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臨場分析技術應用於分析人工光合作用之催化中間態 Analyzed intermediate of electrocatalyst toward artificial photosynthesis by in-situ mythology

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研究重點

For electrocatalysts, the key factor of activity is the intermediate state of catalyst. Hence, my research focused on determining the intermediate toward artificial photosynthesis by both in-situ XAS and XRD. For the anode part, metal oxides of the spinel family have shown great potential. By utilizing several in situ analyses, we could conclude a universal rule that the activities for OER in the metal oxide systems were determined by the occurrence of a phase transformation, and this structural transformation could work well in both crystallographic sites (Td and Oh sites). In addition, the phase transition would happen within the non-oxide catalyst, the reactive species that are really in charge of the target reactions are evidently not the initial phases in alkaline electrolyte. After determining the real phase during reaction, the mechanism of OER can also be revealed by in-situ XAS. A new catalyst which is made of nanoclusters of γ -FeOOH covalently linked to a γ -NiOOH support may allow a reaction path involving iron as the oxygen evolving center and a nearby terrace O site on the γ -NiOOH support oxide as a hydrogen acceptor, and it can achieve higher activity. On the other hand, In situ XAS revealed the active sites to be discrete Fe³⁺ ions, coordinated to pyrrolic nitrogen (N) atoms of the N-doped carbon support, that maintain their +3 oxidation state during CO₂ reduction, probably through electronic coupling to the conductive carbon support. Electrochemical data suggest that the Fe³⁺ sites derive their superior activity from faster CO₂ adsorption and weaker CO adsorption than that of conventional Fe²⁺ sites. Besides, the stability of atomically dispersed type catalyst can also be revealed. In iron case, the oxidation state would be reduced under higher applied voltage. And the same situation would also happen in another element. The Cu atom would assemble into cluster after -0.8V, and the selectivity of product would be reduced at this potential. It can be realized that the selectivity displayed as Cu cluster rather than atomically dispersed Cu. In summary, in-situ method can reveal the intermediate of catalyst efficiently and can understand the factor to the activity.

研究成果

Valence- and element-dependent water oxidation behaviors: in situ X-ray diffraction, absorption and electrochemical impedance spectroscopies

