

专家鉴定意见

本人作为纳米材料与技术领域的专业研究人员，经审核确认，Cobalt Nanoclusters-Modulated Platinum-Tin Intermetallic for pH-Universal Hydrogen Evolution Electrocatalysis 围绕电催化性能研究展开，与纳米材料与技术专业核心方向高度契合。

本人作为指导老师，对成果的原创性、真实性及学术规范性予以确认。

推荐人签名：陈子尧 张明

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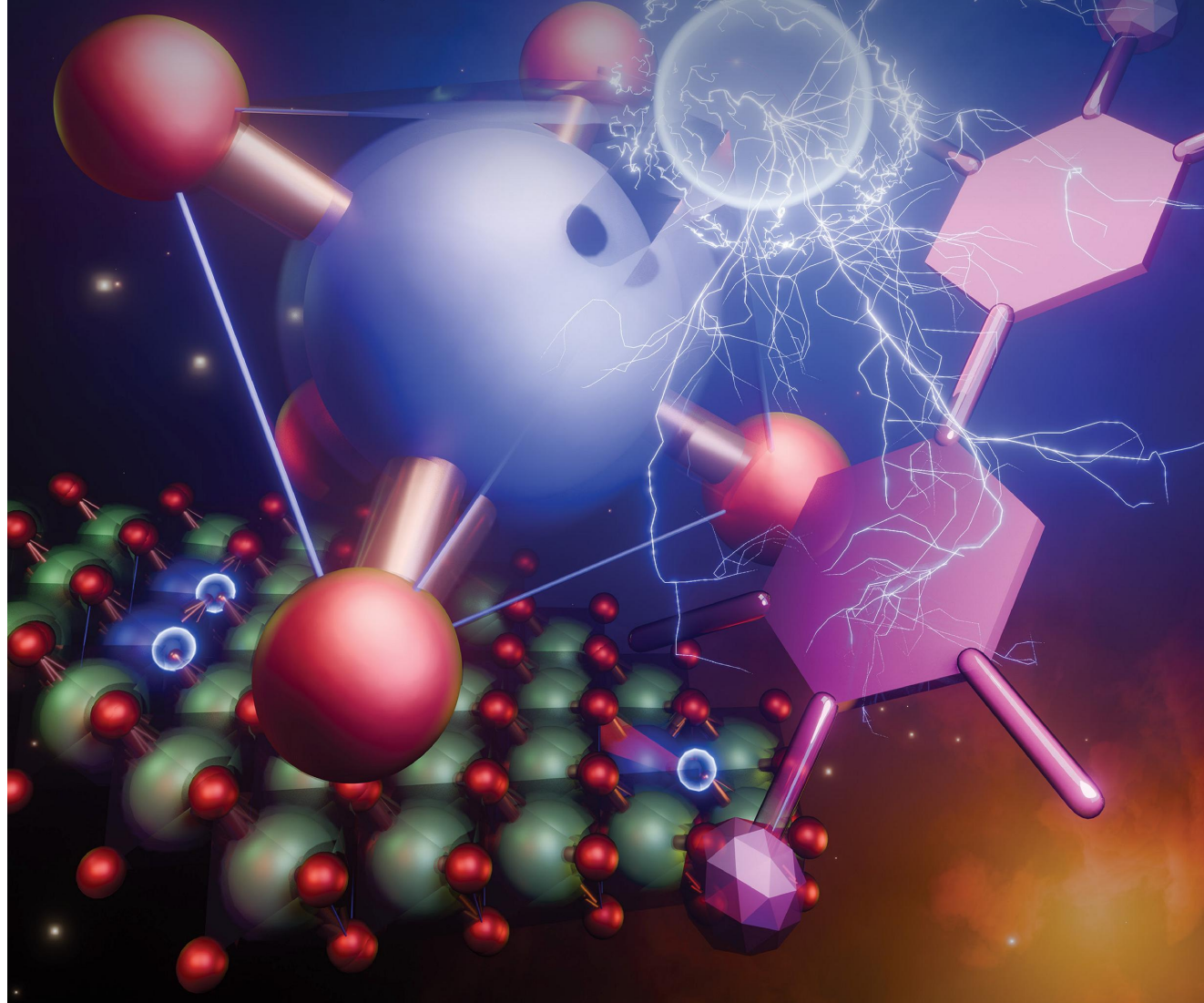
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Genesis Higueros, Qizhang Li, and Po-Chun Hsu*
ACS Materials Letters 2025, 7, 5, 1879-1886 (Perspective)
Publication Date (Web): April 15, 2025



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Perspective on the Next Ten Years of Wearable Passive Radiative Thermoregulation
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ACS Materials Letters 2025, 7, 5, 1879-1886 (Perspective)
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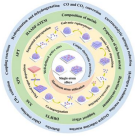
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Atomic-Precision Engineering of Single-Atom Alloy Materials for Green Catalysis and Energy Conversion
Shunwu Wang*, Xinfeng Guo, Ziheng Zhou, Haojiang Cheng*, and Ligang Wang*
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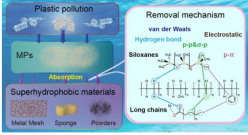
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Oriol Rius-Ayra*, Anhua Ren, and Alisiya Biserova-Tachieva
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Multidimensional Delivery Strategies for Liposomal Transdermal Drug Delivery Systems
Chengyun Wang, Yanhui Wang, Xinyue Lan, Longjiao Zhu, Jiaxuan Gu, Weichen Hou, Baiqiang Zhai, Dantong Li, Hongtao Tian*, and Wentao Xu*
ACS Materials Letters 2025, 7, 5, 1795-1806 (Review)
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1 + 1 > 2 Effect: Constructing Perovskite Heterostructures for Boosting Phototransistor Performance

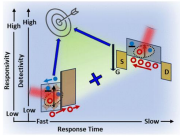
1 + 1 > 2 Effect: Constructing Perovskite Heterostructures for Boosting Phototransistor Performance

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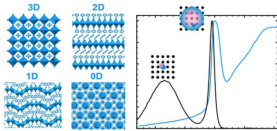
Pathways, Probes, and Puzzles of Broadband Luminescence in "Perovskite-Inspired" Materials

Simon Kahmann*

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Plastics–Fertilizer Homology: Solid-Phase Molecular Assembly Enables Natural Closed-Ring Cycle of Biomass-like Plastics

Jinwan Qi, Hongxin Zhao, Hongjun Jin, Shuitao Gao, Jianbin Huang, Xinxian Ma*, and Yun Yan*

ACS Materials Letters 2025, 7, 5, 1646-1653 (Letter)
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Oxygen-Dependent Sputtered NiO_x for High-Performance Perovskite Solar Cells and Minimodules

Ling Kai Lee, Nengxu Li, Xi Wang, Haoming Liang, Jinxi Chen, Renjun Guo, Zijing Dong, Zhuojie Shi, Tao Wang, Donny Lai, Shunchang Liu, Zhengrong Jia, Yudian Wang, Xiao Guo, Jia Li, Qilin Zhou, Armin Gerhard Aberle, and Yi Hou*

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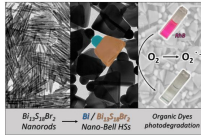
Synthesis, Growth Mechanism, and Photocatalytic Properties of Metallic-Bi/Bi₁₃S₁₈Br₂ Nano-Bell Heterostructures

Anna Cabona, Stefano Toso, Andrea Griesi, Martina Rizzo, Michele Ferri, Pascal Rusch, Giorgio Divitini, Julia Pérez-Prieto*, Raquel E. Gallan*, Ilka Krieger*, and Liberato Manna*

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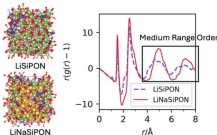
Ab Initio Simulation of Medium-Range Ordering in Ionic Glass Electrolytes LiSiPON and LiNaSiPON

Yuri N. Osetsky, Yuya Shinohara*, German D. Samolyuk, Takeshi Egami, and Andrew S. Westover

