The structure of Pt /CoO(OH) photocatalyst

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Photocatalytic hydrogen evolution based on semiconductor(photocatalyst)-noble metal(cocatalyst) systems has been widely considered as a green and promising approach to convert solar energy into chemical energy. Pt-CoOOH nanosheet has a high photocatalytic water splitting performance.[1,2] The CoOOH nanosheet (with bandgap of ~2.5 eV) covers the ultraviolet- and visible-light regions, and their unique 2D nanosheet features could provide sufficient room for Pt nanoparticles. In order to reveal the catalyst structure, we carried out the XAFS measurements.

Quick transmission-mode XAFS measurements for our CoOOH and Pt-CoOOH samples were performed at BL11S2 XAFS station of Aichi Synchrotron Radiation(SR). The EXAFS data of the samples were analyzed by Athena software to determine the atomic structures.

The Co *K*-edge XANES of CoOOH nanosheet shows an absorption-edge energy position of about 7725 eV, very close to that of the CoOOH reference supplied by Aichi-SR in BL11S2 station (Figure 1a). Moreover, CoOOH nanosheet has a similar oscillatory trend in k-space (Figure 1b) and similar Fourier transform in R-space (Figure 1c) to that of the CoOOH reference. These results indicate the successful synthesis of pure CoOOH phase. HRTEM(High Resolution Transmission Electron Microscopy) indicated the presence of CoOOH nanosheet.

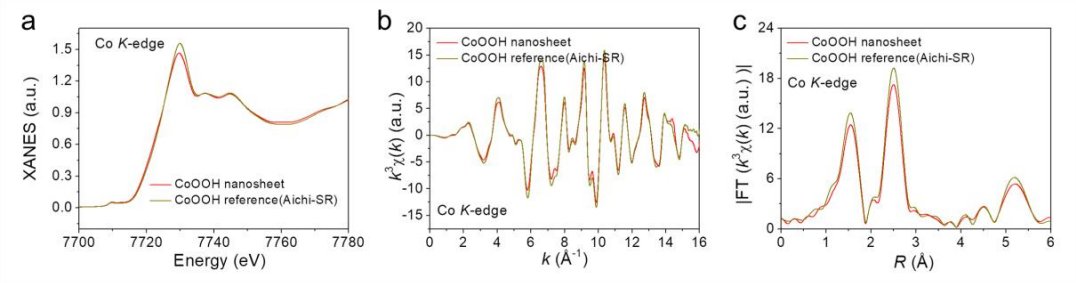

Figure 1. (a) Co *K*-edge XANES spectra, (b) Co *K*-edge $k^3\chi(k)$ oscillations and (c) corresponding Fourier transforms for CoOOH nanosheet and CoOOH reference.

Figure 2a shows that the Pt L_3-edge white-line peak of Pt-CoOOH which has a similar intensity to that of PtO_2 reference compound, indicating the presence of Pt^{4+} species in Pt-CoOOH. Moreover, Pt-CoOOH has a similar EXAFS oscillation trend to that of PtO_2 reference compound in the k range of 2-8 Å (Figure 2b), and there is a peak around 1.67 Å for Pt-CoOOH in its R space (Figure 2c). The XAFS results demonstrate the dominant presence of the atomically-dispersed Pt in Pt-CoOOH sample. Co *K*-edge shows little modification of CoOOH local structure.

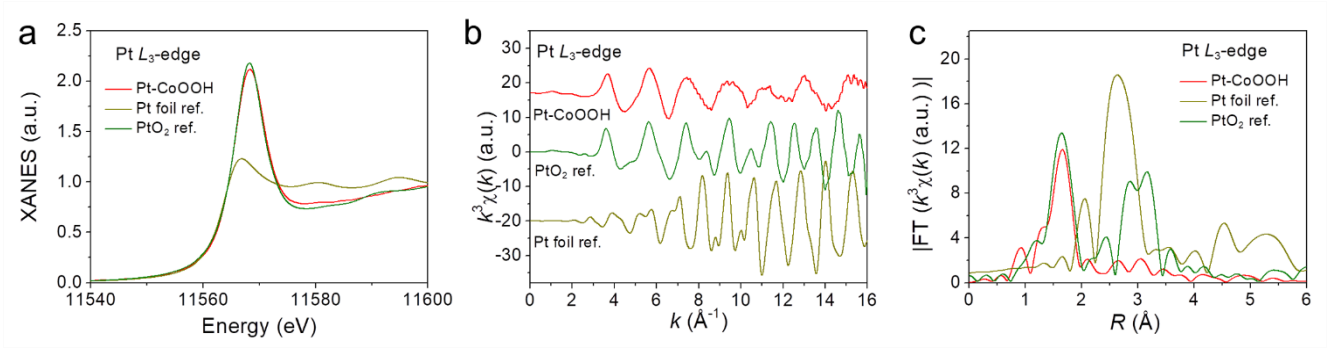

Figure 2. (a) Pt L_3-edge XANES spectra, (b) Pt L_3-edge $k^3\chi(k)$ oscillation curves and (c) corresponding Fourier transform curves for Pt-CoOOH, PtO_2 and Pt foil as reference.

In summary, the XAFS measurements and other analyses have demonstrated that the prepared CoOOH has a CoOOH nanosheet structure, and the Pt species are mainly in the form of atomically-dispersed Pt $^{4+}$ species in Pt-CoOOH.

[1] 1J. Huang, Q. Shang, Y. Huang, F. Tang, Q. Zhang, Q. Liu, S. Jiang, F. Hu, W. Liu, Y. Luo, T. Yao, Y. Jiang, Z. Pan, Z. Sun, S. Wei, *Angewandte Chemie International Edition* **2016**, *55*, 2137-2141 https://doi.org/10.1002/anie.201510642.

[2] F. Tang, W. Cheng, H. Su, X. Zhao, Q. Liu, *ACS Appl. Mater. Interfaces* **2018**, *10*, 6228-6234 https://doi.org/10.1021/acsami.7b15674.