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Advanced nanomaterials for energy conversion and storage: current status and future opportunities

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Energy science has witnessed a surge of interest over the past 10 years, mostly motivated by progress in nanoscience and nanotechnology. For the sustainable development of human beings, extensive research has been dedicated to renewable energy, and its conversion and storage, owing to the increasing concerns about global climate change and the growing demand for energy. In April 2021, the CO₂ concentration was measured at 418.46 ppm, and compared to April 2020 (415.59 ppm) even through coronavirus times the increase is massive. As a result, searching for promising new options is crucial to align human development with the United Nation's Sustainable Development Goals.

In particular, downsizing functional materials to the nanoscale can manifest intriguing properties and performances compared to their bulk structures.

Fabricating nanostructured materials with tailored properties is at the forefront of technological exploration.¹ At present, novel strategies such as size/facet control, structural engineering, vacancy engineering, atomic regulation, and construction of nanocomposites alter the physicochemical properties (e.g. electronic, optical, band and textural) of the active sites.^{2,3} Hence, this gives rise to a momentous improvement in the performance of nanomaterials toward energy conversion and storage. Research in this energy realm necessitates an interdisciplinary approach with synergistic collaboration from all disciplines such as chemistry, engineering, nanotechnology, computation, as well as industrial thinking to accomplish high-performance energy systems.

The themed collection of *Nanoscale* entitled “advanced nanomaterials for energy conversion and storage” aims to showcase the state-of-the-art knowledge on the development of nanomaterials with tunable properties for diverse energy applications. This themed collection consists of 23 Full Papers, 4 Communications and 5 Reviews, focusing on designing advanced materials and building a structure–activity–stability relationship in electrocatalysis, photocatalysis, photoelectrocatalysis, batteries, fuel cells and so forth.

Xiong *et al.* (DOI: 10.1039/D0NR02596H) highlight the development of engineering active sites on surfaces and in open frameworks with respect to surface vacancies, doped heteroatoms, loaded metal nano-

particles, crystal facets and metal nodes/organic linkers in metal–organic frameworks for application in photocatalytic CO₂ reduction. In addition to the advances in CO₂ photoreduction, Zhang *et al.* (DOI: 10.1039/D0NR03178J) have reviewed the use of carbon-based nanomaterials and their hybrids for photo- and electrocatalytic hydrogen peroxide (H₂O₂) production *via* both reductive and oxidative reaction pathways. Apart from photochemistry, inspired by the merits of 2D nanostructures, Tsang’s group (DOI: 10.1039/D0NR01295E) present a minireview on the recent discoveries in hetero-single atom-doped MoS₂ nanosheets for electrochemical hydrogen evolution reaction (HER) from water by reviewing the nature of the dopants, doping positions and the polytypes of MoS₂. In view of the importance of morphological engineering in energy applications, Wang *et al.* (DOI: 10.1039/D0NR03425H) focus on the primary issues facing one-dimensional (1D) electrospun carbon nanofibers in supercapacitors with the aim of ameliorating the conductivity, modulating pore configuration, doping with heteroatoms and increasing mechanical strength. Sun *et al.* (DOI: 10.1039/D0NR05475E) summarize the most recent updates on the structure–activity relationship of random alloy and intermetallic (ordered structure) nanocrystals for electrochemical fuel cells with robust activity and superb stability.

By mimicking natural photosynthesis, artificial photosynthesis using nanocatalysts is described by several research groups.⁴ For enhancing the light absorp-

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tion and inhibiting the electron–hole recombination, morphological modification and surface engineering are facile techniques to boost photocatalysis.^{5–7} Tang *et al.* (DOI: 10.1039/D0NR00226G) have prepared graphitic carbon embedded inside hollow graphitic carbon nitride ($\text{g-C}_3\text{N}_4$). Yu's group (DOI: 10.1039/C9NR10451H) successfully developed hierarchical Ni–NiS/C/ZnO photocatalysts *via* *in situ* photodeposition of Ni–NiS nanosheets onto C/ZnO electrospun nanofibers for CO_2 reduction to CO and CH_4 . Attributed to the advantages of 2D/2D heterojunction systems, Jing *et al.* (DOI: 10.1039/D0NR02551H) fabricated dimension-matched ultrathin NiMOF/ $\text{g-C}_3\text{N}_4$ heterojunctions with the aid of ultrasound by

