

## Preview

## Efficient electrochemical wastewater treatment on a customized three-phase interface

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The development of high-performance catalysts for organic wastewater treatment has proven itself to be a very challenging chemical problem. In this issue of *Chem Catalysis*, Zhang and co-workers report a Ru-MnO<sub>2</sub>-mTi anode material through a three-phase interface engineering strategy. The Ru-MnO<sub>2</sub>-mTi catalyst demonstrates exceptional efficiency for the electrochlorination degradation of dyes found in wastewater from the textile industry.

The rapid growth of industrialization, especially in less developed areas, has led to numerous environmental challenges, including water scarcity and contamination. These issues are largely due to the high demand for water by the manufacturing industry, particularly the textile industry.<sup>1</sup> This sector alone uses 10% of the world's industrial water supply, which equates to a staggering 93 billion cubic meters of water per year. Additionally, it is estimated that up to 20,000 chemicals are used globally for textile manufacturing, contributing significantly to the release of gaseous and solid wastes and wastewater pollution.<sup>2</sup> Textile dyeing and treatment are responsible for as much as 20% of industrial water pollution, and they not only damage the environment but also put human health at risk.<sup>3</sup> Therefore, to address the challenges posed by the textile industry's wastewater and to promote sustainable water resource management, public health protection, and environmental preservation, it is essential to develop effective methods for organic wastewater treatment.

Annually, the textile industry releases a significant amount of textile dyes into the environment through the discharge of industrial wastewater worldwide. The presence of these dyes in wastewater is a major challenge for wastewater

treatment. Various treatment methods, including physical (adsorption and membrane filtration), biological (enzymes and microorganisms), oxidation (advanced oxidation and chemical oxidation), and electrochemical methods,<sup>4–7</sup> are available for the removal of dyes from this mixture. Electrochemical wastewater treatment in particular offers several advantages. This method operates flexibly at ambient temperature, requires a small operational area, saves time, and provides robust and versatile performance for the degradation of typically uncooperative pollutants in complex textile wastewater. Additionally, electrochemical wastewater treatment can simultaneously perform the separation and degradation of dyes in wastewater, making it an effective and efficient method for the treatment of textile wastewater. Because of the advantages of the electrochemical wastewater treatment technique, extensive efforts are being developed for organic wastewater separation, remediation, and valorization.<sup>8</sup> However, several challenges still serve as impediments to the field of electrochemical wastewater treatment, including the conventional design of catalytic electrode materials and catalytic interfaces.

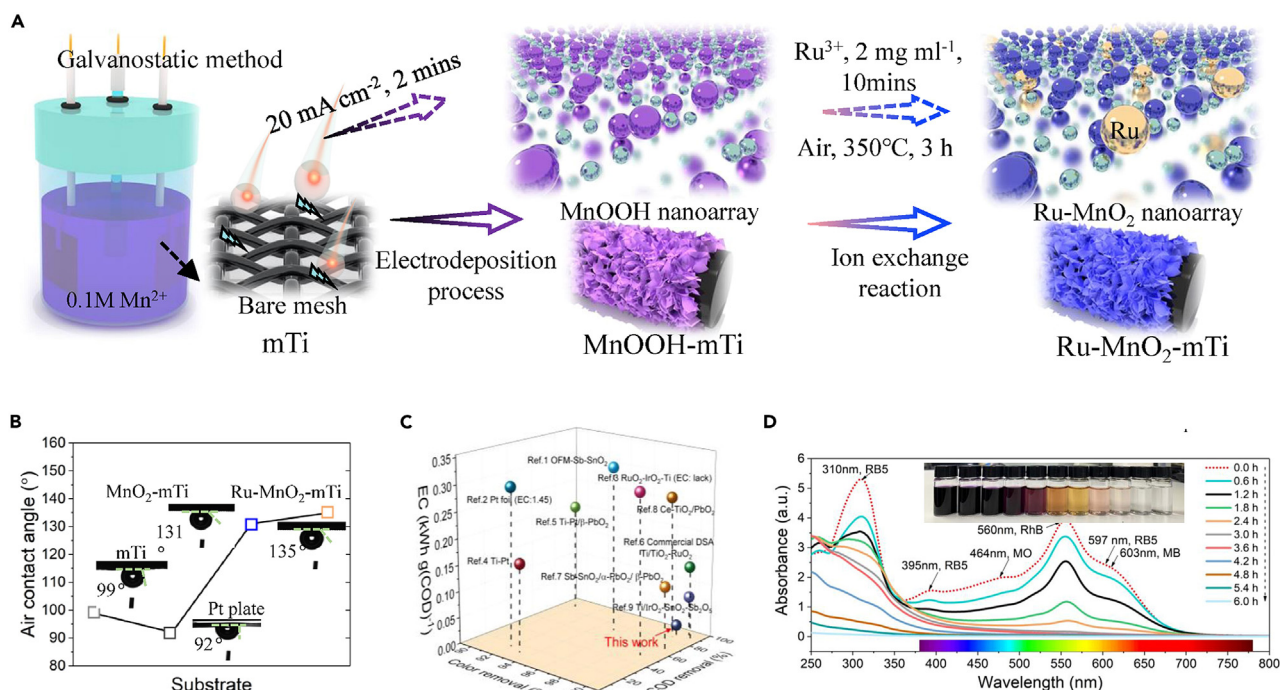
In this issue of *Chem Catalysis*, Zhang et al. report the development of an advanced three-phase interface nano-

