers into viscoelastic bodies/gels (Feng et al., 2021; Y.-Z. Zhang et al., 2020). Despite the simplicity of this method, challenges persist, including inadequate uniform mixing, leading to layered accumulation and aggregation, thus diminishing electrochemical performance. Inhomogeneity may further result in unpredictable impacts on sensing performance, contingent on the orientation and stacking of MXene nanosheets. Interlayer interactions of MXene nanosheets through van der Waals forces and hydrogen bonds encourage spontaneous stacking and clustering, substantially reducing surface group availability and electronic transport abilities. Furthermore, MXene's inherent surface functional groups can cause nanosheet oxidation in aqueous environments, considerably undermining its electrochemical performance, thereby limiting its applicability in hydrogel sensors. Strategies employing metal ions like Na+, Fe2+, K+, and polymeric intercalation to build 3D structures that prevent MXene self-stacking have been effective (Q. Li, Song, et al., 2021; Wu et al., 2020; Zha et al., 2019). Lv et al. utilized divalent metal ions to intercalate MXene, counteracting the electrostatic repulsion between MXene nanosheets and inducing MXene gelation for capacitors (Y. Deng et al., 2019). Zhao et al. effectively prevented nanosheet stacking, achieving a composite hydrogel with excellent conductivity and mechanical attributes (He et al., 2022). Storing MXene in water under ambient conditions poses oxidation challenges, as oxidation often initiates at the nanosheet edges. Techniques involving inert gas low-temperature protection and edge effect reduction through salting have been effectively employed to prevent oxidation (Habib et al., 2019; Lee et al., 2020; Natu et al., 2019; C. J. Zhang et al., 2017). Nonetheless, there continues to be an imperative need to foster the growth and innovation of stable, highly sensitive, and durable MXene hydrogel electronic sensors.

Tannic acid (TA), a polyphenol abundantly present in numerous plants, functions as a polyanion, demonstrating electrostatic affinity for positively charged entities. Recognized for its cost-effectiveness and plentiful phenolic hydroxyl groups, TA forms uniform metal-TA complexes on metal surfaces, achieving antioxidation (P.-F. Zhang, Wu, et al., 2022). This ability has made it a frequent choice as an antioxidant in food and other substances (Yan et al., 2020). Artificial/natural fibers, unique in their structural hierarchy and mostly fibrous in nature, are widely used as inclusions in elastomers/hydrogels to enhance mechanical strength. Bacterial cellulose (BC), a natural biopolymer polysaccharide with advantages such as low cost, renewability, easy processability, biodegradability, high purity, and high network structural strength, is extensively applied in the fabrication of hydrogels (J. Lu et al., 2022; Pan et al., 2023; D. Zhang, Jian, et al., 2022). As an exemplary additive, BC nanofiber networks can equip hydrogels with enhanced mechanical properties, while the hydrophilic character of the hydroxyl groups on the BC surface contributes to the hydrogel's water retention capacity (Jin et al., 2022; Murugarren et al., 2022; Z. Yang et al., 2022).

In this study, we introduce a dual-network hydrogel system MXene/TEMPO bacterial cellulose (TOBC) (designated as PBMG), tailored for flexible electronic devices to overcome existing challenges. Upon refinement, the PBMG hydrogel exhibits remarkable low-temperature (−20 °C) and high-temperature (60 °C) tolerance, superior conductivity, and notable self-healing characteristics. The success of this approach relies on the synergistic interaction between TEMPO bacterial cellulose and MXene. It effectively navigates around the MXene flocculation issue with polymer bacterial cellulose, resulting in a stable dynamic three-dimensional network system. This system efficiently inhibits MXene nanosheet stacking, maximizing its conductive function in the hydrogel, and amplifying the detection sensitivity of the hydrogel. Simultaneously, the formation of a cohesive dynamic 3D network structure between TOBC and MXene nanosheets imparts the hydrogel with exceptional mechanical strength (fracture stress approximately 420 kPa) and stretchability (fracture strain around 2800 %), without sacrificing flexibility. Tannic acid can bind to MXene edge positively charged groups, successfully inhibiting oxidation and enhancing the hydrogel's longevity in flexible electronic devices. This streamlined and potent strategy not only confers the PBMG hydrogel with extensive temperature resilience but also substantially improves its mechanical fortitude, stretchability, sensitivity, detection range, and endurance. These enhancements collectively underscore the potential and innovative pathways for the utilization of MXene in hydrogel-based flexible electronic devices.