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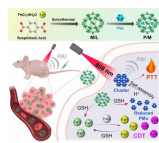
Tumor-Activated Nanoassemblies with Positive Feedback Loop for Photoacoustic Imaging-Guided Precise Cancer Therapy

Xuan Wang, Xiaotong Xing, Ming-Jie Dong*, Huiyu Liu, Zijia Zhou, Jing Zheng, and Haifeng Dong*

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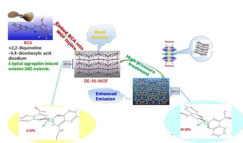
Pressure-Induced Luminescence Enhancement of Aggregation-Induced Emission Molecules Confined in Two-Dimensional MOF Layers

Dedi Liu, Dapeng Dong, Tingyu Liu, Shuang Liu, Zhen Yao, Qianjun Li*, Bo Liu, Ran Liu, Lei Yue, Xiumei Yin, Zhenghua Li, Jinhai Niu, Naisen Yu, Zhenyi Zhang*, and Bingbing Liu*

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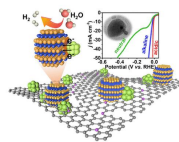
Cobalt Nanoclusters-Modulated Platinum–Tin Intermetallic for pH-Universal Hydrogen Evolution Electrocatalysis

Chuhan Dai, Ruiqi Wang*, Shouyu Yao, Qianqian Liu, Hongyuan Yang, Wanfei Li, Miao Cheng, Ziliang Chen, Jing Hu, Tao Wei, Yun Ling, Prashanth W. Menezes*, and Bo Liu*

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Cost-Effective and Humid Air-Stable Fluoride Solid Electrolyte with High Ionic Conductivity Induced by Microstructural Modulation

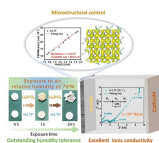
Cost-Effective and Humid Air-Stable Fluoride Solid Electrolyte with High Ionic Conductivity Induced by Microstructural Modulation

Xianhui Nie, Meng Lei, Jialin Hu*, and Chilin Li*

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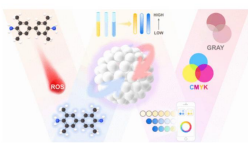
Defect-Engineered CoFe Layered Double Hydroxide Quantum Dots: Oxygen Vacancy-Driven Boost in Peroxidase-Mimic Catalysis for Multiplex Biomarker Sensing

Zhongwei Yang, Xiaoyu Zhang, Longwei Wang, Jian Zhang, Na Ren, Longhua Ding, Shenghao Xu, Zheng Wang*, Aizhu Wang*, Hong Liu, and Xin Yu*

ACS Materials Letters 2025, 7, 5, 1777-1785 (Letter)
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Controlled Assembly of Chiral One-Dimensional Helical Coordination

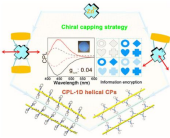
Controlled Assembly of Chiral One-Dimensional Helical Coordination Polymers for Circularly Polarized Luminescence and Polydimethylsiloxane-Assisted Signal Inversion and Amplification

Hongyu Dong, Ziwen Song, Liping Wang, Haitao Li, Xin-Tao Wu, and Yuehong Wen*

ACS Materials Letters 2025, 7, 5, 1786-1794 (Letter)
Publication Date (Web): April 9, 2025

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Intelligent, Personalized Scientific Assistant via Large Language Models for Solid-State Battery Research

Yan Leng, Yi Zhong, Zhi Gu, Peli Li, Haoting Cui, Xing Li, Yang Liu, and Jiayu Wan

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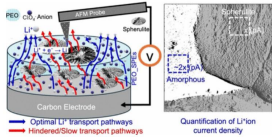
Linking Local Ionic Conductivity, Microstructure, and Nanomechanical Properties to Bulk Performance for Enhanced Design of Solid Polymer Electrolytes

Vinay Saini, Gleb Bobrov, Hai Le, Philip Egberts*, and Milana Trifkovic*

ACS Materials Letters 2025, 7, 5, 1830-1836 (Letter)
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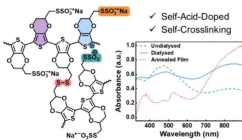
A Self-Acid-Doped and Self-Cross-Linked PEDOT Derivative Using a Simple and Effective Thiosulfate Addition

Kristina Fidanovski, Modi Gu, Jiaxin Wu, Antonio Lauto, Daniel Ta, David Miskovic, Pawel Wagner, Klaudia Wagner, Zezhong Deng, David Officer, and Damia Mawad*

ACS Materials Letters 2025, 7, 5, 1837-1844 (Letter)
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Ambiently Stable Two-Dimensional β -CuI Monolayers with Self-Trapping

Ambiently Stable Two-Dimensional β -CuI Monolayers with Self-Trapping Exciton Luminescence

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ACS Materials Letters 2025, 7, 5, 1845-1851 (Letter)
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Cobalt Metal–Organic Framework as a Standalone Material for Supercapattery Electrodes: Achieving Superior Power Density among Advanced Energy Storage Devices

Govu Radha, Sreya Kondapalli, T. Leelasree, and Himanshu Aggarwal*

ACS Materials Letters 2025, 7, 5, 1852-1859 (Letter)
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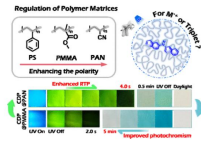
Harnessing Polymer Matrices for Tuning the Luminescence and Photochromism Properties of Organic Photoresponsive Materials

Mingda Shan, Aisen Li, Man Wang, Yujie Yang, Jiaqiang Wang, Kun Yang*, Ben Zhong Tang*, and Zhen Li*

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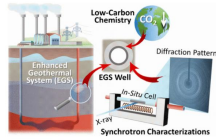
Geo-Responsive Chemomechanics in Aluminum Oxyhydroxide via Alkali-Driven Dehydroxylation for Supercritical Geothermal Systems

Sizhan Liu, Michelle Devoe, Devon M. Samuel, Waltraud M. Kriven, Jianming Bai*, Anastasia G. Ilgen*, Toshifumi Sugama, and Tatiana Pyatina*

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Superimposed Effect of Intramolecular Modular Assembling and Silver Coordination to Amplify Superoxide Anion Radical for Antitumor and Antibacterial Photodynamic therapy

Siwen Wei, Haoran Hou, Yingnan Wu, Wenlong Chen, Gaobo Hong, Dapeng Liu*, Meng Zhou*, and Fengling Song*

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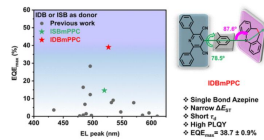
Azepine Modulation in Thermally Activated Delayed Fluorescence Emitters for OLEDs Achieving Nearly 40% EQE

Jian Lei, Yi-Kuan Chen, Min-Jie Wang, Chang-Lin Ko, Wen-Yi Hung, Liang-Yan Hsu*, Tien-Lin Wu*, and Chien-Hong Cheng*

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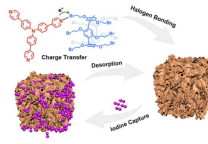
Halogen Bonding-Driven Supramolecular Polymers Based on Pillararenes for Efficient Iodine Capture

Chun-Li Song, Meng-Hao Li, Gengxin Wu, Chunyu Wang, and Ying-Wei Yang*

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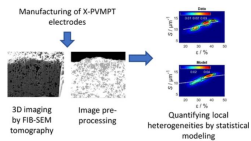
Quantifying Local Heterogeneities in the 3D Morphology of X-PVMPT Battery Electrodes Based on FIB-SEM Measurements

Lukas Dodel, Matthias Neumann*, Markus Osenberg, André Hilger, Gauthier Studer, Birgit Esser, Ingo Manke, and Volker Schmidt

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Three-Dimensional to Layered Halide Perovskites: A Parameter-Free Hybrid Functional Method for Predicting Electronic Band Gaps

Ibrahim Buba Garba, Lorenzo Trombini, Claudine Katan, Jacky Even, Marios Zacharias, Mikael Kepenekian, and George Volonakis*

