Abstract

Hydrogen energy has emerged as a promising clean energy source for achieving global carbon neutrality. However, metal hydrogen embrittlement and leakage pose severe safety risks in hydrogen storage and transportation. This highlights the urgent need for real-time monitoring of metal pipelines for hydrogen transportation, as well as high-performance hydrogen barrier coatings to minimize embrittlement in metal pipelines. Rational design of polymer composites under multi-scale considerations, reinforced with 2D nanostructures like graphene oxide (GO) and MXene, offers a compelling pathway to develop such composite materials as both sensing materials and coatings owing to their tunable structures and multifunctional properties.

This dissertation, after a thorough review of the relevant literature and theoretical background of hydrogen embrittlement monitoring in pipelines and hydrogen barrier coatings (Chapter 1), systematically explores both internal and external monitoring of hydrogen pipelines, as well as the scalable production of 2D MXene materials and their integration with polymers for advanced hydrogen barrier systems, covering four key aspects:

In **Chapter 2**, through rational microstructural design and multiscale modulation, a conductive antifreeze organohydrogel (PGOPPy) was developed using a DMSO/water solvent system with a tunable freezing point and wettability. Designed for flexible electronics under extreme conditions, this hydrogel also shows great potential for monitoring external geometric deformation of hydrogen pipelines at low temperatures down to cryogenic temperatures (–75 °C). The PGOPPy organohydrogel was constructed from carboxyl-modified polyvinyl alcohol (PVA) as the gel matrix and graphene oxide (GO)-assembled polypyrrole (PPy) nanowires as functional reinforcements, it demonstrated reliable conductivity and mechanical adaptability. Beyond its application in low-temperature sensing, this study also provides fundamental insights into how microstructural design principles and multiscale regulation of 2D materials within polymer matrices can be extended to the development of hydrogen barrier films.

In **Chapter 3**, inspired by the DMSO/water system employed in Chapter 2, a novel Temperature-Induced DElamination (TIDE) method was developed using an

ethanol/water solvent system to achieve scalable preparation of large-sized, defect-free $Ti_3C_2T_x$ MXene nanosheets. By exploiting the reversible volumetric changes of low-freezing-point solvent mixtures, this method enabled efficient intercalation and uniform delamination of multilayer MXene. After five TIDE cycles with the ethanol/water mixture, the interlayer spacing expanded to 6.6 Å, approaching the theoretical value of 7.2 Å, thereby producing large (>10 μm), highly conductive (~6000 S/cm), defect-free monolayers and few-layer nanosheets with a high yield (61 wt%).

In **Chapter 4**, the obtained large-sized, defect-free $Ti_3C_2T_x$ nanosheets were used as fillers with highly amorphous polyvinyl alcohol (HAVOH)/polyacrylic acid (PAA) matrix to realize structurally hydrogen barrier films. At the optimal composition, consisting of 50 wt% HAVOH, 50 wt% PAA, and 3 wt% MXene relative to the total polymer weight ($H_{50}P_{50}MX_3$), the film exhibited a hydrogen transmission rate (H_2TR) below the detection limit of the instrument (< 0.3 $cm^3/(m^2 \cdot 24\ h)$) under both 41 °C/0% relative humidity (RH) and 41 °C/41% RH, representing a substantial improvement over pristine HAVOH (3.6 $cm^3/(m^2 \cdot 24\ h)$).

In **Chapter 5**, the effects of four crosslinking agents – BORAX (B), glutaraldehyde (GA), citric acid (CA), and 1,2,3,4-butanetetracarboxylic acid (BTCA) – on the structure and hydrogen barrier performance of HAVOH/MXene films were systematically investigated. Notably, the $H_{100}BT_{30}MX_3$ film (with BTCA accounting for 30% of HAVOH weight and MXene comprising 3 wt% of the total HAVOH/BTCA weight) exhibited an ultralow H_2TR of 2.0 $cm^3/(m^2 \cdot 24\ h)$ at 50 °C and 50% RH, while maintaining a swelling ratio below 10%, a gel fraction of 99%, and a water absorption as low as 21%, collectively indicating outstanding dimensional stability under harsh conditions. Additionally, the laser-processed HAVOH/BTCA/MXene films showed a linear relationship between electrical resistance and pressure, making them effective sensors for real-time monitoring of internal hydrogen leaks in pipelines.

In summary, this dissertation establishes an integrated framework, spanning from antifreeze conductive hydrogels for cryogenic monitoring of external pipeline deformation to scalable production of defect-free MXene nanosheets and water-resistant hydrogen barrier composites with built-in leakage-sensing functionality. These advances not only refine microstructural design strategies for functional materials but also provide practical solutions for health monitoring of hydrogen pipelines and preventing hydrogen leakage, thereby offering both theoretical foundations and technological support for real-time hydrogen safety management across storage, transportation, and intelligent pipeline operation.