

ANSO Highlight is to share the new ideas, methodologies, datasets and technologies of sustainability research by summarizing the latest progress and achievements of scientific projects funded by ANSO and ANSO partners. Through this publication, we would like to stimulate active collaboration and communication among ANSO members and partners.

International Collaborative Research Project ANSO-CAS Joint Project

Research into Valorizing Atmospheric Carbon Dioxide via Its Sustainable Capture

PI Affiliation:

Royal Scientific Society of Jordan

Collaborating Organizations:

Mohammed VI Polytechnic University, Morocco;

Istanbul Technical University, Turkey;

ShanghaiTech University, China.

Summary

Our research activities focused on the synthesis of porous materials with a high affinity for CO₂, particularly at very low pressure to enable carbon capture from the gas stream that mimics air concentration. Our initial search was focusing on the synthesis of polymeric and metal-organic framework (MOF) materials. However, our selection settled on porous polymers for many aspects such as ease of fabrication, low cost of production, scalability, and reasonable stability, because polymers normally can withstand humidity and acidic gases. Different polymers were synthesized and examined for surface area and CO₂ uptake. Brunauer-Emmett-Teller (BET) surface area analysis measurement showed moderate surface areas of the synthesized polymers in the range of 106 to 420 m²·g⁻¹ with types I and IV adsorption isotherms that prove material microporosity or mesoporosity of the resulting polymers. The synthesized microporous Polymer (MPP) showed significant performance for CO₂ affinity represented by the relatively sharp CO₂ uptake at low pressure (< 100 torr) compared to other reported and synthesized MPPs.

Period: January 2021-December 2023

PI: Bassem Al-Maythality

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Cost-effective Preparation and Industrialization of Thermal Shielding Coatings for Tropical Industrial Factories

PI Affiliation:

Shanghai Institute of Ceramics, Chinese Academy of Sciences

Collaborating Organizations:

Philippine Economic Zone Authority (PEZA)

Hotta Palad Marble Corporation

Haotu Research and Development on Engineering

ShanghaiTech University, China.

Summary

Research background: Recognizing that environment and resources are the focus of China's foreign cooperation, this project is based on the advantages of new material technology of the Chinese Academy of Sciences and it is the foundation of cooperation with the Philippines, Thailand and other Southeast Asian "Belt and Road" countries. Tailings from the processing of rich coral reef and marble mineral resources from the Philippines and other countries are used to create energy-saving heat shielding coatings for buildings, tailored for the climate and economic conditions of Southeast Asian countries. The product will fill a gap in the Philippine market, and will be of interest to ANSO members.

Period: January 2021-December 2023

PI: CAO Xun

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Research into Valorizing Atmospheric Carbon Dioxide via Its Sustainable Capture

Objectives

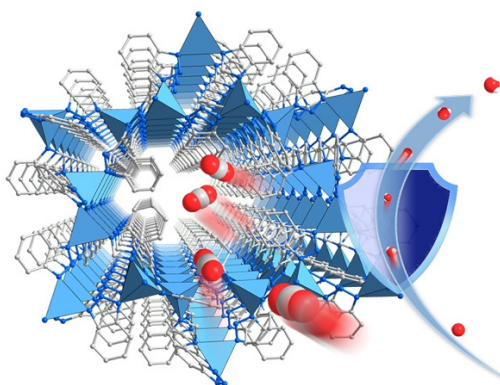
The development of advanced 'artificial trees' in the form of compact, energy-efficient carbon capture devices could have an immediate positive impact on decreasing carbon dioxide levels in the atmosphere and on purifying captured carbon dioxide for use as a high-quality product for different commercial applications.

Research Contents

This project brings together researchers with unique expertise and experience from China, Turkey, Jordan, and Morocco to discover new solid adsorbents that can effectively act as 'artificial trees' by capturing carbon dioxide directly from air. These adsorbents are then re-shaped into different forms – from membranes to fixed beds – and integrated within a cost-efficient prototype device that is capable of capturing waste carbon dioxide directly from air for use in small-scale commercial applications.