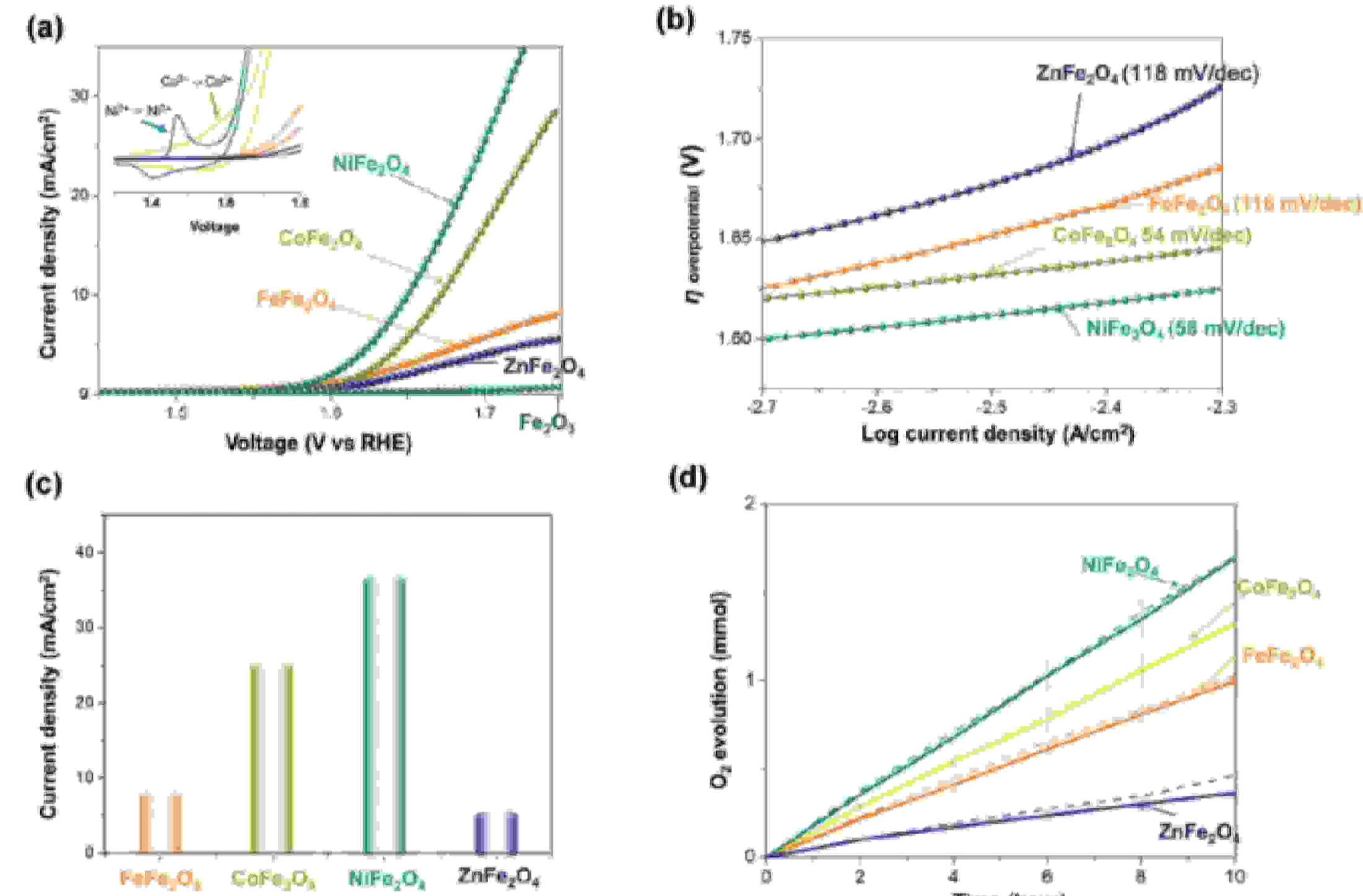


Fig. 1 Electrochemical performance and gas evolution for a series of samples of MFe₂O₄ (M = Fe, Co, Ni, Zn). (a) OER polarization curves were performed upon a RDE system in alkaline electrolyte (0.5 M KOH; pH 13.6). Inset: Cyclic voltammogram of each sample. (b) Steady-state Tafel (overpotential vs. log current density) measurements in alkaline electrolyte. (c) Comparison of current density from OER polarization curves were determined at Z = 0.43 V. (d) Oxygen gas evolution (solid line) with the error bar and the charge throughout the circuit (dashed line) for each sample. Uncertainties are standard deviation of five identically measurements, standard deviation are plotted as error bars.