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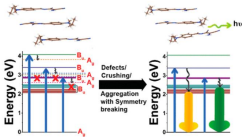
Unveiling the Inversion-Symmetry-Driven Excitation Switching in Aggregation-Induced Emission

Charya J. Senanayake, Thalpage Don Dinithi Kavindi, D. H. Sanduni Deenalattha, Dinushika Kotudura Arachchige, Kaushanie Gunaratne, P. M. Anuradha Bandaranayake, U. Dulanjali Rodrigo, Nuwan de Silva, and Neranga Abeyasinghe*

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Non-fluorinated Triazine-Functionalized Pentiptycene-Based Nanoporous Organic Polymer for Highly Efficient SF₆/N₂ Separation

Xinyu Yang, Qilin Wang, Jiangli Zhu, Jun Yan*, and Shengwei Guo

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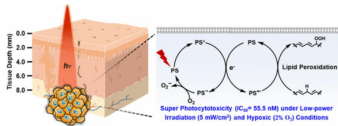
BODIPY-Based Photosensitizer with Outstanding Photocytotoxicity for Deep-Tissue Photodynamic Therapy

Bin-Kai Liu, Kun-Xu Teng, Li-Ya Niu, and Qing-Zheng Yang*

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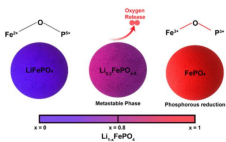
Anion Activity and Metastable Phase Formation in Li_{1-x}FePO₄ Investigated Using Soft-to-Hard X-ray Absorption and Emission Spectroscopy

Abiram Krishnan, Doyoub Kim, Chemo Jaye, and Faisal M Alamgir*

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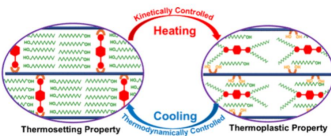
Kinetically and Thermodynamically Controlled Cross-Linking in Sustainable Digital Light Processing Printing: Enabling Thermoset Reprocessing via Thermal Leveling Effect

Yi Ting Chong, Suxi Wang, Sirawit Pruksawan, Zhuang Mao Png*, Qiang Zhu, Zibiao Li, and FuKe Wang*

ACS Materials Letters 2025, 7, 5, 1963-1972 (Letter)
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A Chiral Amino Acid-Modified pH-Responsive Nanoplatfrom Coactivates

A Chiral Amino Acid-Modified pH-Responsive Nanoplatfom Coactivates Cuproptosis and cGAS-STING Signaling Pathways for Cancer Therapy

Lin Li, Guanheng Wang, Biao Xue, Xueao Li, Jiapeng Wang, Wenjun Wang, Chang Liu*, Chunlei Li*, and Xiuwen Zheng*

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Ionic-Bond Regulated Cross-Linking Polyurethane with Multilevel Energy Dissipation, Enhanced Chain Rearrangement and Solvent Reprocessability

Qingyun Zhao, Linzhu Xu, Birong Zeng*, Yiting Xu, Weiang Luo, Conghui Yuan, and Lizong Dai*

ACS Materials Letters 2025, 7, 5, 1984-1992 (Letter)
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Reliability Challenges in Equivalent-Oxide-Thickness Scaling with High-k

Reliability Challenges in Equivalent-Oxide-Thickness Scaling with High-k Er₂O₃ Dielectrics on Two-Dimensional MoS₂ Field-Effect Transistors

Shuhong Li, Ryotaro Otake, Tomonori Nishimura, Takashi Taniguchi, Kenji Watanabe, Yoshiki Sakuma, and Kosuke Nagashio*

ACS Materials Letters 2025, 7, 5, 1993-2001 (Letter)
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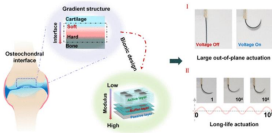
Biomimetic Gradient Structured Dielectric Elastomer Actuators for Long-Term Large Out-of-Plane Actuation

Huifeng Dong, Zike Chen, Jiangshan Zhuo, Rufen Tang, Junbo Peng, Lvting Wang, Shengchao Jiang, Rui Xiao*, and Ye Shi*

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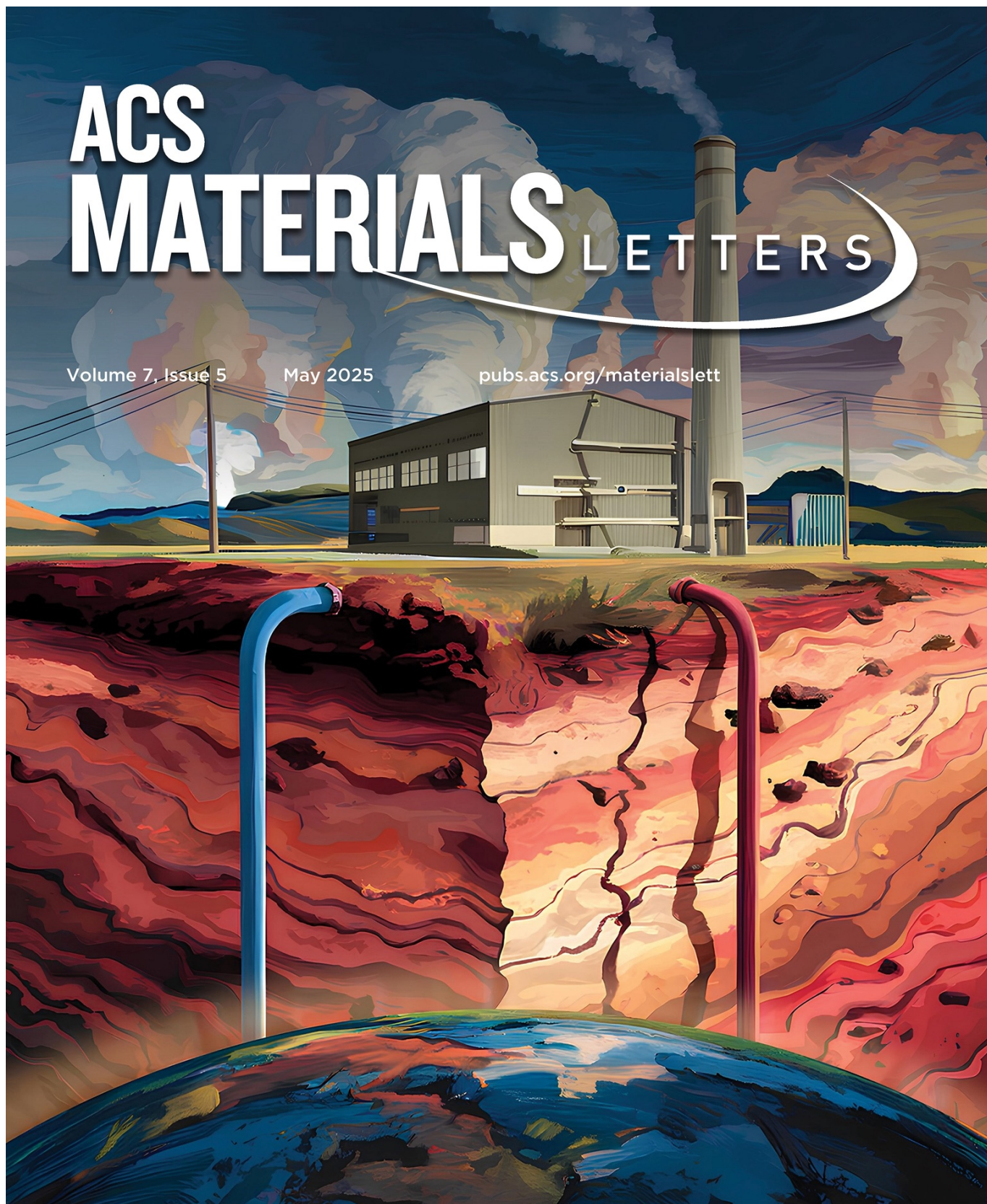
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Cobalt Nanoclusters-Modulated Platinum–Tin Intermetallic for pH-Universal Hydrogen Evolution Electrocatalysis