Main Progress and Highlights

The research consortium has invented and synthesized a series of porous polymers, metal-organic frameworks (MOFs), and zeolitic imidazolate frameworks (ZIFs), characterized their structures on the atomic level through advanced techniques, and proven their ability to selectively capture carbon dioxide in the presence of other contaminant gases.



A newly invented zeolitic imidazolate framework, termed ZIF-1001, that was demonstrated to successfully capture carbon dioxide from complex gas mixtures. A series of compounds with similar carbon-dioxide capturing properties will be reported in a high-impact, international journal in 2022.

The consortium has held one international workshop and training meeting at Istanbul Technical University in Istanbul, Turkey in September 2021 to strategically assess progress, carry out detailed data analysis, and promote communication, cooperation, and further collaboration in advancing the research program among the country partners.



Pictured left to right: Dr Bassem Al-Maythality (Royal Scientific Society, Jordan), Kyle E. Cordova ((Royal Scientific Society, Jordan), Dr Youssef Belmabkhout (University of Mohammad VI Polytechnic, Morocco), Dr Gamze Gur (Istanbul Technical University, Turkey), Dr Karim Adil (Le Mans University, France), and Dr Mert Gur (Istanbul Technical University, Turkey) at the first ANSO-sponsored international workshop and training meeting at Istanbul Technical University in Istanbul, Turkey in September 2021



Dr. Gamze Gur (Istanbul Technical University, Turkey) and her graduate students are demonstrating their research group's gas-phase, heterogeneous catalytic reactor for use during the second and third phase of the consortium's work on carbon dioxide utilization.

Future Plan

In 2022, the consortium focused on synthesizing porous materials for efficient carbon capture at low pressures. We successfully created new Zeolitic Imidazolate Frameworks (ZIFs), namely ZIF-1001 to ZIF-1004, and published their CO₂ uptake results in *Angewandte Chemie*. Additionally, we developed porous polymers with favorable characteristics like cost-effectiveness, scalability, and stability under humid conditions. Our progress involved synthesizing polymers at a larger scale and conducting analyses on their thermodynamic properties, pore size distribution, BET surface area, and dynamic capacity using a breakthrough device we built in-house. These advancements contribute to our ongoing search for effective carbon capture materials.

Publication and Intellectual Property

The results of the consortium's research work have led to three research articles published in high-impact, international journals:

1. Robust Barium Phosphonate Metal-Organic Frameworks Synthesized under Aqueous Conditions, *ACS Materials Letters*, 2021, 3, 1010-1015.
2. Control over Interpenetration for Boosting Methane Storage Capacity in Metal-Organic Frameworks, *Journal of Materials Chemistry A*, 2021, 9, 24857-24862.
3. Cross-linked, Porous Imidazolium-based Polys (Ionic Liquid) for CO₂ Capture and Utilisation, *New Journal of Chemistry*, 2021, 45, 16452-16460.
4. Zeolite NPO-Type Azolate Frameworks. *Angewandte Chemie* 2022, DOI: 10.1002/ange.202207467.
5. The Chemistry of Metal-Organic Frameworks with Face-Centered Cubic Topology, *Coordination Chemistry Reviews*, 2022, 468, 214644.
6. Back Cover: Zeolite NPO-Type Azolate Frameworks (*Angew. Chem. Int. Ed.* 39/2022)
7. Flexible Metal-Organic Frameworks as CO₂ Adsorbents en Route to Energy-Efficient Carbon Capture. *Small Structures*, 2022, 5, 2100209.
8. Covalent functionalization of ZIF-90 for improving mixed matrix membranes performance in CO₂ separation, 2022, SSRN 4136344.
9. Environmentally Adaptive MOF-based Device Enables Continuous Self-Optimizing Atmospheric Water Harvesting, *Nature Communications*, 2022, 13, 4873.
10. Functionality-Induced Locking of Zeolitic Imidazolate Frameworks, *Chemistry of Materials*, 2023, DOI: 10.1021/acs.chemmater.2c02832.

One patent application has been submitted in China for the invention of zeolite NPO-type azolate frameworks and a second international patent application will be submitted once the Chinese patent is granted. The inventors include researchers from ShanghaiTech University, China and Royal Scientific Society, Jordan.



