COMMENTARY

A universal strategy for fabrication of dual atom materials for multifunctional electrocatalysis

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Green hydrogen (H_2) produced from water splitting using renewable electricity is required for a sustainable hydrogen economy. Water splitting system (WSS) generally harnesses rechargeable batteries, such as metal-air batteries, for the storage of the renewable electricity. Three half reactions, i.e., oxygen reduction reaction (ORR), oxygen evolution reaction (OER), and hydrogen evolution reaction (HER), are usually involved in WSS. Therefore, enhancing the efficiency of electrochemical H_2 production requires critical improvements be made to the performance of ORR/OER/HER. To this end, the development of efficient catalysts holds the key. In the quest for suitable catalysts for the ORR/OER/HER, conventional precious metal-based nanoparticle catalysts and also the emerging field of single atom catalysts (SACs) have both shown great improvement in reaction efficiencies.[1] However, it can be challenging to achieve both multifunctionality and fast reaction kinetics with these catalyst materials.

Dual atom catalysts (DACs), with their unique structure of adjacent dual atom sites facilitating tailored synergistic effects, provide a promising solution to obtain highly efficient catalysts.[2] For example, a "pre-constrained metal twins" strategy was developed by Bu et al. to fabricate FeCo DACs, achieving bifunctional activity in both ORR and OER.[3] Zhang et al. reported the formation of Ni dual-atom sites for boosted CO_2 electroreduction kinetics via an in-situ conversion strategy.[4] The formation mechanism revealed that Ni nanoparticles firstly formed at a relatively lower pyrolysis temperature. With the rising of the pyrolysis temperature, the Ni atoms evaporated and were captured by the double carbon vacancies in the carbon matrix, thus forming the Ni dual atom sites. To fully realize the potential of DACs, it requires a deeper fundamental knowledge of this new catalyst system, with such understanding enabling the future rational design of DACs for optimal performance.

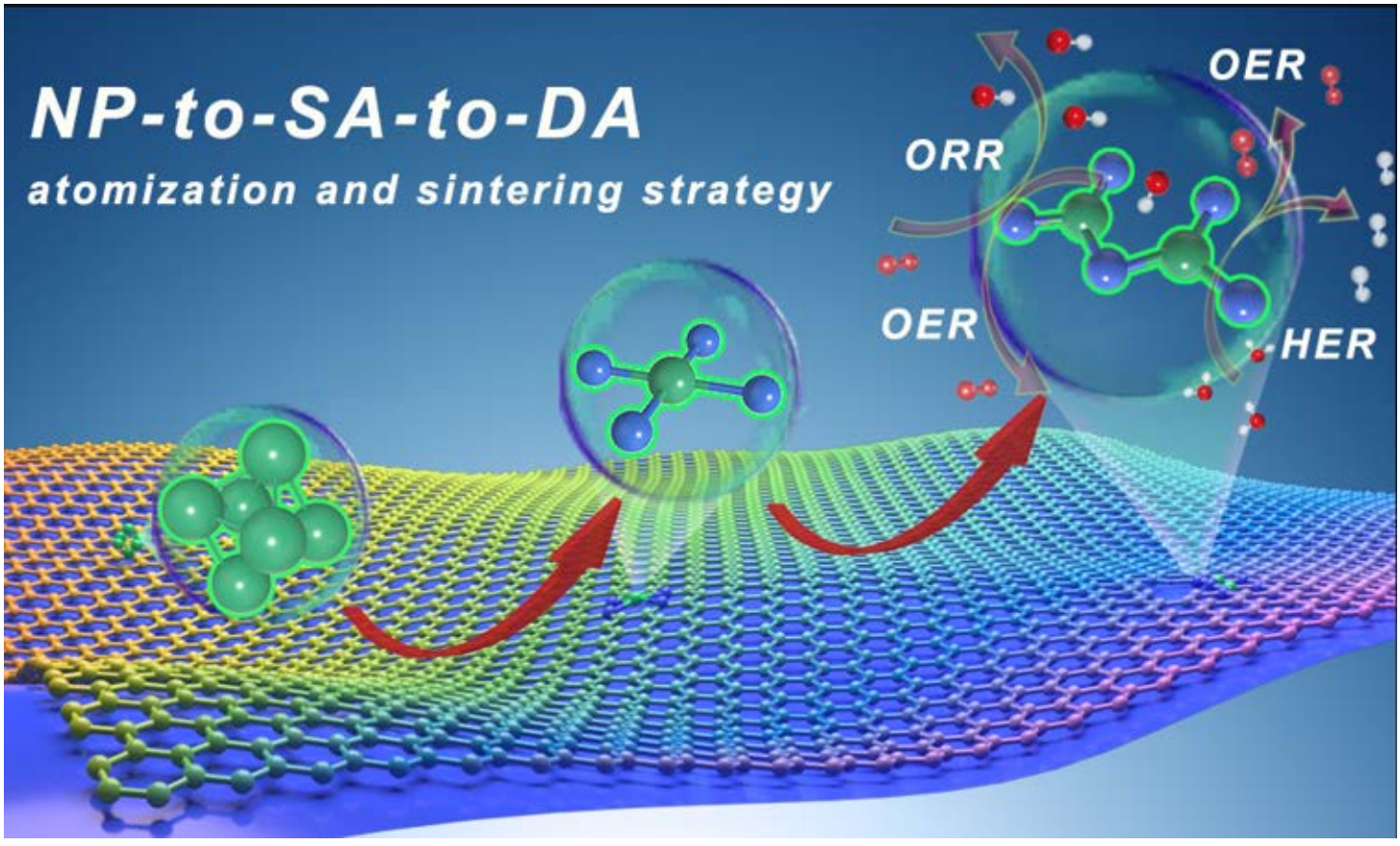

Figure 1. Schematic of the atomization and sintering strategy.

