Rationally designed metal and carbon composites for efficient electrocatalysis

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Owing to the significant technological advances during the past few decades, the energy conversion efficiency of photovoltaic (PV) cells has increased dramatically meanwhile the fabrication costs being significantly lowered, which make PV cells the dominant apparatus to harness solar energy in the foreseen future. By admitting that, it needs to be taken into account that solar energy is intermittent, therefore a continuous usage of solar energy will require efficient manners to store the extra-electricity generated by PV cells when the sunlight shines, either in its initial form or the form of other energy carriers, for instance, hydrogen. PV cells powered electrochemical energy conversion systems plays a crucial role in the conversion of solar energy. For instance, PV powered electrolytic water splitting system is capable of converting solar energy to hydrogen (H_2), which can be easily stored, distributed and re-used in a hydrogen fuel cell (1,2). Besides that, PV cells powered electrochemical CO_2 reduction reactions (CO_2RR) not only can store solar energy in the forms of chemical fuels such as CO, formate and methanol, but also reduce the already high concentration of CO_2 in the atmosphere, thereby alleviating the greenhouse effect (3,4). However, the sluggish reaction kinetics of the electrocatalysis processes have rendered these systems energy inefficient and constrained their potential large-scale applications. As a result, earth-abundant material-based catalysts that exhibit high activity as well as stability are highly sought after.

Herein, I will present some of our recent results in tuning the interplay between carbon and metal for highly selective and active electrocatalytic processes. For instance, by wrapping NiCoFe alloyed nanoparticles inside graphitic carbon shells (NiCoFe@C), a versatile catalyst is obtained that exhibits high catalytic activity towards OER, ORR and HER. The encapsulation of the NiCoFe alloyed core induces the electronic structure change of the outer graphitic carbon shell, which tunes the binding strength of reaction intermediates thereby improving the catalytic activity (5). Besides that, Fe atoms embedding inside carbon matrix that are coordinated by nitrogen and phosphorus atoms (FeNPC) are capable of catalyzing the ORR with an onset potential of 1.03 V and a half-wave potential of 0.88 V (both *vs.* the reversible hydrogen electrode) in alkaline solution, outperforming the commercial Pt/C catalyst under identical conditions. Experimental results and theoretical simulations reveal that the *quasi*-octahedral O_2-FeN_xP_y species are the active sites of the FeNPC composite that modify the electronic configuration of Fe centers and weaken the adsorption of the OH* intermediate (6,7). Our study reveals the important role of the carbon/metal interaction in affecting electrocatalytic reactions, and the relation between these interactions and certain reactions has been established. We believe such findings can be used as useful designing guidelines to fabricate cost-effective and highly efficient energy conversion systems that are powered by PV cells, which can be used in small scale and localized applications.

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