Carbon dioxide capture

CO₂

CO₂



Principal Investigator

Bassem Al-Maythality, Professor

Prof. Bassem received his Ph.D. in Chemistry in 2010 from King Fahd University of Petroleum and Minerals (KFUPM), Saudi Arabia, in the field of organometallic synthesis. After graduation, he moved on to work at King Abdullah University of Science and Technology (KAUST) as a Postdoctoral Fellow at the Center for Advanced Membranes and Porous Materials. During his post-doctoral period, he was actively involved in research projects in the field of Metal-Organic Frameworks (MOFs) development and MOF-based membranes. In 2014, Bassem joined King Fahd University of Petroleum and Minerals again as a Research Scientist under the Center for Technological Innovation - Carbon on Capture and Segregation (KACST-TIC-CCS). At King Fahd University of Petroleum and Minerals, Bassem focused on the synthesis of new materials, and on the exploration of different materials for practical applications. During his career at KFUPM, he got several funded projects in the fields of MOFs, membranes, and porous polymers. Bassem's scientific research output has exceeded 34 publications spread across journal papers, article reviews, patents, conference proceedings, and one book chapter in the field of inorganic, kinetic, and membrane chemistry. His research activities are appreciated by reputable publishers Nature, American Chemical Society (ACS), Elsevier, Wiley, and Royal Society of Chemistry (RSC). In December 2019, Bassem joined the Royal Scientific Society (RSS) in the research and development sector where he established the Advanced Research Center and led the Materials Discovery Unit concerned with the synthesis of new materials for practical applications.

CO₂

Cost-effective Preparation and Industrialization of Thermal Shielding Coatings for Tropical Industrial Factories

Objectives

To fulfill specific requirements, several high-performance heat shield coatings were developed, and promoted in the Philippines and Thailand. An aim is to extend the product across tropical countries in the entire “Belt and Road” region, and so to promote energy-saving transformations in industrial processing

Research Contents

Research methods: Utilizing the properties of coral reef/marble tailings in the Philippines, this project prepares high-performance heat shielding coatings through research methods such as composition analysis, formulation design and surface modification.

Technical route: Utilize the abundant local resources of ore tailings in the Philippines, through broad-spectrum heat shielding formula design, solid particle size control, surface modification and dispersion, as well as coating processing, rust construction, anti-corrosion services and other technological breakthroughs, more than two types of high-performance heat shielding coatings have been developed.

Cooperation mechanism: Prepare roof heat shielding coatings for industrial buildings, and promote sales after completing field experiments in the Philippines and Thailand to fill a gap in the local market.