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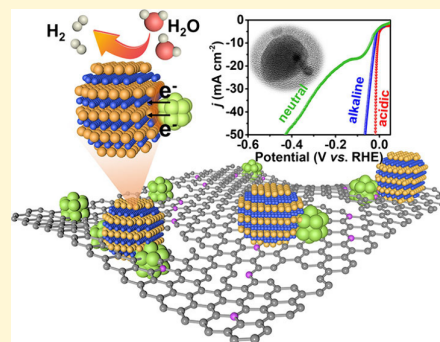


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Supporting Information

ABSTRACT: Achieving satisfactory electrocatalytic activity and stability of platinum (Pt)-based catalysts for hydrogen evolution reaction (HER) in wide-pH media remains a formidable challenge. In this context, a heterostructure composed of platinum–tin intermetallic nanoparticles and cobalt nanoclusters, evenly confined in a nitrogen-doped carbon mesh (Pt₃Sn/Co@N-CM), is designed that acts as an efficient HER catalyst. Alloying Sn effectively reduces Pt usage and ensures high electrical conductivity during catalysis. Notably, the Co clusters not only accelerate water dissociation in the HER process but also form strong coupling with ordered Pt₃Sn particles, thus optimizing the Gibbs free energy for pH-universal HER intermediates. Consequently, Pt₃Sn/Co@N-CM attains 10 mA cm^{−2} current densities at low overpotentials of ~8, ~20, and ~41 mV in acidic, alkaline, and neutral solutions, respectively, outperforming most reported Pt-based counterparts. Additionally, excellent structural and operational stability is achieved, displaying its promising prospects. This study paves a simple avenue for developing high-performance, pH-universal HER electrocatalysts.



Electrochemical water splitting driven by renewable energy to produce green hydrogen (H₂) has become a worldwide research focus. Importantly, its core half-reaction, hydrogen evolution reaction (HER), typically requires active electrocatalysts to reduce the energy barriers and reaction overpotentials.^{1–3} Numerous catalysts based on nonprecious, earth-abundant metals have recently been reported for all-pH electrolytes. However, their catalytic performance is often far from satisfactory.^{4,5} In particular, industrially, the acid water electrolysis (e.g., the proton exchange membrane electrolyzer cell-based cells) predominantly relies on noble metal-based catalysts for electrodes, as they can efficiently and durably sustain large current densities, something that precious metal-free catalysts hardly achieve.^{6,7} Therefore, the development of precious Pt-based electrocatalysts for wide-pH HER remains highly relevant.^{8,9} However, (i) Pt features a high cost and extreme scarcity; thus, reducing its usage is pivotal for large-scale applications. (ii) The pH-universal capabilities of such catalysts are typically not satisfactory, probably because it is difficult to fulfill different thermodynamic features under distinct electrolyte scenarios. (iii) In most cases, their observed HER stability still needs to be further improved due to the corrosive loss of the catalytic sites and aggregation of the active phase.^{10–13}

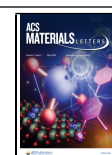
To solve the above issues, over the years, previous research has discovered that (i) Alloying Pt with non-noble metal (M) to form an ordered Pt-M intermetallic has attracted extensive attention, which can substantially lower the utilization of Pt. Meanwhile, intermetallics are characteristic of distinct chemical bonding and ordered structures with voids, thus exhibiting high electric conductivity, good electrochemical stability, and numerous active sites.^{14–17} (ii) Heterogeneously coupling another phase has been verified to effectively adjust the d-band center of Pt, thus optimizing the adsorption strengths of the reaction intermediates during the electrocatalysis process.^{18–21} Considering that the favorable water dissociation and combination of H intermediate (H*) into H₂ product are both demanded by alkaline and neutral HER, only the latter is necessary in the acid case.^{11,13} Regulating the d-band center of the active Pt offers the opportunity to realize the

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thermodynamic requirements for HER in different electrolytes. (iii) Introducing carbon-based support with high porosity into a catalyst system can significantly accelerate the mass/ion transport.^{22–24} At the same time, the presence of carbon-based support can confine the dispersed active nanocatalysts from aggregation and corrosion during the electrochemical process. Thus, both activity and stability can be significantly enhanced.^{25–27} Meanwhile, doping with foreign atoms can create more effective anchor sites toward the targeted catalysts to be deposited.^{28–30} Bearing these concerns in mind, it is conceivable that a Pt–M intermetallic, coupled with functional species and anchored on a heteroatom-doped carbon support, could potentially achieve excellent HER performances across wide-pH electrolytes. Nevertheless, this type of catalyst has not been explored yet.

Herein, the intermetallic platinum–tin nanoparticles, which were decorated by cobalt nanoclusters and encapsulated by porous nitrogen-doped carbon mesh (Pt₃Sn/Co@N-CM), were developed via a facile zeolitic imidazolate framework (ZIF)-template method. Through alloying Sn to form such an intermetallic at low temperature, the Pt utilization was lowered and thereby its mass activity was enhanced. Besides, the Co clusters not only promoted the dissociation of water molecules, thus accelerating the Volmer step of alkaline and neutral HER activities, but also form a strong heterogeneous electronic interaction with Pt₃Sn, positively shifting the d-band of Pt and improving its Gibbs free energy toward HER intermediates. Furthermore, the rich surface anchoring sites enable N-CM to be intimately combined with the Pt₃Sn/Co, leading to the increased exposure of active sites and improved structural stability. Consequently, Pt₃Sn/Co@N-CM exhibited low overpotentials of ~8, ~20, and ~41 mV to drive 10 mA cm^{−2} current density in acidic, alkaline, and neutral media, respectively, which outmatched most of the state-of-the-art Pt-based catalysts. Also, the Pt₃Sn/Co@N-CM catalyst exhibited excellent HER stability. In particular, a high current density of 100 mA cm^{−2} can be stably maintained over 138 h in the acidic electrolyte. Our work introduces a simple approach to preparing low-Pt content composite for outstanding HER electrocatalysts across all-pH electrolytes and highlights its significant economic and practical value.

The synthesis process of the Pt₃Sn/Co@N-CM catalyst is depicted in Figure S1. The morphology and microstructure of as-obtained samples were first characterized. The scanning electron microscope (SEM) images of the ZnCo-ZIF-L precursor and its derived Co@N-CM illustrated that both of them had a two-dimensional (2D) thin structure (Figures S2 and S3). Analogous results were observed on the Zn-ZIF-L precursor and N-CM derivate (Figures S4 and S5). The powder X-ray diffraction (XRD) patterns of both Co@N-CM and N-CM were further collected (Figure S6). In the former case, no obvious diffraction peaks can be attributed to the metallic Co phase, demonstrating that Co was likely to exist in the form of atomic sites or clusters within Co@N-CM. Afterward, the SEM images of Pt₃Sn/Co@N-CM uncovered that amounts of nanoparticles were uniformly rooted into the 2D carbon support (Figure 1a and b). More detailed microstructure information was demonstrated by its transmission electron microscope (TEM) image in Figure 1c: numerous nanoparticles with a main diameter of 25.6 ± 0.7 nm were distributed on porous carbon mesh. The high-resolution TEM (HRTEM) of Pt₃Sn/Co@N-CM further uncovered that such carbon-supported nanoparticles were surrounded by

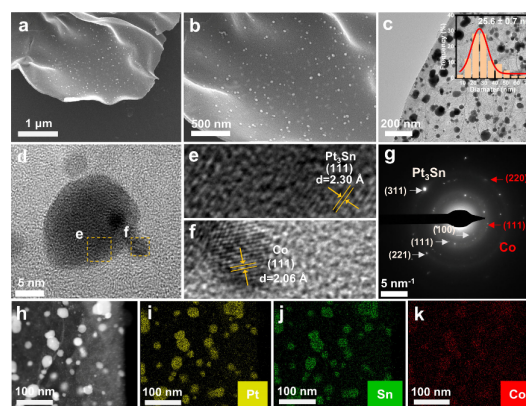


Figure 1. (a, b) SEM images, (c) TEM image (Inset: Histograms of particle size distribution for Pt₃Sn in Pt₃Sn/Co@N-CM), (d–f) HRTEM images, (g) SAED pattern of Pt₃Sn/Co@N-CM, and (h) HAADF-STEM pattern and EDX elemental mapping of (i) Pt, (j) Sn, and (k) Co for the selected region of Pt₃Sn/Co@N-CM.

