Narrative Progress Report

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Enhancing Cu Nanowire Catalysis for Selective Electrochemical Reduction of CO_2 to Ethylene

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This proposal focuses on studying Cu nanowire (NW)-based catalyst for selective electrochemical reduction of CO_2 to ethylene ($H_2C{=}CH_2$ or C_2H_4). C_2H_4 is widely used in chemical industry and is a starting material for many reactions, such as polymerization, oxidation, halogenation and drohalgenation, alkylation, and hydroformylation. Previous studies have indicated that single crystal Cu(100) is more selective for the reduction of CO_2 to C_2H_4, but CH_4 is always co-produced in previous studies on Cu-catalyzed CO_2 reduction. Here we propose to synthesize Cu NWs surrounded by (100) planes to maximize (100) area and to further enhance Cu catalysis for C_2H_4 formation.

We prepared Cu NWs by the reduction of CuCl in a heated oleylamine solution. In the process, oleylamine served both as a reducing agent (to reduce CuCl to Cu) and a NW stabilizer. We obtained 25 nm and 50 nm wide Cu NWs by controlling the heating temperature in the reaction process. **Figure 1** shows transmission electron microscopy (TEM) images of two kinds of Cu NWs we prepared. They are in micrometer long with an average dimeter of 25 nm (**Figure 1A**) or 50 nm (**Figure 1B**). We performed the electrolysis of CO in a conventional H-cell (separated by Nafion 212) filled with 0.1 M $KHCO_3$ solution (pH = 8.3) by bubbling CO at room temperature. The gaseous products analyzed by gas chromatography (GC) contained C_2H_4, C_2H_6 and H_2 with net total Faradaic efficiency (FE) at 100%±3%. There was no liquid product that could be detected by ^1H NMR. The 50 nm Cu NWs showed the maximum FE of C_2H_4 + C_2H_6 at 60%. When CO was replaced by CO_2, the reduction still yielded C_2 products (C_2H_4 + C_2H_6) but with lower FE's (<20%). In this reduction process, trace amount of CO was also detected (FE below 0.5%).

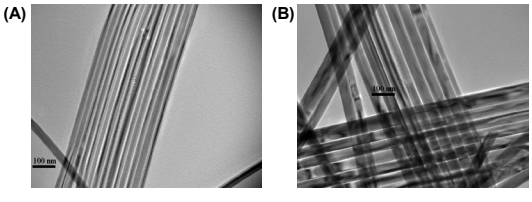

Figure 1. TEM images of (A) 25 nm and (B) 50 nm wide Cu NWs.

Reasoning that Cu NWs can catalyze CO reduction more selectively to C_2H_4, and Au NPs are selective for CO_2 conversion to CO, we made nanocomposites of 50 nm Cu NWs and 8 nm Au nanoparticles (NPs) by anchoring Au NPs on the NW surface (**Figure 2**). Testing the catalysis of Au-Cu composite catalyst for the CO_2 reduction, we found that CO was the main product at low reduction potentials, but at higher reduction potentials, more multi-carbon products were produced and FE's for liquid products and gas multi-carbon products were increased with the reduction potentials. For example, at -0.5 V, the total FE of carbon products is at 80%, among which 70% belongs to the formation CO, while at -0.9 V, the total FE of carbon products reaches 90% with C2 (C_2H_4, CH_3CHO and CH_3COOH) product FE at 50%. Interestingly, CH_3CHO dominates the liquid phase product with 75% selectivity.

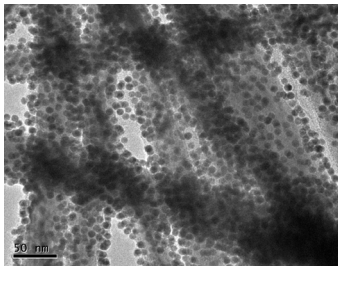

Figure 2. TEM image of the Au-Cu nanocomposite catalyst with Au NPs anchored on Cu NW surface for CO_2 reduction.

To further improve Cu-catalysis for the CO_2 reduction to C_2H_4, we tested Cu_3N nanocubes as a new catalyst for CO_2 reduction. These Cu_3N nanocubes were prepared by reductive decomposition of $Cu(NO_3)_2 \cdot 3H_2O$ in oleylamine. By controlling reaction times and temperatures, we could tune the nanocube sizes from 10 nm to 50 nm. Studying Cu_3N catalysis for the CO_2 reduction in the same reaction condition as described above, we found 25 nm Cu nanocubes (**Figure 3**) to be especially active and selective for the CO_2 reduction with C_2H_4 being the main gas product (60% FE) (CH_4 is minor product and C_2H_4/CH_4 ratio > 2000) and HCOOH (33% FE) and CH_3CH_2OH (5.7% FE) dominating the liquid products.

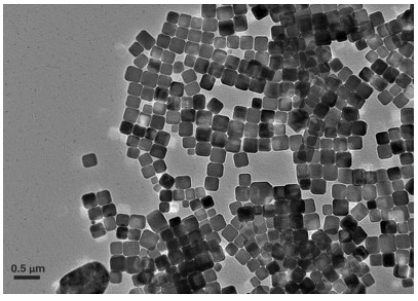

Figure 3. TEM image of the as-synthesized 25 nm Cu_3N nanocubes used for electrochemical reduction of CO_2.

In summary, our ACS-PRF studies have led to the development of three interesting catalyst systems based on Cu: Cu NWs, Au-Cu NWs, and Cu_3N nanocubes. 50 nm Cu NWs are more selective for the CO reduction to $C_2H_4 + C_2H_6$ (60% FE) than for the CO_2 reduction (< 20% FE). Anchoring Au NPs on the 50 nm Cu NWs improves the composite catalysis for the CO_2 reduction with a total carbon product FE at 90% and C2 (C_2H_4, CH_3CHO and CH_3COOH) product FE at 50%. CH_3CHO dominates the liquid phase product at 75% selectivity. 25 nm Cu_3N nanocubes are the best catalyst for selective CO_2 reduction C_2H_4 with the FE reaching 60% and that of liquid $HCOOH/CH_3CH_2OH$ at 38.8%.

The work was initiated by my former postdoc Qing Li, who now is Professor of Materials Sciences and Engineering of Huazhong University of Technology of China. My former graduate student Hongyi Zhang, who now works as an analyst for a non-profit organization in New York City, then took over and demonstrated the catalysis of Cu NWs for CO and CO_2 reduction. She also collaborated with a visiting student, Jiaju Fu, of Nanjing University and graduate students in my group, Zhouyang Yin and Yuyang Li, on demonstrating the synergistic effect between Au and Cu NWs for selective CO_2 reduction to hydrocarbons. The work was raised to a new level by my current graduate student, Zhouyang Yin, on demonstrating Cu_3N nanocubes to be an efficient catalyst for CO_2 reduction to C_2H_4.