performance for
heat shield coa
heat shield

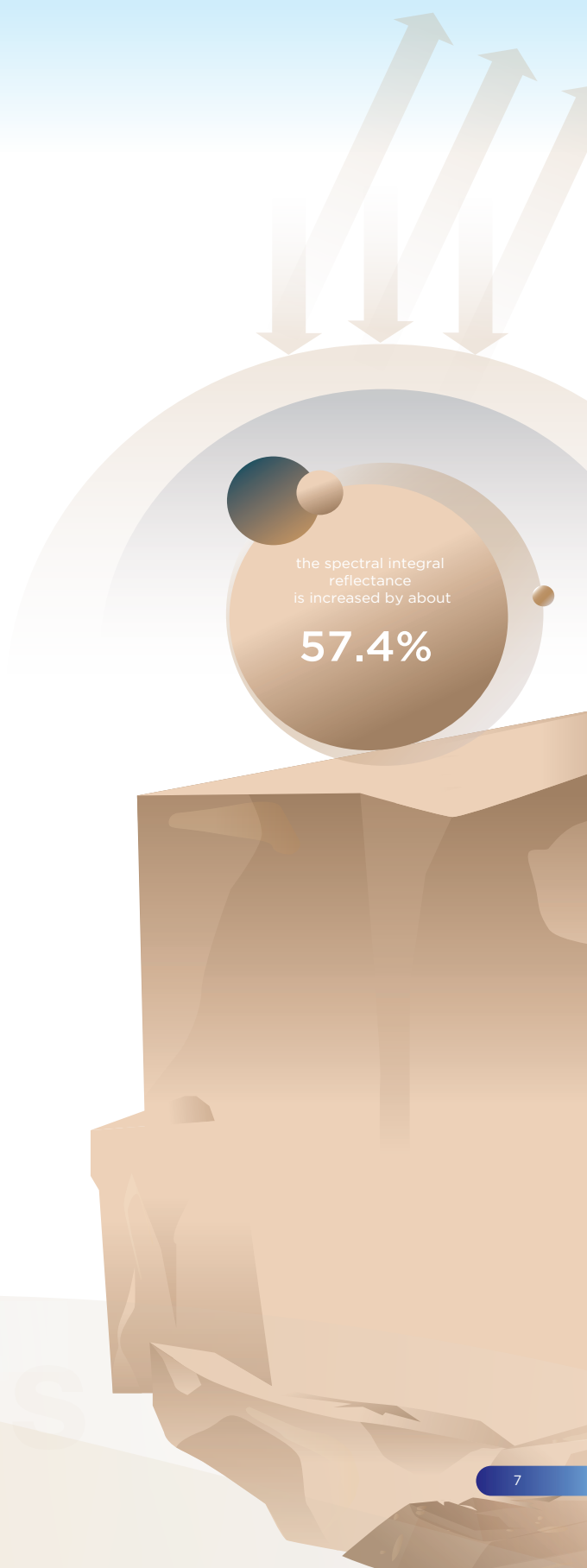
Main Progress and Highlights

Characterization of performance

The coating products have been tested by a third-party authoritative organization (as shown in Figure 1), which proves that they have excellent performance. The coated sample has good sunlight reflection ability, and the spectral integral reflectance is increased by about 57.4% compared with the blank substrate. In order to expand ANSO's local influence, it is planned to design and print the logo and product model number (as shown in Figure 2) with "ANSO" and "SICCAS" on the delivered products (primer + topcoat), so as to improve the quality of the products. It is good to carry out promotion and publicity under the guidance of ANSO.

Domestic pilot test

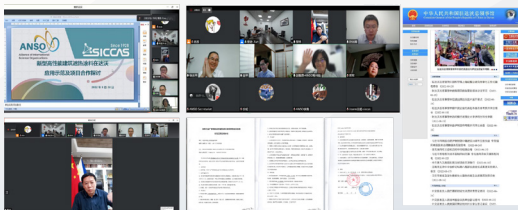
At present a cooperation agreement has been reached with a partner, Guohua Construction Co., Ltd. The partner can provide 5000 m² of color steel plates. This project has completed the preparation of coatings for a 5000 m² domestic industrial plant, including primer and topcoat, a total of 3 tons of new heat shielding coatings (Figure 4).