In a recent work published in Nature Communications, Huang et al. developed an universal atomization and sintering strategy to synthesize dual atom materials in a rational and controllable way for multifunctional catalysis (Figure 1).[5] Through pyrolyzing the Co-hollow polymer sphere (Co-HPS) precursor without or with melamine and tuning the pyrolysis time, Co_{NP}/HCS-900 with Co nanoparticles, Co_{SA}-N-HCS-900 with CoN_4 single atoms, and Co_2-N-HCS-900 with paired Co_2N_5 dual atoms could be obtained, respectively. Co_2-N-HCS-900 was formed from the thermal migration and coupling of

single Co atoms. Density functional theory (DFT) calculations showed that the reaction paths from two neighboring or randomly dispersed CoN_4 single atoms to Co_2N_6 and to Co_2N_5 dual atom were both exothermic with Co_2N_5 dual atom as the most stable structure. The sintering from CoN_4 single atoms to Co_2N_5 dual atoms was deduced to be a spontaneous process. It is worth mentioning that this synthesis method was found to be applicable to the fabrication of 22 distinct DAC configurations.

The authors calculated the Gibbs free energy of H* (ΔG_{H*}) and the Gibbs free energy difference between ΔG_{OOH*} and ΔG_{OH*} ($|\Delta G_{OOH*-OH*}|$) to probe the reaction activities of HER/ORR/OER over the Co nanoparticle, CoN_4 single atom, and Co_2N_5 dual atom models. Distinct from the CoN_4 single atom and Co_{10} nanoparticle with an average $|\Delta G_{OOH*-OH*}|$ value of 3.2 eV, the Co_2N_5 dual atom exhibited a $|\Delta G_{OOH*-OH*}|$ value very close to 2.46 eV for ideal catalysis toward ORR/OER. This means that Co_2N_5 dual atom breaks the universal ΔG_{OOH*} to ΔG_{OH*} scaling relation, which helps achieve boosted ORR/OER activities. The Co_2N_5 dual atom was also ideal for HER with its highest ΔG_{H*} close to the ideal value of 0 eV among other models. The free energy diagrams of CoN_4 and Co_2N_5 models for ORR/OER/HER further demonstrated the moderated and balanced adsorption and desorption of those reaction intermediates, which favor enhanced catalytic performance.

The atomic coordination structure of the Co_2N_5 dual atom site was analyzed by a series of techniques including high-resolution transmission electron microscope (HRTEM), aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (AC HAADF-STEM), X-ray absorption spectroscopy (XAS), X-band electron paramagnetic resonance (EPR) measurement, and others. The results showed that the Co_2N_5 dual atom structure was successfully constructed in Co_2-N-HCS-900. The work function and valance band maximum calculated from the ultraviolet photoemission spectroscopy (UPS) revealed that Co_2-N-HCS-900 was more favorable for the interaction between the intermediates and active sites, leading to higher reaction activity. Additionally, Co_2-N-HCS-900 was proven to possess more accessible active Co sites than Co_{SA}-N-HCS-900 and Co nanoparticles due to the larger Brunauer–Emmett–Teller (BET) surface area and Co content determined by inductively coupled plasma optical emission spectrometry (ICP-OES).

With the theoretical and structural investigations showing the superior properties of the Co_2N_5 dual atom catalyst for ORR/OER/HER, the authors further evaluated the electrochemical performance of Co_2-N-HCS-900. Firstly, Co_2-N-HCS-900 displayed advanced trifunctional activities for all three reactions including lowering their onset potential, faster reaction kinetics, and lower overpotential, together with long-term performance stability. Secondly, in view of its excellent activity for ORR/OER and OER/HER, Co_2-N-HCS-900 was used as a catalyst to assemble liquid Zn-air batteries (ZABs) and water electrolysis devices, respectively. The performance of ZABs with Co_2-N-HCS-900 surpassed commercial noble metal based ZABs for properties including the open-circuit potential, specific capacity, and peak power density. The Co_2-N-HCS-900-based ZABs also suggested practical application promise with sustained operation for over 600 cycles under a current density of 50 mA cm^{-2}, together with a round-trip efficiency of 58.1% at 5 mA cm^{-2} and a lifespan of over 800 h. The Co_2-N-HCS-900-based water splitting devices can be operated steadily for 1000 h with almost unchanged potential. Finally, the authors prepared a proof-of-concept solar-powered WSS integrating polycrystalline Si solar panels, three tandem ZABs, and water electrolysis devices using Co_2-N-HCS-900 for continuous H_2 production.

In summary, Huang et al. developed a universal strategy applicable to 22 types of metals or their alloys for dual atom catalyst site fabrication. The as-synthesized Co_2-N-HCS-900 with Co_2N_5 dual atoms displayed trifunctionalities with excellent catalytic performance in ORR/OER/HER. The solar-powered WSS constructed based on Co_2-N-HCS-900 enabled continuous H_2 production for over 48 h. Their work provides a deeper understanding of the formation mechanism of dual atom materials as well as a design strategy of multifunctional catalysts for renewable energy production.

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DECLARATION OF INTERESTS

The authors declare no competing interests.