pore-network-regulated Ru-MnO<sub>2</sub>-mTi catalyst, which demonstrates high efficiency in the electrochlorination degradation of dyes present in the organic wastewater from textile industries.<sup>9</sup> This work presents a cost-effective and simple strategy for producing a catalytic interface by using Ru-MnO<sub>2</sub> nanoarrays regulated with a nanopore-network structure. The fabrication process involves the electrodeposition of a MnOOH nanoarray precursor onto the bare surface of the Ti mesh anode, an ion-exchange reaction of Ru<sup>3+</sup> ions, and a crystal-phase transfer through mild annealing in the air (Figure 1A). The as-prepared Ru-MnO<sub>2</sub>-mTi anode maintains the original three-dimensional architecture of the vertically aligned MnOOH nanoarrays. This unique structure offers vertical-standing channels for rapid transportation of species during the electrochemical process. The atomic-scale Ru sites are well dispersed and anchored onto the surface of the MnO<sub>2</sub> nanoarray, allowing them to exhibit good mechanical stability between the catalyst and substrate, as well as maintain high catalytic activity during the electrochemical degradation process. Compared with conventional flat anode surfaces, such as Pt and mTi plates, which have high adhesion forces of 214 and 158 μN, respectively, the Ru-MnO<sub>2</sub>-mTi anode features a low adhesion force of only 49 μN. As a result of the microstructure of nanoarrays and this low adhesion force of the interface, the Ru-MnO<sub>2</sub>-mTi anode exhibits a superaerophobic characteristic with a bubble equilibrium contact angle of 135° (Figure 1B), which favors the detachment of produced chlorine bubbles.<sup>10</sup> The regulated release of chlorine bubbles further alleviates the blockage of the active sites,

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**Figure 1. Synthesis of Ru-MnO<sub>2</sub>-mTi and its applications in wastewater treatment**

(A) Schematic illustration of the synthetic process of the nanopore-network-regulated Ru-MnO<sub>2</sub>-mTi.

(B) Bubble equilibrium contact angle of anode substrates.

(C) Performance comparison with other reported anode materials.

(D) Dye removal of wastewater by the scale-up Ru-MnO<sub>2</sub>-mTi catalyst.

Adapted from Zhang et al.<sup>9</sup>

leading to improved electrocatalytic efficiency. Furthermore, the controllable generation and detachment of chlorine bubbles enhance the utilization of chlorine resources and prevent the hazards that can be associated with chlorine gas leakage.

Compared with commercial Pt plates, the Ru-MnO<sub>2</sub>-mTi anode displays not only superior chlorine evolution reaction (CER) activity but also good stability. The results demonstrate that the Ru-MnO<sub>2</sub>-mTi anode provides superior SER selectivity at almost 100%. Chronopotentiometry tests performed at a current density of 20 mA cm<sup>-2</sup> for 10 h revealed that the average voltage platform of the Ru-MnO<sub>2</sub>-mTi anode is significantly lower than that of the Pt plate and MnO<sub>2</sub>-mTi (1.741 versus 2.692 and 3.377 V, respectively). Additionally, the voltage platform of the Ru-MnO<sub>2</sub>-mTi anode remained nearly constant over

time and manifested the lowest overpotential losses, indicating its stable and efficient electrocatalytic performance during wastewater treatment. Meanwhile, the results of treatment tests with real wastewater samples show that the Ru-MnO<sub>2</sub>-mTi anode is highly effective at breaking down chromophores in that it achieved nearly 100% color removal in just 4 h. The kinetic rate constant of chromophore breaking was higher for the Ru-MnO<sub>2</sub>-mTi anode than for both the Pt plate and MnO<sub>2</sub>-mTi. Also, the usage of Ru-MnO<sub>2</sub>-mTi resulted in an impressive chemical oxygen demand (COD) removal rate of approximately 90.0% after 11 h of electrolysis, and when achieving an 80% COD removal rate, the Ru-MnO<sub>2</sub>-mTi anode consumed only 12.237 kWh m<sup>-3</sup> of electricity, which was approximately half of the energy consumed by the commercial Pt plate (24.087 kWh m<sup>-3</sup>). Compared with other reported works, the developed three-