nanoclusters (Figure 1d). Together with the associated selected area electron diffraction (SAED) pattern, Figure 1d–g further confirmed that the (111) plane of Pt₃Sn intermetallic phase (*Pm3m* space group, a *d*-spacing of 2.30 Å) was heterogeneously coupled with the (111) plane of metallic Co phase (*Fm3m* space group, a *d*-spacing of 2.06 Å) (See detailed information on coordination environment of the metal centers for Pt₃Sn and Co in Note S1). In addition, the high-angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) pattern and the associated energy dispersive X-ray spectroscopy (EDX) element mapping (Figure 1h–k and Figure S7) further visualized that Pt₃Sn nanoparticles decorated by Co nanoclusters were dispersed on N-doped carbon mesh, consistent with the above findings. Moreover, the microstructure of the reference catalyst, Pt₃Sn@N-CM, was also characterized by TEM (Figure S8), which unveiled that Pt₃Sn nanoparticles with a similar average size (focus on 27.3 ± 0.4 nm) to the case of Pt₃Sn/Co@N-CM were uniformly anchored on porous carbon mesh. Moreover, a lower *d*-spacing of 2.30 Å for (111) lattice plane of Pt₃Sn was found in Pt₃Sn/Co@N-CM compared to that in Pt₃Sn@N-CM (2.34 Å), revealing that the lattice contraction of Pt₃Sn might be induced by the coupling of Co (Figure S9).

The crystal phases of Pt₃Sn/Co@N-CM and Pt₃Sn@N-CM were analyzed based on their powder XRD patterns in Figure 2a, which were calibrated by Si standards. Specifically, both of these two samples possessed diffraction peaks indexed to the presence of (100), (110), (111), (200), (220), and (311) planes of Pt₃Sn intermetallic phase (JCPDS card No. 35-1360). This signified that the N-CM supports of Pt₃Sn/Co@N-CM and Pt₃Sn@N-CM were all amorphous (see detailed Raman information on N-CM supports in Figure S10). Moreover, no diffraction peaks of metallic Co were observed in the pattern of Pt₃Sn/Co@N-CM, probably because Co existed in the form of nanoclusters, as affirmed by the above TEM findings. In addition, the position of characteristic diffraction peaks of Si is consistent in two XRD patterns, but the diffraction peak of Pt₃Sn/Co@N-CM has a positive shift compared with that in Pt₃Sn@N-CM (Figure 2b), indicating the lattice contraction of Pt₃Sn in Pt₃Sn/Co@N-CM might be induced by the coupling of Co.^{31,32} Subsequently, the metal contents of the Pt₃Sn/Co@N-CM catalyst were investigated

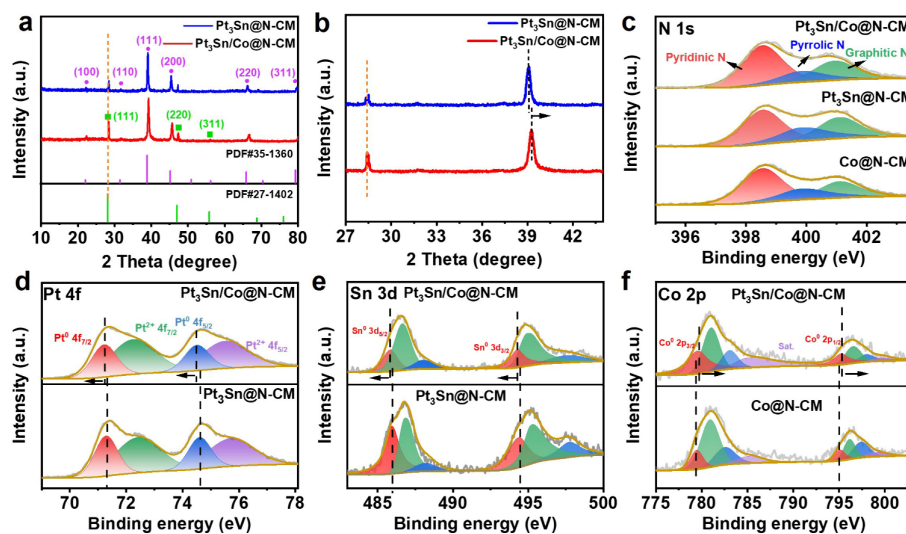


Figure 2. (a, b) Powder XRD patterns of Pt₃Sn/Co@N-CM and Pt₃Sn@N-CM. The high-resolution XPS spectra of (c) N 1s for Pt₃Sn/Co@N-CM, Pt₃Sn@N-CM, and Co@N-CM, (d) Pt 4f and (e) Sn 3d for Pt₃Sn/Co@N-CM and Pt₃Sn@N-CM, as well as (f) Co 2p for Pt₃Sn/Co@N-CM and Co@N-CM.