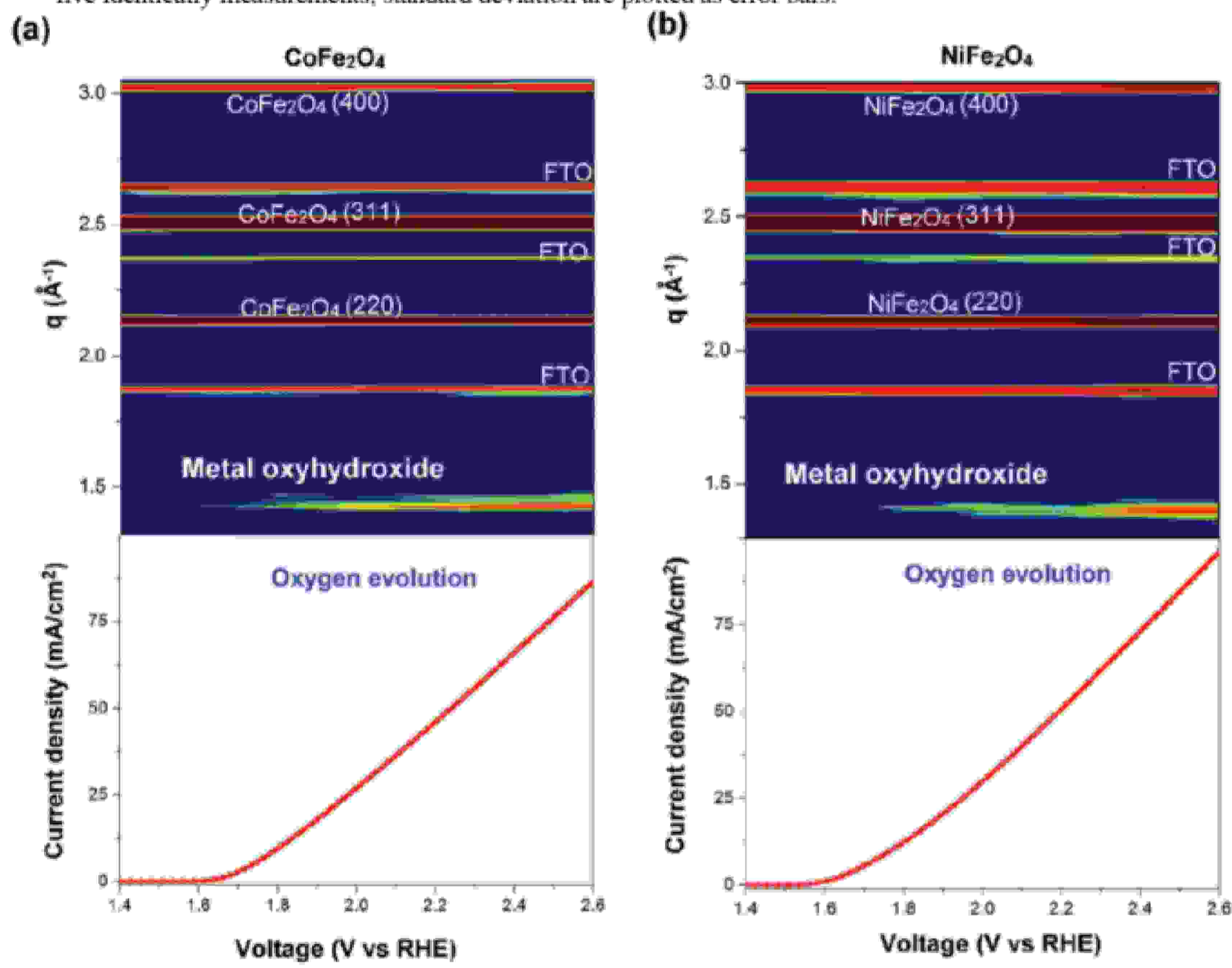


Fig. 2 Contour plots of in situ grazing-angle X-ray diffraction signals of CoFe₂O₄ and NiFe₂O₄ samples in an aqueous solution with relevant current density as function of applied voltage in both cases.

研究生活與心得

我自碩班開始我的研究生涯，我的研究主題核心為透過臨場技術的分析，需要用到大量的同步輻射技術，而除了同步輻射的技術外，我也致力於發展臨場電化學穿透式電子顯微鏡，透過光譜能有效了解催化劑的性質變化，而顯微鏡則能看出催化劑的形貌變化，結合這兩個技術就能更完整的描述催化過程，雖然在臨場電化學穿透式電子顯微鏡會遇到許多問題要克服，但在慢慢摸索的過程中慢慢的到可用的數據那是最振奮人心的；在這段期間除了自己研究的主題外，也很高興能有機會和其他老師的合作，在這些合作的過程中我覺得是最好的學習機會，可以累積自己的經驗以及對數據的判斷及解析，然而在這些經驗外也讓我覺得還有許多地方仍然不足，在接下來的求學過程希望能更加充實我的知識及技術，也希望能在學術期刊的發表上能有更好的成績，非常感謝我的指導教授的支持以及中技社對我的肯定，這對於現階段的我而言是最好的鼓勵。

Operando Unraveling of the Structural and Chemical Stability of P-Substituted CoSe₂ Electrocatalysts toward Hydrogen and Oxygen Evolution Reactions in Alkaline Electrolyte