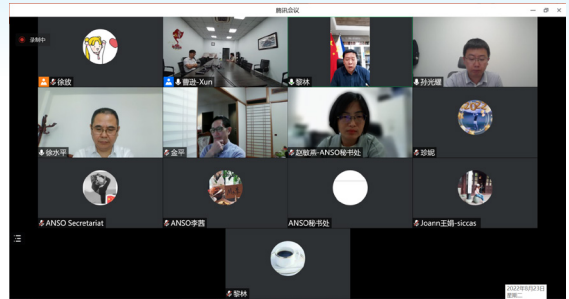
Performance
Coatings
Coatings

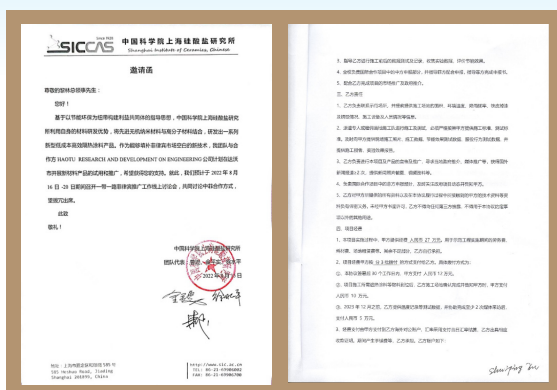
Foreign demonstration sites

The demonstration project will be established in Davao, Philippines, and an agreement will be signed with HAOTU RESEARCH AND DEVELOPMENT ON ENGINEERING on cooperation in the establishment of the demonstration project. The Consulate General of the China in Davao City and schools within the jurisdiction of Davao City will be taken as demonstration sites, and priority will be given to energy-saving transformation. Figure 7 shows a video conference with the Consulate General of the China in Davao, Philippines, to demonstrate the application of high-performance building thermal control technology. The conference invited Li Lin, Consul General of the People's Republic of China in Davao, Zhao Minyan, ANSO Project Management Office, and Philippine cooperation companies. The conference carried out news publicity on the homepage of the official website of the Consulate General in Davao. The design and implementation of the demonstration project will help solve practical problems such as overheating of local buildings, and play a good role in promoting the construction of the "the Belt and Road" between China and the Philippines.



Exploring the Application Demonstration of High Performance Building Thermal Control Technology with the Philippine Consulate in Davao





Highlight

- This project develops a series of high-performance heat shielding coatings according to the actual situation of the place of use. The products and technologies are mainly promoted in the Philippines and Thailand.
- Complete the establishment of a 2200m² foreign demonstration site, and carry out energy-saving renovations for industrial plants, producing a total of 2.34 tons of transport coating products.
- Complete the coating preparation and transportation of the 5000 m² domestic industrial plant, send the products to the Philippines through international logistics, and conduct local construction and field verification.

Future Plan

- In the next step, field tests will be conducted at the construction sites of domestic and foreign demonstration sites, and the heat shielding effect of the coating products will be verified.
- It is planned to use its existing 1,000-square-meter factory building through local investment in the Philippines to build a production base according to the formula of the project technology.
- Meet the needs of related companies in South Asia and Southeast Asia like those in the Philippines and Thailand, and conduct sales to achieve the planned goal of promoting the use of high-performance heat shielding coatings in Southeast Asia.

Publication and Intellectual Property

Published 2 papers in ACS Appl. Mater. Interfaces (zone 1, IF=10.383) and Chemical Engineering Journal (zone 1, IF=16.744), and ANSO marked the first place in the paper.

- Z. Li, S. Zhao, Z. Shao, H. Jia, A. Huang, P. Jin, X. Cao,* Deterioration mechanism of vanadium dioxide smart coatings during natural aging: Uncovering the role of water, Chemical Engineering Journal, 447 (2022) 137556. DOI: 10.1016/j.cej.2022.137556
- C. Cao, H. Bin, G. Tu, X. Ji, Z. Li, F. Xu, T. Chang, P. Jin, X. Cao,* Sputtering Flexible VO₂ Films for Effective Thermal Modulation, ACS Applied Materials & Interfaces, 14(24) (2022) 28105-28113. DOI:10.1021/acsami.2c05482

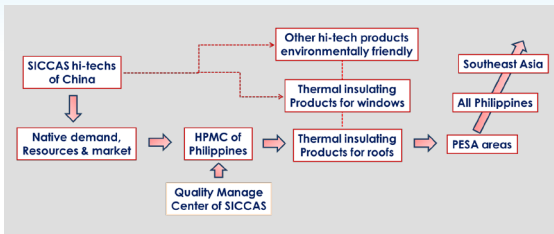


Principal Investigator

CAO Xun, Professor

Prof. CAO Xun obtained his Ph.D. from Shanghai Institute of Ceramics, Chinese Academy of Sciences (SICCAS), China, in 2010. He joined University of California, Berkeley in 2015 as a visiting research fellow. In 2016, he returned SICCAS working as a full professor and Deputy Director of Ancient Ceramics Research Center, as well as Head of Research Group of Smart Materials for Energy Modulation. His research interests include processing and characterization of functional oxides films, chromogenic materials and advanced coatings for the applications of energy-efficient project. Prof. Cao has published over 100 papers (containing Nature Electronics, Nature Communications etc.), 4 book chapters, and made more than 30 patents. He has presided over 15 national, provincial and ministerial projects, including National Key Research & Development Program and National Natural Science Foundation of China et. al. In 2022, he was awarded as National High-Level Young Talents and Excellent Member of the Youth Promotion Association of the Chinese Academy of Sciences. In 2023, he was elected as Fellow of the Royal Society of Chemistry (FRSC).