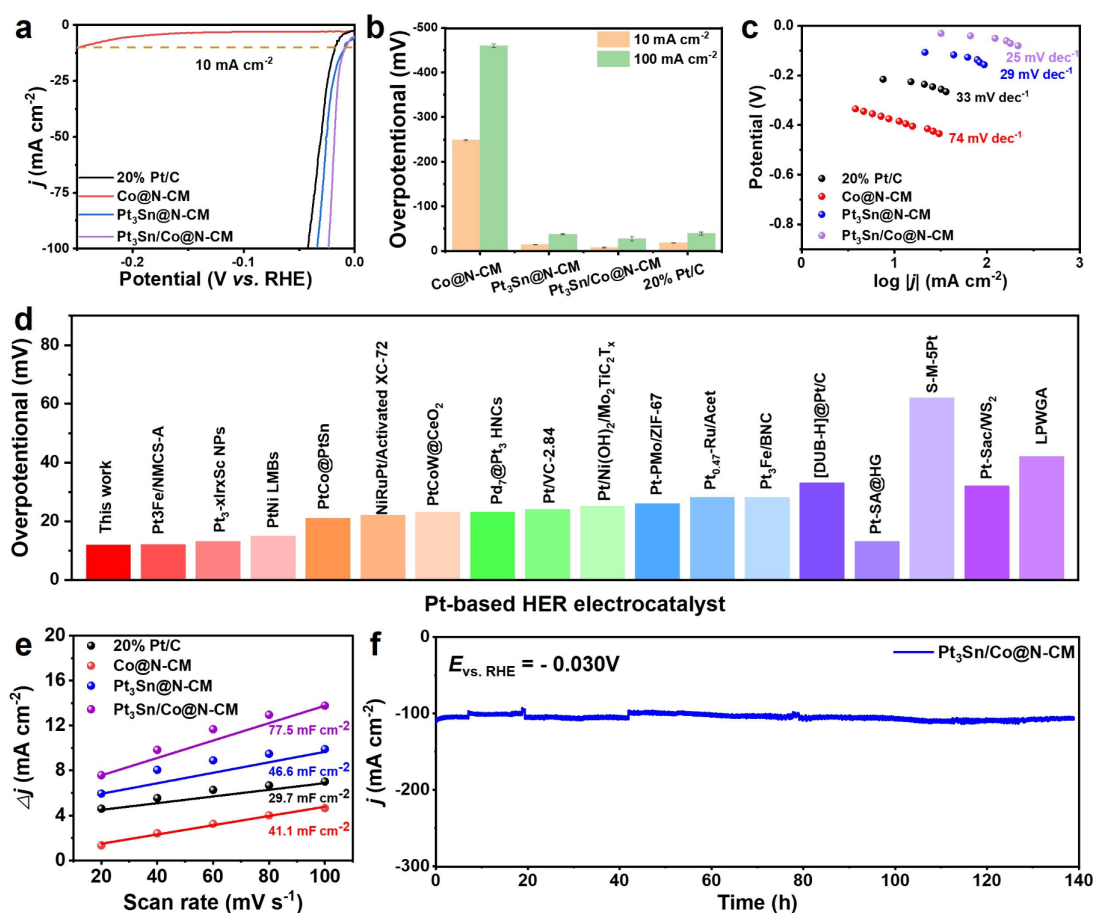


Figure 3. (a) *iR*-corrected LSV curves and (b) overpotential comparison at different current densities for Pt₃Sn/Co@N-CM and its reference samples, including Pt₃Sn@N-CM, Co@N-CM, and commercial 20% Pt/C. (d) Comparison of HER activity of Pt₃Sn/Co@N-CM with its Pt-based counterparts at 10 mA cm⁻² current density. (c) Tafel slopes and (e) *C_{dl}* values of Pt₃Sn/Co@N-CM, Pt₃Sn@N-CM, Co@N-CM, and 20% Pt/C. (f) CA curve of Pt₃Sn/Co@N-CM at a current density of ~100 mA cm⁻² (*E*_{vs. RHE} = -0.030 V). Note that all electrochemistry herein was conducted in 0.5 M H₂SO₄ aqueous electrolyte under room temperature.

by inductively coupled plasma optical emission spectrometer (ICP-OES) measurement. As shown in Table S1, the atomic ratio of Pt, Sn, and Co was $\sim 3.2:1:1.3$. Notably, the ratio of Pt and Sn was close to the theoretical value of Pt_3Sn phase. Moreover, the N_2 adsorption–desorption result showed that $\text{Pt}_3\text{Sn}/\text{Co@N-CM}$ presented typical IV-type isotherms with a high BET surface area of $1207.91 \text{ m}^2 \text{ g}^{-1}$ and a pore volume that reached $\sim 1.1 \text{ cm}^3 \text{ g}^{-1}$ (Figure S11), which were beneficial to facilitating the exposure of active sites and enhancing the mass transfer ability during the electrocatalysis process.^{33,34}

The X-ray photoelectron spectroscopy (XPS) characterizations were further performed to explore the chemical state of each element in the samples. In Figure S12, the full spectrum of $\text{Pt}_3\text{Sn}/\text{Co@N-CM}$ proved the presence of Pt, Sn, Co, C, and N. The high-resolution XPS spectra of Pt, Sn, Co, C, and N were further analyzed and the specific parameters were recorded, as shown in Table S2. The high-resolution C 1s XPS spectra of these three samples in Figure S13 can be fitted into three peaks at ~ 284.8 , ~ 285.8 , and $\sim 289 \text{ eV}$, corresponding to C–C, C–O, and C–N bonds, respectively.³⁵ Regarding the N 1s XPS spectra, three main peaks at ~ 398.55 , ~ 399.79 , and $\sim 401.10 \text{ eV}$ were recognized (Figure 2c), indicative of the pyridinic-N, pyrrolic-N, and graphitic-N, respectively.³⁶ Note that graphitic nitrogen in carbon can improve the electronic conductivity of carbon support, thus enhancing the catalytic reaction efficiency.³⁷ In the high-resolution Pt 4f XPS spectrum of $\text{Pt}_3\text{Sn}/\text{Co@N-CM}$, the fitted peaks at ~ 71.2 and $\sim 74.5 \text{ eV}$ were ascribed to $\text{Pt}^0 4f_{7/2}$ and $\text{Pt}^0 4f_{5/2}$, respectively, and other peaks at ~ 72.5 and $\sim 75.7 \text{ eV}$ were ascribed to $\text{Pt}^{2+} 4f_{7/2}$ and $\text{Pt}^{2+} 4f_{5/2}$, respectively.^{35,38} More importantly, they were located at lower binding energies than those of $\text{Pt}_3\text{Sn@N-CM}$ (Figure 2d). In the case of Sn 3d XPS, the peaks at ~ 485.84 and $\sim 494.27 \text{ eV}$ in the spectrum of $\text{Pt}_3\text{Sn}/\text{Co@N-CM}$ were indicative of the presence of Sn^0 (Figure 2e),³⁹ which negatively shifted compared with those of $\text{Pt}_3\text{Sn@N-CM}$. Similarly, the Co 2p XPS spectrum of $\text{Pt}_3\text{Sn}/\text{Co@N-CM}$ also exhibited differentiable peaks of Co^0 ,⁴⁰ yet, the associated binding energies were more positive than those of Co@N-CM (Figure 2f). These binding energy changes suggested that the electrons were transferred from Co clusters to Pt_3Sn nanoparticles when they were coupled with each other within $\text{Pt}_3\text{Sn}/\text{Co@N-CM}$, which resulted in the optimizing electronic structure for Pt sites.^{23,40}

The acidic HER electrochemistry of $\text{Pt}_3\text{Sn}/\text{Co@N-CM}$ and its reference samples was carried out in $0.5 \text{ M H}_2\text{SO}_4$ aqueous solution electrolyte. The detailed experimental pH values of the electrolyte and the calibration curves of the reference electrode can be seen in Figures S14 and S15. In Figure 3a, the linear sweep voltammetry (LSV) curves of these samples revealed that $\text{Pt}_3\text{Sn}/\text{Co@N-CM}$ merely needed ~ 8 and $\sim 27 \text{ mV}$ overpotentials to deliver the current density of 10 and 100 mA cm^{-2} , lower than those of $\text{Pt}_3\text{Sn@N-CM}$ ($\sim 14 \text{ mV}$, $\sim 38 \text{ mV}$), Co@N-CM ($\sim 248 \text{ mV}$, $\sim 460 \text{ mV}$), and 20% Pt/C ($\sim 18 \text{ mV}$ and $\sim 39 \text{ mV}$) (Figure 3a and b). The activity of $\text{Pt}_3\text{Sn}/\text{Co@N-CM}$ was also superior to most of its reported Pt-based counterparts (Table S3 and Figure 3d). The Tafel slopes of these catalysts were also compared. As shown in Figure 3c, $\text{Pt}_3\text{Sn}/\text{Co@N-CM}$ has a Tafel slope of $\sim 25 \text{ mV dec}^{-1}$, smaller than those of $\text{Pt}_3\text{Sn@N-CM}$ ($\sim 29 \text{ mV dec}^{-1}$), Co@N-CM ($\sim 74 \text{ mV dec}^{-1}$), and 20% Pt/C ($\sim 33 \text{ mV dec}^{-1}$). All of this indicated that the coupling of the Co nanocluster endowed the Pt_3Sn intermetallic with enhanced HER kinetics. Furthermore, the charge transfer resistance (R_{ct}) of $\text{Pt}_3\text{Sn}/\text{Co@N-CM}$

obtained based on electrochemical impedance spectroscopy (EIS) measurements was $\sim 1.35 \Omega$, the smallest among the probed samples (Figure S16, Table S4), substantiating the improved charge transfer ability of intermetallic Pt_3Sn modified by Co and N-CM. Additionally, the double-layer capacitance (C_{dl}), which is proportional to electrochemical specific surface area (ECSA), was also evaluated for these four samples. As depicted in Figures S17 and 3e, $\text{Pt}_3\text{Sn}/\text{Co@N-CM}$ displayed the highest C_{dl} ($\sim 77.5 \text{ mF cm}^{-2}$), followed by $\text{Pt}_3\text{Sn@N-CM}$ ($\sim 46.6 \text{ mF cm}^{-2}$), Co@N-CM ($\sim 41.1 \text{ mF cm}^{-2}$), and 20% Pt/C ($\sim 29.7 \text{ mF cm}^{-2}$). These results demonstrated that $\text{Pt}_3\text{Sn}/\text{Co@N-CM}$ was endowed with increased active area and more active sites. Besides, the chronoamperometry (CA) measurement was performed to evaluate the long-term stability of the $\text{Pt}_3\text{Sn}/\text{Co@N-CM}$ catalyst. As displayed in Figure 3f, a stable high current density of $\sim 100 \text{ mA cm}^{-2}$ ($E_{vs. RHE} = -0.030 \text{ V}$) was maintained over 138 h without obvious decay, confirming the superior catalytic durability of $\text{Pt}_3\text{Sn}/\text{Co@N-CM}$ for acidic HER.