growing NiMOF nanosheets on hydroxylated and 1,4-aminobenzoic acid-functionalized $\text{g-C}_3\text{N}_4$ nanosheets for improved CO_2 reduction. To aim for energy sustainability as opposed to the energy-intensive industrial Haber–Bosch process, Tang *et al.* (DOI: 10.1039/D0NR02527E) designed a ternary heterostructure consisting of ruthenium species on $\text{g-C}_3\text{N}_4$ ($\text{Ru/RuO}_2/\text{g-C}_3\text{N}_4$) for ammonia photosynthesis, in which Ru and RuO_2 functioned as electron and hole storage sites, respectively. Furthermore, Zhang *et al.* (DOI: 10.1039/D0NR03393F) report W-doped TiO_2 for boosted photothermocatalytic CO_2 reduction to CO due to the presence of more active sites with increased W doping. By applying an external bias,

Jorge *et al.* (DOI: 10.1039/D0NR06139E) introduce a carbon underlayer derived from carbon dots *via* a hydrothermal process between the fluorine-doped tin oxide substrate and the hematite photoanodes, which has remarkably enhanced the photocurrent density and charge transfer efficiency of up to *ca.* 80% at 1.25 V *vs.* RHE. Besides energy conversion, An's group (DOI: 10.1039/D0NR01027H) has synthesized well-aligned 2D Ni-MOF nanosheet arrays vertically grown on porous nickel foam (Ni-MOF/NF) without lateral stacking *via* solvothermal processes for the removal of ethyl acetate. Falaras's group (DOI: 10.1039/D0NR02562C) designed an innovative interface engineering approach to utilize an organic chromophore as an



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interlayer between a perovskite absorber and hole transporter, which preserved 83% of the original efficiency despite storing the device for 37 days in the dark and under open-circuit conditions.

In addition to light-driven reactions, research in the field of electrocatalysis for water splitting and CO_2 reduction is a prime focus of sustainable energy research.^{8–11} As a low-cost alternative to Pt, Yamashita's group (DOI: 10.1039/D0NR02525A) employed the noble-metal-free hybrid phase 1T/2H- MoS_2 with tunable 1T concentration for electrochemical hydrogen evolution. Oh *et al.* (DOI: 10.1039/D0NR02951C) studied the pH influence on the electro-activation of IrNi alloy nanoparticles supported on carbon (IrNi/C) toward water oxidation, where different pH conditions led to extraordinary electronic structure by modifying the alloy catalysts. Liu *et al.* (DOI: 10.1039/D0NR03378B) developed trifunctional electrocatalysts for hydrogen evolution (HER), oxygen evolution (OER) and oxygen reduction reactions (ORR), which are composed of a hierarchically-structured Pt/NiO/Ni/CNT with around 2 nm of Pt nanoparticles *via* substrate-enhanced electroless deposition. Beyond water splitting for hydrogen and oxygen evolution reactions, Luo *et al.* (DOI: 10.1039/D0NR02591G) synthesized nanostructured Cu@ $\text{Cu}_2(\text{OH})_3\text{NO}_3$ electrodes *via* a molten salt decomposition method (MSDM) for CO_2 electroreduction to C_2H_4 in KHCO_3 solution with a high faradaic efficiency of 31.8% and robust stability of over 20 h. In another investigation, Chen's group (DOI: 10.1039/D0NR03475D) unravelled the effect of the dynamic chemical state on the selective CO_2 reduction to CO and formate using Zn electrocatalysts *via* *in situ* Raman spectroscopy, X-ray absorption spectroscopy (XAS) and X-ray diffraction, in which Zn(II) and Zn(0) species played a dominant role in CO and formate production, respectively. Li *et al.* (DOI: 10.1039/C9NR10304J) employed a series of an electrochemical method and *in situ* SERS to elucidate the size effects of Pt on the activity of Pt-on-Au nanocatalysts with a Au-core Pt-satellite superstructure toward CO and metha-

nol electrooxidation. Other than that, by taking the merits of the appealing optoelectronic and electrochemical attributes of MXene, Gogotsi *et al.* (DOI: 10.1039/D0NR02673E) fabricated solution processable transparent conducting electrodes for three-electrode electrochromic cells by employing titanium carbide MXenes. Along another energy conversion route, Hong *et al.* (DOI: 10.1039/D0NR03303K) examined thermoelectricity in molecular junctions developed from oligophenylene-ethynylene derivatives.

