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In Situ TEM Observation of Spinel-Structured $ZnFe_2O_4$ as a Low-Temperature CO_2 Splitting Agent

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Carbon dioxide (CO_2) is a greenhouse gas and its continuous increase in the atmosphere results in the global warming issue. An appealing solution to alleviate CO_2 emissions is to convert them into value-added products such as fuels and daily chemicals products [1]. One of the methods to convert CO_2 into CO by breaking the strong C=O bond is called solar-driven thermochemical CO_2 reduction [2]. Take redox metal oxides (MO_x) as an example and the two steps of CO_2 splitting are as follows:
MO_x + solar energy = MO_{x-y} + y/2 O_2; MO_{x-y} + y CO_2 = MO_x + y CO
However, this process requires a very high operation temperature [3]. Herein, we demonstrate a low-temperature CO_2 splitting method by using zinc ferrite ($ZnFe_2O_4$) with hydrogen:
MO_x + yH_2 = MO_{x-y} + y H_2O; MO_{x-y} + y CO_2 = MO_x + y CO

Nowadays, the *in situ* scanning transmission electron microscopy (STEM) technique is widely applied to characterize the morphology and property changes of catalysts in real-time by introducing light, heat signals, electricity and gas during the measurement. In this work, we performed the *in situ* gas (S)TEM to study $ZnFe_2O_4$ nanoparticles in the CO_2 reduction process. The experiment was conducted using Norcada's micro-electromechanical systems (MEMS)-based chips in Hitachi Blaze heating-gas holder (Figure 1a) in operando inside an environmental transmission electron microscope (ETEM, Hitachi HF-3300). The low-magnification STEM-bright field (BF) image in Figure 1b illustrates the distribution of $ZnFe_2O_4$ nanoparticles at room temperature. The experimental details of the CO_2 reduction process are shown in Figure 1c, and all the reactions occurred at 300 °C. From the high-resolution TEM (HRTEM) images in Figures 2a and b, the lattice extracted from the particle center region remains at about 2.55 Å during the redox reactions. Interestingly, when the nanoparticles are exposed to H_2, the lattice expands to 2.700 Å at the surface region and then shrinks to the original value in the CO_2 atmosphere.

In addition to the structural changes, the dynamic observation of chemical reactions could be also achieved by combining STEM with electron energy-loss spectroscopy (EELS). Since the relative intensities of the Fe L_3 and L_2 white lines are related to the electronic state of Fe, the intensity ratio (L_3/L_2) can be used to measure the oxidation number of Fe. As shown in Figures 2c and d, the calculated intensity ratio decreases to 4.04 in H_2 and then increases to 4.64 in CO_2. This result indicates that H_2 can partially reduce the Fe(III) to Fe (II) on the sample surface, while the original oxidation state of Fe can be recovered when exposing to the CO_2 environment as a result of a CO_2 reduction reaction. Therefore, our findings suggest that $ZnFe_2O_4$ can be used as a cost-effective material for low temperature CO_2 conversion [4].

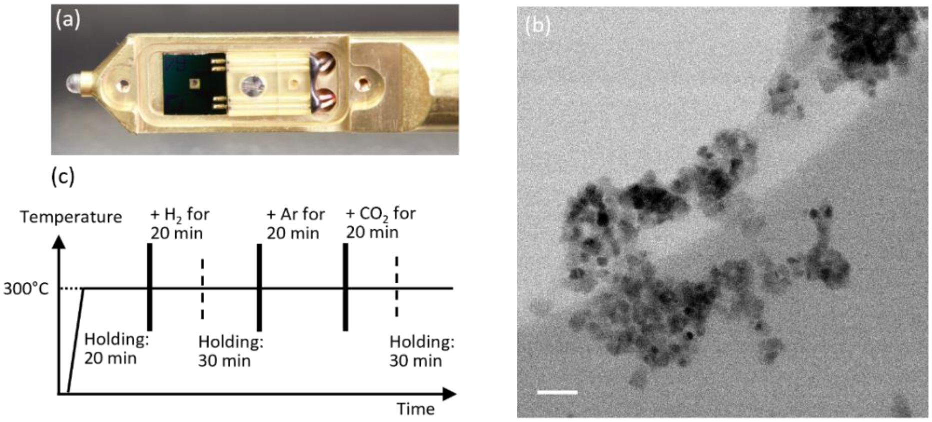

Figure 1. (a) Hitachi Blaze heating-gas holder with a Norcada MEMS heating chip. (b) The STEM-BF image of $ZnFe_2O_4$ nanoparticles. Scale bar: 50 nm. (c) The temperature profile from the *in situ* gas TEM experiment.

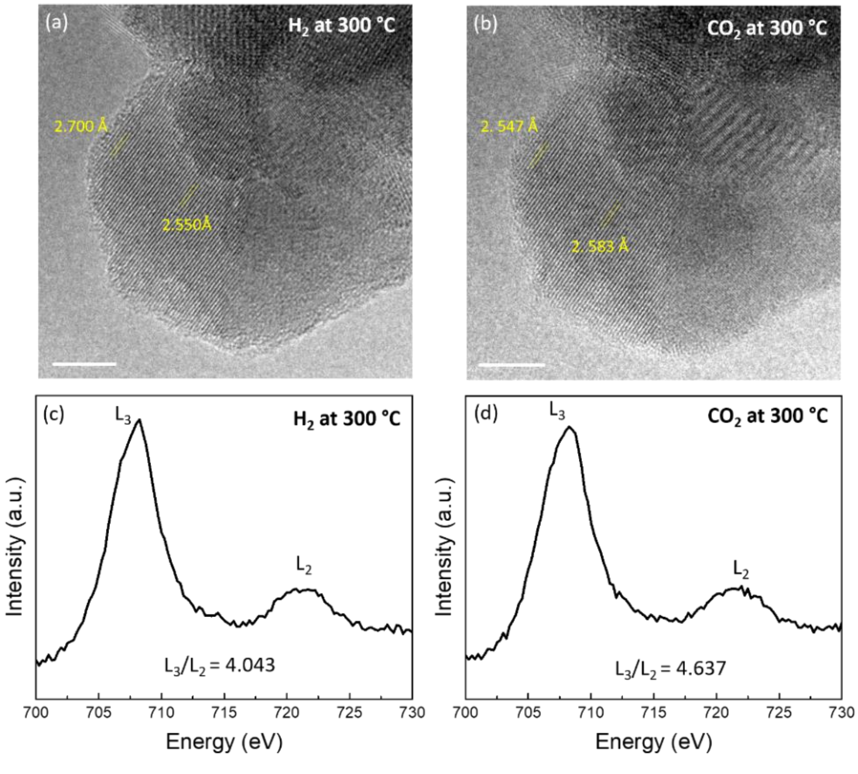

Figure 2. (a,b) The HRTEM images of $ZnFe_2O_4$ nanoparticles when exposed to H_2 and CO_2 at 300 °C, respectively. Scale bars: 5 nm. (c,d) The Fe EEL spectra extracted from the $ZnFe_2O_4$ nanoparticles when exposed to H_2 and CO_2 at 300 °C, respectively.

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