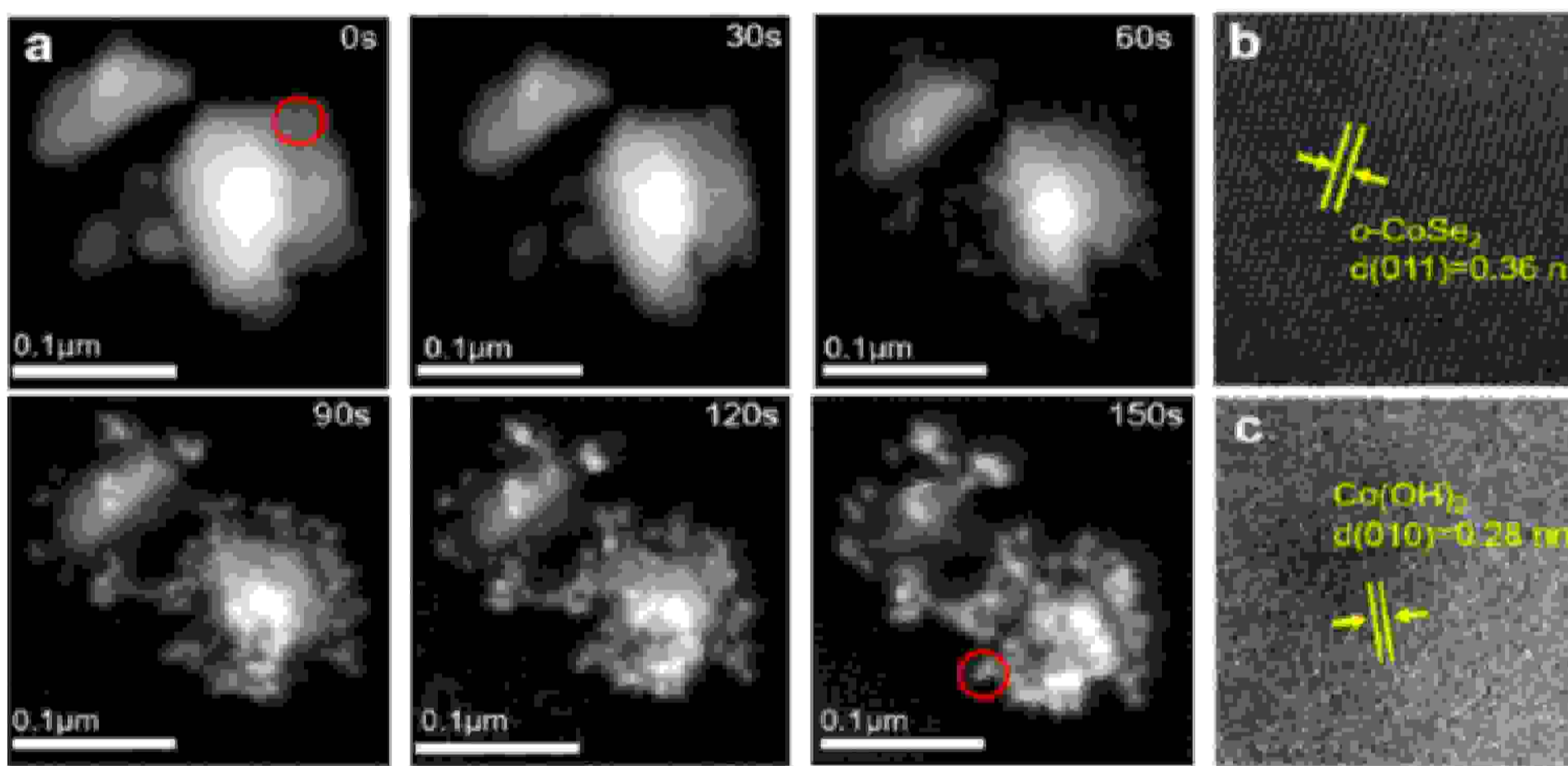


Fig.3. (a) In situ STEM images of the CoSe_{1.26}P_{1.42} catalyst taken at different times after immersing in the KOH solution. HRTEM images of the selected region of the (b) initial and (c) final state of the CoSe_{1.26}P_{1.42}.