Future development plan



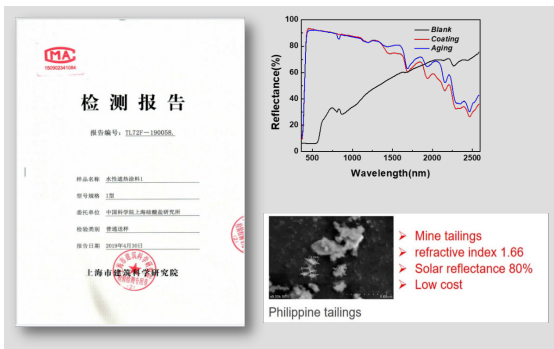
Photos of 2200 m² color steel plate and coating products in the Philippines



Coating product transportation route



Photos of 5000 m² factory, coating products and on-site construction



Third-party inspection report and performance test



The physical picture, logo and model of the new heat shielding coating product



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Deterioration mechanism of vanadium dioxide smart coatings during natural aging: Uncovering the role of water

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ABSTRACT

Vanadium dioxide (VO₂) has already been widely concerned as a thermochromic smart window material. However, the full-life test of VO₂ is rare owing to degradation by water and oxygen in the air, which has limited its commercialization. Until now, it was remained unclear what effect water has on the deterioration of VO₂ hindering the selection of this ceramic. In this work, the degradation mechanism of VO₂ during natural aging was proposed based on density functional theory (DFT) calculation and experimental analysis, and the role of water in the degradation process was discussed in detail. The results showed that water affects the deterioration reaction by influencing the adsorption behavior of oxygen on the VO₂ surface, destroying the dense structure, and participating in the reaction in the form of combined water. This work fills the degradation mechanism gap of VO₂, helps to design high performance structures of VO₂-based smart coatings, and provides theoretical guidance to solve the problem of VO₂ sustainability.

1. Introduction

Buildings consume nearly 40% of the global energy consumption and account for one-third of global greenhouse gas emissions, which is contrary to the goal of global carbon neutrality [1–3]. Achieving energy efficiency in buildings while improving the comfort of the living condition has become the aim of researchers in recent years [4–6]. Thermochromic materials are considered reliable solutions because of their simple structure, zero-energy consumption, and passive light modulation [7–9]. When applied to walls, roofs, and windows, thermochromic coatings can offer tremendous opportunities for energy savings in buildings [10,11]. Vanadium dioxide (VO₂), as an archetypal phase-transition material, has a pronounced metal-insulator transition (MIT) behavior at the critical transition temperature ($T_c \approx 68^\circ\text{C}$) [12], and it is considered one of the most promising candidates for thermochromic coating materials [13–15].

VO₂ coatings have been intensively studied for over 30 years, the problems of insufficient thermochromic performance (the luminous

transmittance (T_{vis}) and solar modulation ability (ΔT_{sol}), the high critical temperature (T_c), and unacceptable inherent color of VO₂ coatings have been addressed in varying degrees [16–20]. However, its commercialization in the construction sector remains a challenge because VO₂ has poor durability and transforms into more stable vanadium oxide phases or its hydroxides in the air [21–23]. Current research has focused only on solving the problem, with almost no detailed study of the degradation mechanism. VO₂-based smart coatings are usually fabricated by hydrothermal, sol-gel, chemical vapor deposition (CVD), and physical vapor deposition (PVD) methods [24–26]. Based on the above preparation methods, VO₂ is present in the form of nanoparticles or thin films in the smart coating. Up to now, the main approach to the durability enhancement of VO₂ nanoparticles is to coat the outer layer with a “shell” forming core-shell structures, for example, SiO₂, ZnO, and MgO [27–30]. The “shell” material is chemically stable and protects VO₂ from moisture and oxygen. For thin films prepared using the deposition technologies, the preparation of a protective layer on the top surface of VO₂ is considered an effective way to improve their

