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Dual-Coordinated Nickel Single Atoms Stabilized in a Triazine-thiadiazole Based Organic Polymer for the Oxygen Evolution Reaction

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Experimental and theoretical investigations have demonstrated the potential of single atom catalysts (SACs) in driving energy conversion processes. In our previous work, we reported the efficiency of carbon nitride (CN) in stabilizing Ni single atoms. [N. Rossetti, et al. *J. Mater. Chem. A*, 2024, **12**, 6652–6662] Now, we have tried to increase the catalytic activity of the Ni centers by modifying the metal coordination. With this purpose, we have synthesized a new triazine-thiadiazole based organic polymer (SCN) to create dual N-S metal anchoring sites. In this way, we expect to modify the electronic density of the metal center and, therefore, tune its catalytic activity and stability. The polymer was obtained by co-polymerization of cyanuric chloride and 1,3,4-thiadiazole-2,5-diamine following three step of temperature (0, 25 and 140 °C). Subsequently, it was metalated at low temperature to limit the formation of metal aggregates. Transmission electron microscopy and X-ray diffraction characterizations revealed a graphitic-like structure with well exfoliated nanosheets of some hundreds of nanometers. X-ray photoemission spectroscopy confirmed the presence of C, N and S chemical species in the polymer building block. The presence of single Ni atoms was proved by STEM and X-ray absorption spectroscopy. Ni-SCN was tested as oxygen evolution electrocatalyst. Results showed an increase of the activity with the introduction of S in terms of onset potential (50 mV shift towards lower potential) and current density (doubled at 1.7 V vs RHE), respect to Ni-CN. The Tafel analysis revealed a decrease of the Tafel slope from 51.0 mV dec^{-1} to 43.4 mV dec^{-1}, suggesting an effect of the S heteroatom in the catalytic reaction pathway. Therefore, we can conclude that the direct modification of the Ni environment is a good approach to improve the activity and stability of SACs and brings this type of material closer to its industrial application.

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