Preparation of Cu-doped TiO_2 catalyst for electrochemical CO_2 reduction

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Electrochemical reduction of CO_2 (ECO_2R) has recently attracted attention as a highly useful technology for CO_2 recycling. Cu exhibits high activity for ECO_2R[1] but still suffers from unsatisfactory selectivity towards CH_4, which is an extensively used fuel having a high energy density. CH_4 formation proceeds by the addition of 8 electrons and 8 protons to CO_2 ($CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$). In this process, CH_4 formation is thought to occur via *CHO formation by protonation of *CO. The *CHO formation competes with both the C-C coupling of two *CO and hydrogen evolution reaction (HER), which makes it difficult to achieve a highly selective ECO_2R to CH_4. The construction of isolated Cu sites has been found to effectively improve the selectivity for CH_4 production by suppressing the unfavorable C-C coupling.[2] In this study, we develop Cu-doped TiO_2 electrocatalysts presenting isolated Cu sites with high dispersion for the selective CH_4 production and examine their ECO_2R activity in detail.

Precursors of TiO_2 and Cu-doped TiO_2 (Cu-TiO_2) were prepared via a one-pot solvothermal method and calcined under air or H_2 atmosphere to obtain the desired TiO_2-y and xCu-TiO_2-y samples, where x and y are the doping amount of Cu (wt.%) and the calcination atmosphere, air or H_2. X-ray diffraction (XRD) patterns of xCu-TiO_2-y samples (x = 0–5 wt.%) showed characteristic diffraction pattern attributable to the formation of anatase TiO_2 with a few weight percentage of brookite TiO_2 without no intensity from crystaline Cu. Fig. 1 shows high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of the 3Cu-TiO_2-H_2 sample. Cu species with sizes of 1–3 nm, which are appeared as white dot-like objects, were well dispersed over a TiO_2 grain, indicating that isolated Cu clusters are formed on 3Cu-TiO_2-H_2. LSV measurements in CO_2-saturated KOH solution showed the reduction current, indicating that both 3Cu-TiO_2-air and 3Cu-TiO_2-H_2 exhibit ECO_2R activity (Fig. 2). The current density of hydrogen-treated 3Cu-TiO_2-H_2 was higher than that of the other samples, which suggests that hydrogen treatment increases the ECO_2R activity.

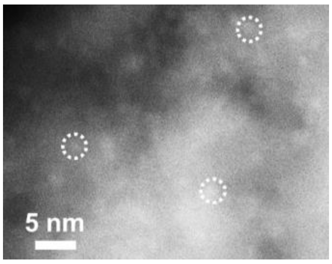

Fig. 1. HAADF STEM image of 3Cu-TiO_2-H_2. A few of clusters are highlited with a dotted circle.

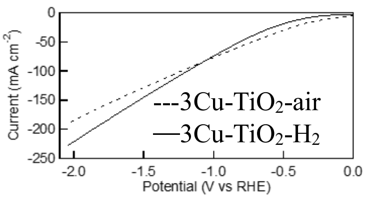

Fig. 2. LSV curves measured in a CO_2-saturated 1 M KOH.

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