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Research Article

Spattering Flexible VO₂ Films for Effective Thermal Modulation

Cuicui Cao, Bin Hu, Guoli Tu, Xiaowei Ji, Zhongshao Li, Fang Xu, Tianci Chang, Ping Jin, and Xun Cao^{*}

☆ <https://doi.org/10.1016/j.apl.2023.050482>

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Supporting Information

ABSTRACT: Flexible vanadium dioxide (VO₂) thermochromic films show great potential for large-scale fabrication and possess broader applications compared with VO₂ coatings on rigid substrates. However, the fabrication of flexible VO₂ films remains a challenge so far, leading to the scarcity of research on flexible VO₂ films for smart windows. With the aim to obtain a flexible VO₂-based film with excellent optical properties and a long service life, we designed and successfully fabricated a flexible ITO/VO₂/ITO (IVI) film on the colorless transparent polyimide substrate, which could be directly attached to glasses for indoor temperature modulation. This flexible IVI film effectively enhances the luminous transmittance (T_{vis}) and solar modulation ability (ΔT_{sol}) (15 and 68% increase relative to a VO₂ single layer), reduces the thermal emissivity (ϵ_p) (50.7% decrease relative to a VO₂ single layer), and exhibits better durability than previously reported structures. Such excellent comprehensive performance offers it great potential in practical applications on smart windows. This work is supposed to provide a new strategy for facile direct fabrication of flexible VO₂ films and broaden the applications of flexible VO₂ in more coatings and devices.

KEYWORDS: vanadium dioxide; flexible; colorless polyimide; smart window; durability

1. INTRODUCTION

The issue of building energy consumption has received rapidly growing attention over the past few decades as there is almost 30–40% of primary energy consumption in buildings. Heat losses from windows account for 50% of the overall building energy consumption. Therefore, thermal management of windows is one of the key ways to reducing building energy consumption. Utilization of chromogenic materials on building fenestration is considered an effective way to save energy, among which thermochromic materials are widely used due to their intelligent temperature response and zero power input. Vanadium dioxide (VO₂), as a typical thermochromic material, undergoes a metal-insulator transition (MIT) at the critical temperature T_c of $\sim 68^\circ\text{C}$. Through the MIT process, VO₂ shows reversible and dramatic optical property changes, especially the transmittance at the near-infrared region (NIR), which has facilitated its promising energy-efficient applications in smart windows.

However, the VO₂-based thermochromic smart window still faces challenges for practical applications. First, there exists a trade-off between luminous transmittance (T_{vis} , 380–780 nm) and solar modulation ability (ΔT_{sol} , 380–2500 nm), which makes it difficult to improve T_{vis} and ΔT_{sol} simultaneously. Second, the VO₂ film generally exhibits thermal emissivity (ϵ_p , 2.5–15 μm) as high as 0.83, which means that there is a strong heat exchange between the window surface and the

surrounding environment, thereby weakening the thermal insulation properties of the windows. Third, fabrication of high-quality flexible VO₂ films remains a challenge due to the high sputtering temperature. However, flexible VO₂ films are needed in many circumstances because they can be produced in large scale and cut into required shapes and size. Last, VO₂ suffered durability issues because it is unstable in humid conditions and will gradually be oxidized into the most thermodynamically stable phase of vanadium pentoxide (V₂O₅), losing its thermochromic properties.

Recently, researchers have developed numerous strategies to solve these problems. Fabricating multilayer films,^[1–11] microstructures,^[12–15] and nanocomposites^[16–21] can effectively enhance the T_{vis} and ΔT_{sol} simultaneously. To reduce ϵ_p , transparent conductive oxides such as F-doped SnO₂ (FTO) and indium tin oxide (ITO) have been introduced into VO₂-based multilayer films.^[22–26] Regarding to the fabrication of flexible VO₂ films, a commonly used method is dispersing VO₂

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Project article results

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