An Unconventional Iron Nickel Catalyst for the Oxygen Evolution Reaction

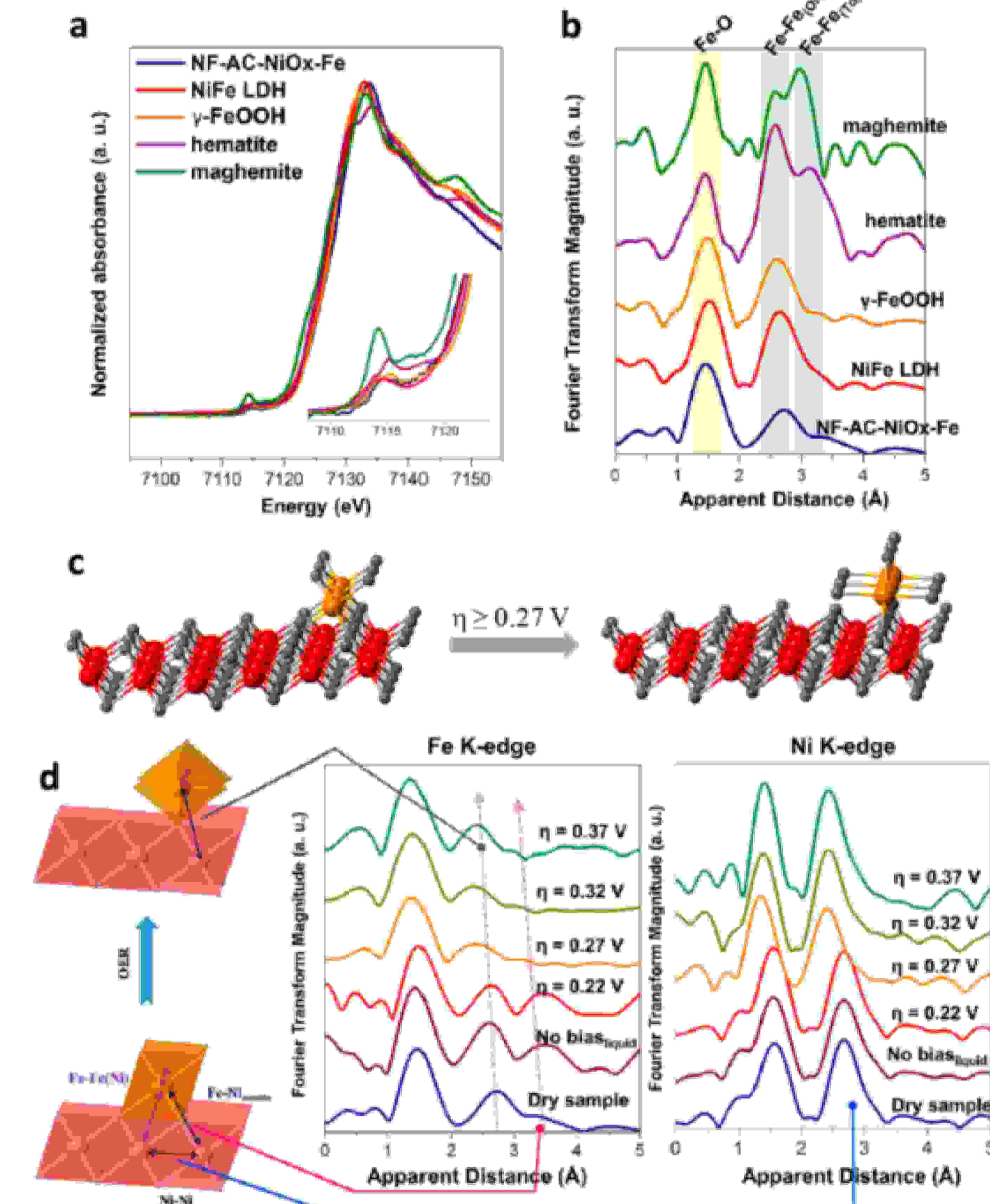


Fig.4. In situ X-ray absorption spectroscopy. (a) XANES spectra, inset shows the pre-edge features of all spectra. (b) Fourier transform of Fe K-edge EXAFS spectra for NF-AC-NiOx-Fe and the corresponding references. (c) Proposed structural model of NF-AC-NiOx-Fe showing γ -FeOOH sitting on the surface of NiOOH; upon application of an overpotential of more than 0.27 V the structure reorganizes with a tilt. (d) In situ FTXAFS spectra of Fe K-edge and Ni K-edge for Au-NiOx-Fe during the OER.