Advances in energy storage devices using nanotechnology is another global trend of energy research.^{9,12,13} Xu *et al.* (DOI: 10.1039/D0NR02016H) prepared multilayered nickel-cobalt organic framework (NiCo-MOF) nanosheets as robust electrode materials for excellent electrochemical energy storage over 3000 cycles at 5 A g⁻¹. Kovalenko *et al.* (DOI: 10.1039/D0NR02930K) present the synthesis of homogeneously embedded Sb nanoparticles in a silicon oxycarbide (SiOC) matrix, which was able to provide a reasonably high Li-ion storage capacity. Hwang *et al.* (DOI: 10.1039/D0NR02569K) designed the intercalative hybridization of MoS_2 with chromium hydroxide nanoclusters, which increase the basal spacing, accelerate charge kinetics and stabilize the open porous stacking structure for boosted charge storage capacity and rate performance for Li-ion batteries.⁴ In Li-S batteries, sluggish dynamics of lithium polysulfides (LiPS) conversion results in fast capacity decay and ineffective utilization of active sulfur. Wu *et al.* (DOI: 10.1039/D0NR03528A) designed a hierarchical MXene@ TiO_2 nanoarray *via* *in situ* solvothermal strategies, which is able to retain a stable discharge capacity of 612.7 mA h g⁻¹ after 500 cycles at a rate of 2C in a Li-S battery. In another related work, a ZnS quantum dot@graphene nanosheet (ZnS QD@rGO) catalyst was fabricated by Wei and co-workers (DOI: 10.1039/D0NR02429E) to ameliorate polysulfide conversion for high energy density Li-S batteries. By blocking the LiPS shuttling, the construction of an interlayer with low Li ion diffusion resistance renders a magnificent approach. Lv *et al.* (DOI: 10.1039/

D0NR02607G) constructed a thin porous carbon nanosheet with embedded TiO_2 nanoparticles as an interlayer on the separator, which allows rapid Li ion diffusion and simultaneously blocks the polysulfide diffusion. In another work, Lee *et al.* (DOI: 10.1039/D0NR02258F) engineered a Li metal anode by employing microporous and mesoporous carbon as host materials to avoid degradation during cycling of Li-S batteries.

Other than Li batteries, Dong and Wang *et al.* (DOI: 10.1039/D0NR02604B) reported the design of a walnut-like $\text{MoS}_2@\text{SnS}$ core-shell heterostructure as an anode for sodium-ion batteries, which exemplified superior electrochemical performances ascribed to improved ion diffusion at the heterointerface driven by an internal electric field. To circumvent shortcomings present in organic potassium-ion batteries (PIB), Zhang *et al.* (DOI: 10.1039/D0NR00964D) designed a non-redox-metal potassium metal-organic framework (K-MOF) as an auspicious organic anode for high electrochemical performance and cycling for more than 300 cycles with capacity retention of 92% stemming from the N-K/O-K coordination bonds. Apart from the organic anode, Mai's group (DOI: 10.1039/D0NR01274B) constructed self-adaptive NiS_2 nanoparticles embedded in three-dimensional (3D) graphene oxide as a robust anode with outstanding rate behaviour and high reversible capacity in PIB with reversible transformation from NiS_2 to K_xNiS_2 followed by generating Ni and K_2S_4 products. Bifunctional OER/ORR electrocatalysts composed of N-doped carbon nanotubes containing NiFe alloy nanoparticles were fabricated by Zhang *et al.* (DOI: 10.1039/D0NR02486D), in which an excellent performance for rechargeable zinc-air batteries was ascribed to the high porosity and boosted conductivity, hence benefiting mass and electron transfer processes.

We are certain that this themed collection will inspire the readers to further advance fundamental understanding of the state-of-the-art energy applications to potentially meet the industrial requirements for commercialization and globalization. As Guest Editors, we would like to thank all invited authors for their

excellent contributions as well as all *Nanoscale*'s editors and reviewers for their selfless professional services. On a final note, in conjunction with the Xiamen University's anniversary in 2021, we would like to commemorate and congratulate on the 100th anniversary of Xiamen University, China and the 5th anniversary of Xiamen University Malaysia campus. In view of the university's anniversary, we would like to celebrate the successful launch of the Center of Excellence for NaNo Energy & Catalysis Technology (CONNECT) at Xiamen University Malaysia in 2021.

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