Beyond excellent catalytic activity and stability in acid media, the exceptional HER performances of $\text{Pt}_3\text{Sn}/\text{Co@N-CM}$ in alkaline (1 M KOH) and neutral (1 M phosphate-buffered saline, PBS) aqueous electrolytes were also validated. Notably, $\text{Pt}_3\text{Sn}/\text{Co@N-CM}$ required low overpotentials of ~ 20 and $\sim 41 \text{ mV}$ to afford 10 mA cm^{-2} in 1 M KOH and 1 M PBS media, respectively. Note that the attained activities were much superior to most of the state-of-the-art Pt-based electrocatalysts for alkaline and neutral electrolytes (Tables S5 and S6). Furthermore, $\text{Pt}_3\text{Sn}/\text{Co@N-CM}$ had low Tafel slopes of ~ 32 and $\sim 63 \text{ mV dec}^{-1}$, large C_{dl} values of ~ 60.1 and $\sim 42.7 \text{ mF cm}^{-2}$, as well as small R_{ct} values of ~ 11.35 and $\sim 29.49 \Omega$ under alkaline and neutral media, respectively. All of these parameters were superior to those of the reference samples, i.e., $\text{Pt}_3\text{Sn@N-CM}$, Co@N-CM , and 20% Pt/C, measured under identical conditions (Figures S18–S22, Table S4). Moreover, $\text{Pt}_3\text{Sn}/\text{Co@N-CM}$ possessed good HER stabilities for over 60 h in both 1.0 M KOH and 1.0 M PBS media (Figures S18f and S20f). All the above data comprehensively demonstrated the outstanding pH-universal HER activity of $\text{Pt}_3\text{Sn}/\text{Co@N-CM}$.

Next, to further probe the inherent activity of the active sites, ECSA-normalized LSV polarization curves were plotted and the turnover frequency (TOF) was calculated (see details in Supporting Information).^{41,42} As shown in Figure S23 and Figure S24a–c, it is noted that the $\text{Pt}_3\text{Sn}/\text{Co@N-CM}$ possessed the highest j_{ECSA} and highest TOF values in comparison with the other catalysts in acidic, neutral, and alkaline electrolytes, respectively, implying its superior intrinsic activity. In addition, the mass activities of Pt in $\text{Pt}_3\text{Sn}/\text{Co@N-CM}$ were about 20, 21, and 10 times those of 20% Pt/C under the overpotential of 30 mV in acidic, neutral, and alkaline electrolytes, respectively (Figure S24d–f). These results demonstrated the excellent intrinsic activity of $\text{Pt}_3\text{Sn}/\text{Co@N-CM}$ under a wide-pH working environment and its exceptional application potential.

Hereafter, a series of post-HER characterizations on $\text{Pt}_3\text{Sn}/\text{Co@N-CM}$ were conducted to determine whether the active phase's transformation/corrosion/decomposition was triggered during the HER. First of all, the ICP-OES findings in $0.5 \text{ M H}_2\text{SO}_4$ electrolytes unveiled that few Pt, Sn, and Co leached from $\text{Pt}_3\text{Sn}/\text{Co@N-CM}$ during long-term CA under high current density (Table S7). In addition, from the LSV curves of $\text{Pt}_3\text{Sn}/\text{Co@N-CM}$ before and after the CA test in 0.5

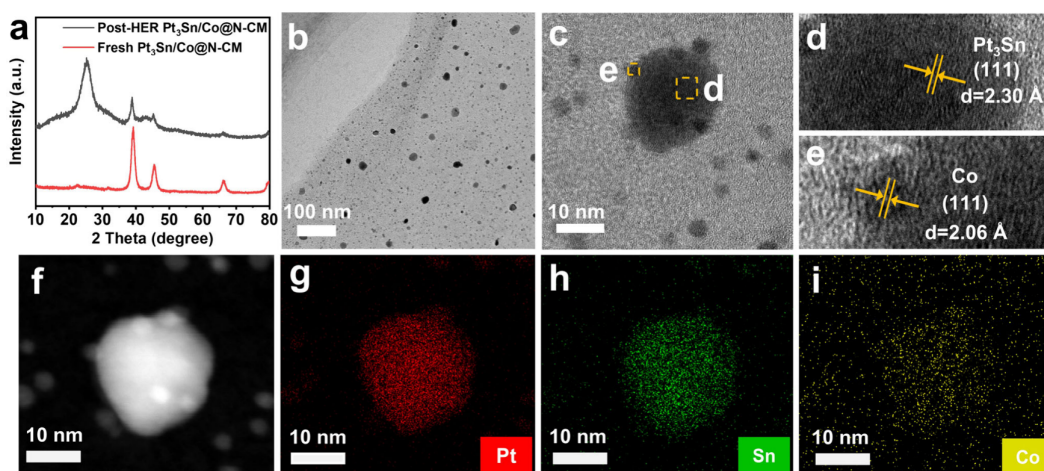


Figure 4. (a) Powder XRD patterns of the fresh and post-HER $\text{Pt}_3\text{Sn}/\text{Co}@N\text{-CM}$. (b) TEM image and (c–e) HRTEM images of post-HER $\text{Pt}_3\text{Sn}/\text{Co}@N\text{-CM}$. (f) HAADF-STEM pattern and EDX elemental mapping of (g) Pt, (h) Sn, and (i) Co for the selected region of the post-HER $\text{Pt}_3\text{Sn}/\text{Co}@N\text{-CM}$.