phase catalytic interfaces in the nanopore-network-regulated catalyst demonstrate desirable performance in terms of color removal, COD removal, and energy consumption for the treatment of real wastewater (Figure 1C). To evaluate the viability of using the proposed Ru-MnO<sub>2</sub>-mTi anode in large-scale industrial applications, Zhang et al. developed a prototype with a scale-up 100 L wastewater treatment capacity to bridge the gap between laboratory findings and real-world implementation. After 14 h of electrochlorination treatment on simulated wastewater, the optimized design of the scale-up prototype modules achieved an impressive color removal rate of nearly 100% within 6 h (Figure 1D) and a COD removal rate of approximately 90.7%. More impressive, however, was the cost assessment of the Ru-MnO<sub>2</sub>-mTi anode, which was determined to be approximately \$157.1 m<sup>-2</sup>, which is equivalent to just

~5.1% of the cost of a conventional boron-doped diamond (BDD) anode.

This work has developed an advanced three-phase interface engineering strategy for the synthesis of Ru-MnO<sub>2</sub>-mTi anode materials with intrinsic surface activities, a mesoscale commuting network, and a superaerophobic feature. This nanopore-network-regulated catalyst demonstrates a high level of electrochlorination degradation efficiency toward the treatment of real textile wastewater. The implementation of such a customized interface engineering strategy is anticipated to offer novel possibilities for the precise and controllable manufacturing of various catalysts in the future.

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### DECLARATION OF INTERESTS

The authors declare no competing interests.

### REFERENCES

1. Yaseen, D.A., and Scholz, M. (2019). Textile dye wastewater characteristics and constituents of synthetic effluents: a critical review. *Int. J. Environ. Sci. Technol.* *16*, 1193–1226.
2. United Nations. (2017). Wastewater: An untapped resource. UN World Water Development Report 2017. <https://www.unwater.org/publications/un-world-water-development-report-2017>.
3. Niinimäki, K., Peters, G., Dahlbo, H., Perry, P., Rissanen, T., and Gwilt, A. (2020). The environmental price of fast fashion. *Nat. Rev. Earth Environ.* *1*, 189–200.
4. Yang, Q., Wang, B., Chen, Y., Xie, Y., and Li, J. (2019). An anionic In(III)-based metal-organic framework with Lewis basic sites for the selective adsorption and separation of organic cationic dyes. *Chin. Chem. Lett.* *30*, 234–238.
5. Song, Y., Phipps, J., Zhu, C., and Ma, S. (2023). Porous materials for water purification. *Angew. Chem. Int. Ed.* *62*, e202216724.
6. Liu, P., Huang, Z., He, X., Hou, J., Zheng, W., Liu, C., Li, L., and Tang, Z. (2022). Conjugated microporous polymer Janus membrane for dye rejection from water. *J. Membr. Sci.* *644*, 120096.
7. Holkar, C.R., Jadhav, A.J., Pinjari, D.V., Mahamuni, N.M., and Pandit, A.B. (2016). A critical review on textile wastewater treatments: possible approaches. *J. Environ. Manage.* *182*, 351–366.
8. Choi, C., Wang, X., Kwon, S., Hart, J.L., Rooney, C.L., Harmon, N.J., Sam, Q.P., Cha, J.J., Goddard, W.A., Elimelech, M., and Wang, H. (2023). Efficient electrocatalytic valorization of chlorinated organic water pollutant to ethylene. *Nat. Nanotechnol.* *18*, 160–167.
9. Zhang, X., Valencia, A., Deng, Z., Shi, J., Ao, K., and Daoud, W.A. (2023). Three-phase interface engineering enables both activation and transport of electrochlorination for textile organic wastewater degradation. *Chem Catal.* *3*, 100612. <https://doi.org/10.1016/j.cheecat.2023.100612>.
10. Jiang, M., Wang, H., Li, Y., Zhang, H., Zhang, G., Lu, Z., Sun, X., and Jiang, L. (2017). Superaerophobic RuO<sub>2</sub>-based nanostructured electrode for high-performance chlorine evolution reaction. *Small* *13*, 1602240–1602247.