Atomically dispersed Fe³⁺ sites catalyze efficient CO₂ electroreduction to CO

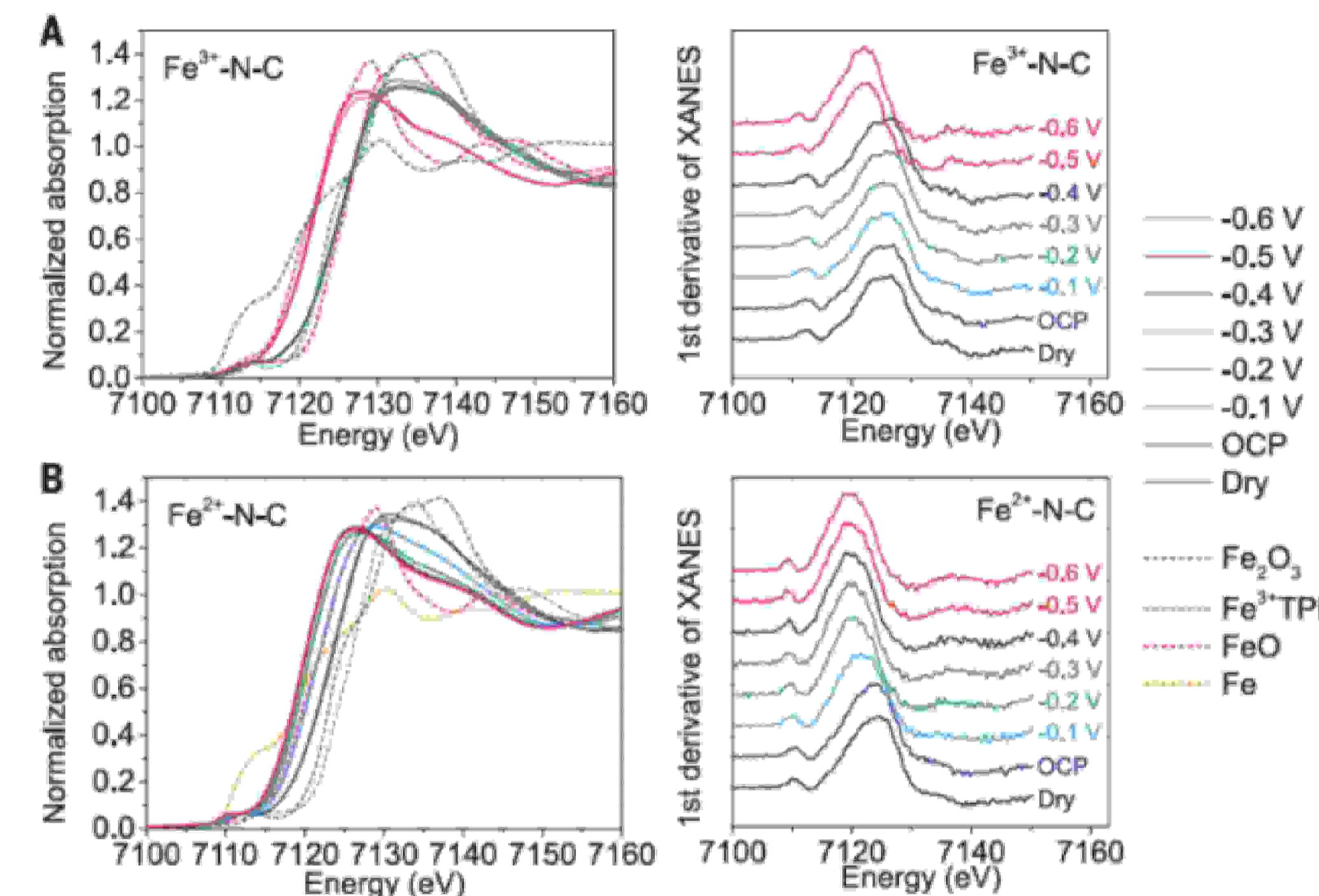


Fig.5. Operando XAS characterization. Fe K-edge XANES spectra (left) and the 1st derivative of the spectra (right) of (A) Fe³⁺-N-C and (B) Fe³⁺-N-C as dry powder (black), and loaded on glassy carbon electrodes at open circuit potential (OCP, blue), -0.1 V (light blue), -0.2 V (green), -0.3 V (dark green), -0.4 V (dark blue), -0.5 V (red) and -0.6 V (pink) vs RHE, with the spectra of Fe₂O₃ (blue dashed), Fe³⁺TPPCI (green dashed), FeO (pink dashed) and Fe foil (orange dashed) as references.