## **Section snippets**

## **Materials**

Ti3AlC2 powder (400 mesh), and lithium fluoride (LiF) were procured from Shandong Xinyan New Materials Technology Co., Ltd., China. Nano bacterial cellulose (BC) dispersion was obtained from Guilin Qihong Technology Co., Ltd., China. Glycerol (Gly), acrylamide (AAm), lauryl methacrylate (LMA), alkyl polyglucoside (APG), tannic acid (TA), ammonium persulfate (APS), N, N′-methylene bisacrylamide (MBA), and tris(hydroxymethyl)aminomethane (Tris) were sourced from Shanghai Macklin Biochemical Co.,

## **Design strategy, synthesis mechanism, and structural characterization of PBMG hydrogels**

PBMG hydrogels are fabricated by cross-linking a conductive three-dimensional (3D) colloidal network of MXene/TOBC with a polyacrylamide (PAM) gel system. Fig. 1 comprehensively delineates the preparation methodology, gel constitution, and intricate physical and chemical interactions within PBMG hydrogels. The MXene surface is replete with reactive functional groups. Following tannic acid (TA) modification and incorporation into the gel matrix, it forms extensive hydrogen bonds with TOBC (L.

## **Conclusion**

In this study, we have successfully developed an MXene class of flexible electronics characterized by temperature tolerance, enhanced durability, self-healing properties, conductivity, and remarkable stretchability for applications in intelligent wearable human-machine interaction. This innovation was realized through the strategic integration of a glycerol-water binary solvent into the MXene/TOBC dual-network hydrogel, employing a solvent substitution method. The deliberate introduction of

## **Ethics declaration**

Consent for the publication of identifiable images of research participants to publish was obtained. The data were obtained with the informed consent of all participants. The Institutional Review Board of Qilu University of Technology approved this study (no. 20230011).

## **CRediT authorship contribution statement**

**Baoting Dong:** Conceptualization, Methodology, Software, Investigation, Writing – original draft. **Dehai Yu:** Conceptualization, Methodology, Software, Investigation, Resources, Supervision, Writing – original draft. **Peng Lu:** Methodology. **Zhaoping Song:** Methodology. **Wei Chen:** Software. **Fengshan Zhang:** Supervision. **Bin Li:** Resources. **Huili Wang:** Supervision, Resources. **Wenxia Liu:** Supervision.

## **Declaration of competing interest**

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

## **Acknowledgements**

This work was supported by the Natural Science Foundation of Shandong Province (No. ZR2020MB128, No. ZR2022MB095); Postdoctoral Research Foundation of China (2023M731168); the QUTJBZ Program (No. 2022JBZ01-05); Shandong Province Key Research and Development Program (No. 2021ZDSYS18). The Project Supported by the Foundation (No. 2023GXZZKFS0) of Guangxi Key Laboratory of Clean Pulp & Papermaking and Pollution Control, College of Light Industry and Food Engineering, Guangxi University.

## **References (64)**

* J. Chen et al.

### [**Tough hydrophobic association hydrogels with self-healing and reforming capabilities achieved by polymeric core-shell nanoparticles**](https://www.sciencedirect.com/science/article/pii/S0928493118326778)

### **Materials Science and Engineering: C**

(2019)

* Y. Dong et al.

### [**Highly sensitive, scrub-resistant, robust breathable wearable silk yarn sensors via interfacial multiple covalent reactions for health management**](https://www.sciencedirect.com/science/article/pii/S2211285523005608)

### **Nano Energy**

(2023)

* C.-Z. Hang et al.

### [**Highly stretchable and self-healing strain sensors for motion detection in wireless human-machine interface**](https://www.sciencedirect.com/science/article/pii/S2211285520306418)

### **Nano Energy**

(2020)

* Y. He et al.

### [**Polysaccharide/Ti3C2Tx MXene adhesive hydrogels with self-healing ability for multifunctional and sensitive sensors**](https://www.sciencedirect.com/science/article/pii/S0144861722004775)

### **Carbohydrate Polymers**

(2022)

* Y. Jia et al.

### [**Rheological behaviors of Pickering emulsions stabilized by TEMPO-oxidized bacterial cellulose**](https://www.sciencedirect.com/science/article/pii/S0144861719303455)

### **Carbohydrate Polymers**

(2019)

* H. Jiang et al.

### [**Hydrophobic association hydrogels with excellent mechanical and self-healing properties**](https://www.sciencedirect.com/science/article/pii/S0014305718315416)

### **European Polymer Journal**

(2019)

* K. Jin et al.

### [**Synthetic biology-powered microbial co-culture strategy and application of bacterial cellulose-based composite materials**](https://www.sciencedirect.com/science/article/pii/S0144861722000753)

### **Carbohydrate Polymers**

(2022)

* S.-N. Li et al.

### [**Environmentally stable, mechanically flexible, self-adhesive, and electrically conductive Ti3C2TX MXene hydrogels for wide-temperature strain sensing**](https://www.sciencedirect.com/science/article/pii/S2211285521007552)

### **Nano Energy**

(2021)

* X. Ou et al.

### [**CO2-sourced anti-freezing hydrogel electrolyte for sustainable Zn-ion batteries**](https://www.sciencedirect.com/science/article/pii/S1385894722005575)

### **Chemical Engineering Journal**

(2022)

* F. Oveissi et al.

### [**Tough hydrogels for soft artificial muscles**](https://www.sciencedirect.com/science/article/pii/S0264127521001623)

### **Materials & Design**

(2021)