The Rougher the Better

The yield of ammonia is improved by controlling the surface shape of the electrocatalyst.

The Haber-Bosch process is still the main method for mass production of industrial ammonia (NH_3). This chemical reaction involves hydrogenation of nitrogen under high temperature and high pressure, for which the raw materials are hydrogen (H_2) and nitrogen (N_2). In the process of obtaining hydrogen, much carbon dioxide is produced, thereby causing serious environmental issues. An important issue is hence to find another method for NH_3 synthesis. Electrochemical N_2 reduction reaction (NRR) is an efficient and sustainable route to convert N_2 to NH_3. The NRR performance is restricted mainly by the poor adsorption and activation of N_2 on catalysts because of the strong N≡N bond and low proton affinity of N_2. There are several ways to improve the efficiency of the electrochemical NRR of electrocatalysts such as size control, composition regulation, defect engineering and ion incorporation, but the effect of surface shape of the electrocatalysts plays an important role in the NRR efficiency. So far, there is no evidence that the surface shape of an electrocatalyst is an important factor affecting the efficiency of NRR.

Xiaoqing Huang's group from Wuhan University in China has synthesized surface-rough Rh_2Sb nanorods (RNR) with high-index facets and surface-smooth Rh_2Sb nanorods (SNR) through hydrothermal synthesis for electrochemical NRR. The NH_3 yield rates of RNR and SNR are 222.85 ± 12.96 and 63.07 ± 4.45 $\mu g h^{-1} mg^{-1}_{Rh}$ at -0.45 V_{RHE}, respectively, which indicate the effectiveness of surface regulation.

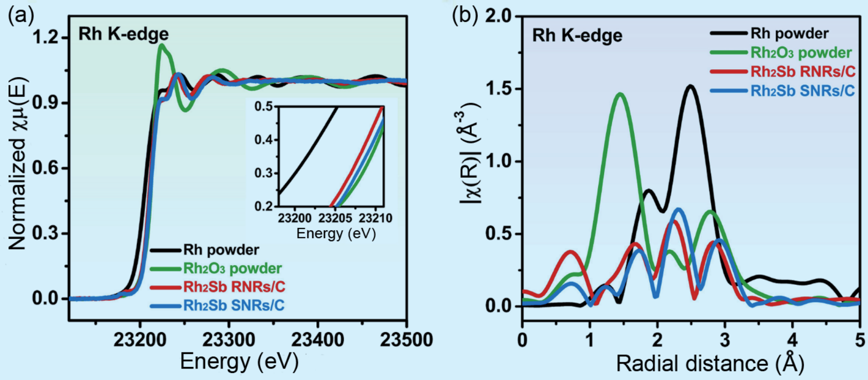

Fig. 1: (a) Normalized XANES spectra and (b) Fourier transform of k^2-weighted EXAFS spectra at the Rh K-edge of Rh powder, Rh_2O_3 powder, Rh_2Sb RNR/C and Rh_2Sb SNR. [Reproduced from Ref. 1]

These workers also recorded X-ray-absorption fine-structure spectra at **TPS 44A1** of NSRRC to investigate the local structure of RNR and SNR on an atomic scale. The Rh K-edge X-ray-absorption near-edge-structure (XANES) (**Fig. 1(a)**) spectra show the coexistence of Rh atoms as metal and in oxidation states; the oxidized Rh is dominant. Moreover, the energy shifts of the white-line absorption edge at the Rh K-edge between the RNR and SNR indicates that the valence state for Rh in RNR is lower than in SNR. The Rh K-edge extended X-ray-absorption fine-structure (EXAFS) spectra (**Fig. 1(b)**) reveal the coordination number around Rh atoms in the RNR sample to be much smaller than in the SNR sample. These results indicate that Rh with unsaturated coordination would be more conducive to activation of small molecules resulting in an enhanced adsorption and activation of N_2 on RNS samples.

In summary, in this work has been synthesized unique Rh_2Sb nanorods with surface-rough and surface-smooth for the first time. The yield rate of electrocatalytic NRR indicate that the surface shape of the electrocatalyst is an important factor affecting the efficiency of NRR. This finding provides a new strategy for creating efficient NRR electrocatalysts. (Reported by Chih-Wen Pao)

This report features the work of Xiaoqing Huang and his collaborators published in Angew. Chem. Int. Edit. ***59****, 8066 (2020).*

TPS 44A Quick-scanning X-ray Absorption Spectroscopy

- XANES, EXAFS, *In-situ/Operando*
- Materials Science, Chemistry, Physics, Environmental Science

Reference

1. N. Zhang, L. Li, J. Wang, Z. Hu, Q. Shao, X. Xiao, X. Huang, Angew. Chem. Int. Edit. **59**, 8066 (2020).