The stability of atomically dispersed Cu toward CO₂ reduction

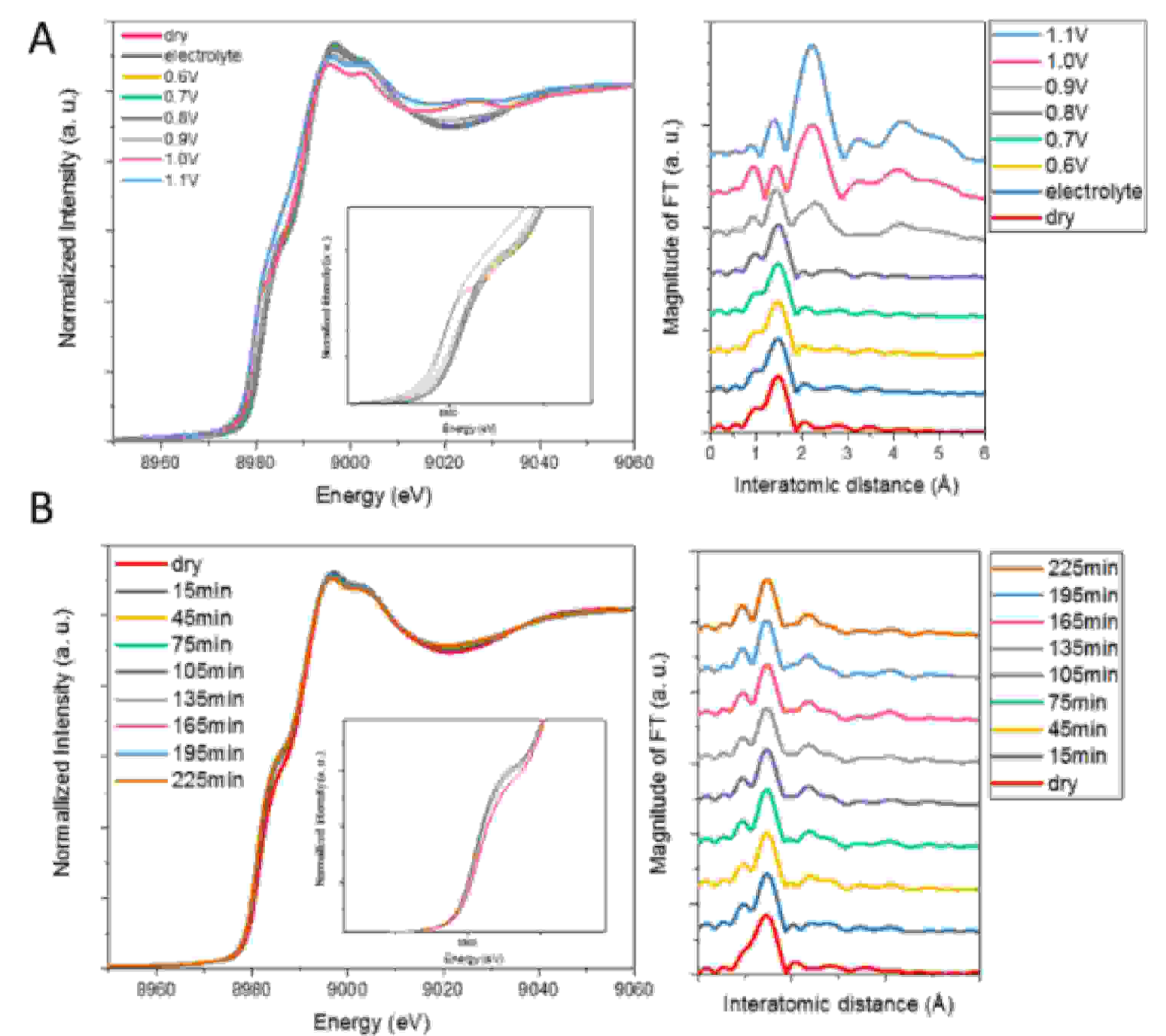


Fig.6. Operando XAS characterization. Cu K-edge XANES spectra (left) and Fourier transform of Cu K-edge EXAFS spectra for Cu-N-C (A) under different potential (B) under constant potential of -0.8V.