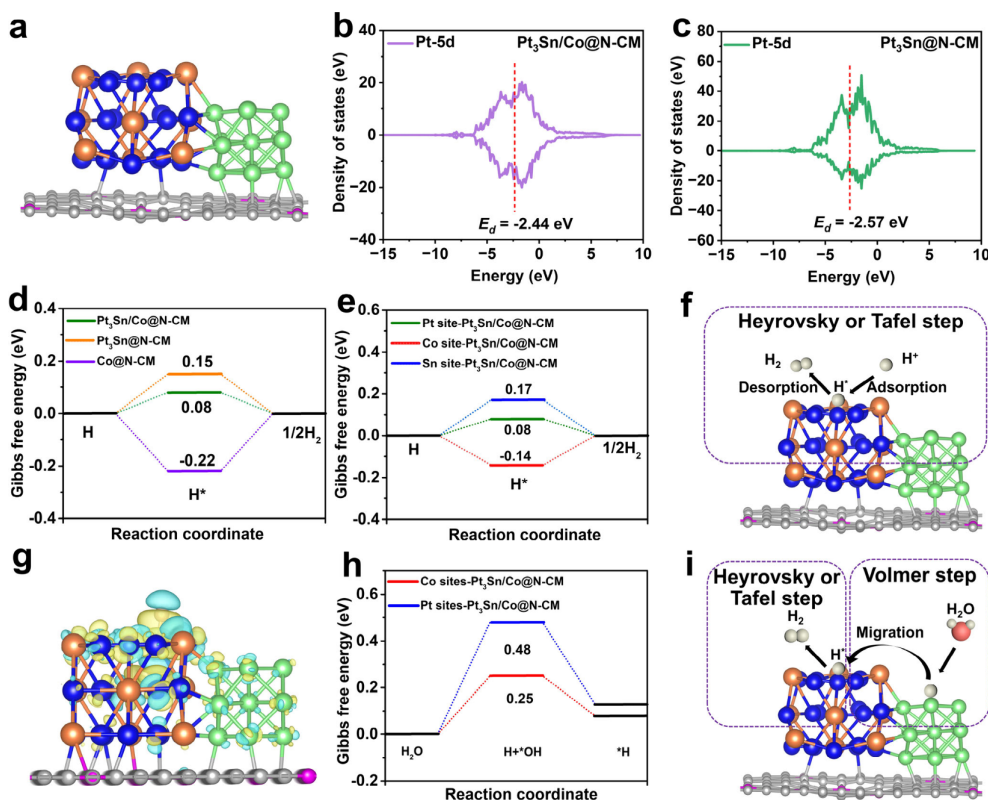


Figure 5. Structure models of the (a) $\text{Pt}_3\text{Sn}/\text{Co}@N\text{-CM}$. DOS of Pt 5d orbitals in (b) $\text{Pt}_3\text{Sn}/\text{Co}@N\text{-CM}$ and (c) $\text{Pt}_3\text{Sn}@N\text{-CM}$. (d) Free-energy diagram of ΔG_{H^*} . (e) Free-energy diagram of ΔG_{H^*} on Pt, Co, and Sn sites in $\text{Pt}_3\text{Sn}/\text{Co}@N\text{-CM}$. (f) Reaction mechanism of HER for $\text{Pt}_3\text{Sn}/\text{Co}@N\text{-CM}$ in acidic media. (g) The charge density redistributions of $\text{Pt}_3\text{Sn}/\text{Co}@N\text{-CM}$ adsorbed H intermediates. (h) Free-energy diagram of ΔG for H_2O dissociation on Pt, Co sites in $\text{Pt}_3\text{Sn}/\text{Co}@N\text{-CM}$. (i) Reaction mechanism of HER for $\text{Pt}_3\text{Sn}/\text{Co}@N\text{-CM}$ in alkaline media, respectively. Herein, the light gray, dark gray, red, pink, green, orange, and blue spheres represented H, C, O, N, Co, Sn, and Pt atoms, respectively.

$\text{M H}_2\text{SO}_4$ (Figure S25a), it also can be observed that there is no significant change in overpotentials. The powder XRD pattern of post-HER $\text{Pt}_3\text{Sn}/\text{Co}@N\text{-CM}$ was also recorded, which presented similar diffraction peaks to those in the PXRD pattern of fresh $\text{Pt}_3\text{Sn}/\text{Co}@N\text{-CM}$ except an additional broad

peak at $\sim 24^\circ$ attributed to the carbon cloth substrate used for the stability test (Figure 4a).⁴³ The post-HER $\text{Pt}_3\text{Sn}/\text{Co}@N\text{-CM}$ was then subjected to TEM characterizations. As shown in Figure 4b, the intermetallic Pt_3Sn nanoparticles coupled with Co nanoclusters were still anchored on the surface of the 2D

porous carbon mesh. Remarkably, no aggregation of Pt₃Sn/Co composites was observed. The HRTEM images, HAADF-STEM pattern, and EDX elemental mapping (Figure 4c–i and Figure S26) further clearly determined that Pt₃Sn/Co@N-CM was well retained during acidic HER without changes in crystallinity, morphology, and composition. This superior catalytic durability of Pt₃Sn/Co@N-CM is also reflected in 1.0 M KOH and 1.0 M PBS, respectively (Figure S25b and c, Tables S8 and S9).

Subsequently, the Density Functional Theory (DFT) calculations were performed to gain deeper insights into how the coupling between Pt₃Sn and Co modifies the electronic structure and to elucidate their corresponding roles in boosting HER activity. Figures 5a and S27 displayed the established structure models of the Pt₃Sn/Co@N-CM, Pt₃Sn@N-CM, and Co@N-CM. On the basis of this, the density of states (DOS) of Pt 5d orbitals for Pt₃Sn/Co@N-CM and Pt₃Sn@N-CM were compared in Figure 5b and 5c. The former featured an energy center ($E_d = -2.44$ eV) which was more positive than the latter case ($E_d = -2.57$ eV). This suggested the upshift of the d-band of Pt 5d when Pt₃Sn was coupled with Co.^{12,41} Besides, the Gibbs free energy of the intermediate H* (ΔG_{H^*}), which is widely used as an effective descriptor to assess the HER activity,^{9,44} was further calculated. As shown in Figure 5d and e, the ΔG_{H^*} value of the Pt site in Pt₃Sn/Co@N-CM was 0.08 eV, almost equal to the optimum theoretic one ($\Delta G_{H^*} = 0$). In contrast, Pt₃Sn@N-CM, Co@N-CM, Sn site, and Co site in Pt₃Sn/Co@N-CM had ΔG_{H^*} values of -0.22 , 0.15 , 0.17 , and -0.14 eV, respectively, implying that the coupling of Co enabled Pt₃Sn with optimized adsorption/desorption ability of active Pt site toward the H intermediate (Heyrovsky or Tafel step) for acid HER (Figure 5f).

Moreover, the charge density redistribution comparison (Figures 5g and S26c) and Bader charge calculations results revealed that 0.37 eV electrons transferred from the Co to Pt₃Sn within the Pt₃Sn/Co heterostructure, manifesting that the construction of such a heterostructure tuned the electronic structure of Pt 5d with a regulated d-band center. Thus, the interaction toward HER intermediate was improved, and an enhanced activity was obtained by Pt₃Sn/Co@N-CM. On the other hand, under the alkaline/neutral conditions, HER contains an extra Volmer step (dissociation of water molecule),⁴⁵ which was catalyzed by the Co site within Pt₃Sn/Co@N-CM. The DFT results in Figure 5h demonstrated that the Gibbs free energy of H₂O dissociation in Co sites was lower than that on Pt sites. This confirmed that for alkaline/neutral HER, Co clusters were responsible for the H₂O dissociation. Subsequently, the Heyrovsky or Tafel step was governed by the Pt site, as depicted in Figure 5i.

In conclusion, the Pt₃Sn intermetallic nanoparticles modified by the coupling of Co nanoclusters and confinement of porous N-CM (Pt₃Sn/Co@N-CM) were developed for HER electrocatalysis. These modifications resulted in enhanced electrical conductivity, an optimized electronic structure with a tuned d-band center, an accelerated H₂O dissociation process, and improved adsorption/desorption toward HER intermediates; additionally, the Pt₃Sn/Co heterostructure displayed reduced aggregation and corrosion. As a result, Pt₃Sn/Co@N-CM demonstrated an outstanding pH-universal HER performance, achieving 10 mA cm⁻² at an exceptionally low overpotential of ~ 8 mV and maintaining a high current density of 100 mA cm⁻² for over 138 h in acidic conditions. Moreover, electrocatalytic HER studies in alkaline and neutral electrolytes

also followed a similar trend where significantly low overpotentials and prolonged stabilities were attained. Overall, this work is expected to pave the way for the development of next-generation, efficient, adaptive, and cost-effective Pt-based electrocatalysts for sustainable green H₂ production.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsmaterialslett.5c00363>.

Experimental section; material characterization results (SEM, TEM, and EDX mapping images, Raman spectra, powder XRD patterns, N₂ sorption isotherm, XPS spectra); electrochemical performance (LSV curves, Tafel plots, CV curves, EIS measurement results, TOF results, mass activity, the durability test result); optimized calculation structures; and tables of ICP, EIS, XPS, and the comparison of electrochemical performances (PDF)

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#Chuhan Dai and Ruirui Wang contributed equally to this work. The manuscript was written through the contributions of all authors. CRediT: **Chuhan Dai** data curation, investigation, methodology, writing - original draft; **Ruirui Wang** formal analysis, investigation, methodology, validation, writing - original draft; **Shouyu Yao** formal analysis, investigation; **Qianqian Liu** data curation, formal analysis, investigation; **Hongyuan Yang** data curation, formal analysis, investigation; **Wanfei Li** investigation, methodology, resources, software, writing - original draft; **Miao Cheng** data curation, formal analysis, investigation; **Ziliang Chen** investigation, methodology, validation, visualization, writing - review & editing; **Jing Hu** data curation, formal analysis, investigation, methodology; **Tao Wei** data curation, investigation, methodology; **Yun Ling** data curation, investigation, methodology; **Prashanth Wilfried Menezes** conceptualization, funding acquisition, resources, supervision, visualization, writing - review & editing; **Bo Liu** conceptualization, funding acquisition, project administration, resources, supervision, writing - review & editing.

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