XAFS study on Cobalt oxide clusters electrocatalyst for overall water splitting

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Electrochemical water splitting, including hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), is considered as the promising technology for renewable energy production. The key aspect is to develop efficient, durable and cheap electrocatalysts, which heavily relies on our understanding of the structure-activity relationships of catalysts. Here, we designed cobalt oxide clusters deposited phosphorous-decorated g-C_3N_4 (CoO_x/PCN) as a high-performance electrocatalyst, and revealed the structure-activity relationships by using XAFS method.

The deposition of CoO_x cluster on PCN was prepared by impregnation of Co precursors followed by pyrolysis reaction. The Co *K*-edge XAFS spectra were measured via transmission mode at 1W1B (BSRF), and the C, O *K*-edge and Co *L*-edge XANES measurements were recorded in the TEY mode at BL12B (NSRL).

The as-obtained CoO_x clusters have uniform size range of 1.5 nm on the PCN, and shows distinct lattice fringe of 2.36 Å that is consistent with the (311) lattice plane of Co_3O_4. Notably, Co K-edge XAFS results revealed the reduced coordination numbers for Co-O coordination, suggesting the unsaturated surface. Furthermore, the Co *L*-edge and O *K*-edge spectra revealed a higher electron density at the O site and a lower electron density at the Co site, probably due to the hybridization effect. Therefore, the XAFS results validate the strong coupling effect between CoO_x and PCN, hence changing the atomic and electronic structures that would bring to the enhanced performance. The resulting hybrid catalyst exhibits excellent overall water splitting activity, reaching 10 mA cm^{-2} current by applying a low voltage of 1.58 V for 10 h. Remarkably, the CoO_x possesses outstandingly intrinsic activity, delivering turnover frequency of 1.69 O_2 s^{-1} and 1.53 H_2 s^{-1} at an overpotential of 300 mV, which are the best among those catalysts reported for water electrolysis.

In summary, the CoO_x clusters were developed for the first time as bifunctional electrocatalysts for overall water splitting. XAFS method combined with first-principles calculation revealed the fact that unsaturated-coordination surface with oxygen vacancies and the strong coupling effect optimizes OH^- and H_2O adsorption energy for OER and HER, respectively, thus retaliating efficient electrocatalytic water splitting.

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