Endotaxially Anchoring Metal/Alloy Nanoparticles for Methanol Synthesis and Steam Reforming

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The main objective of this proposed research focuses on developing highly active and stable catalysts for low temperature methanol synthesis and steam reforming. Methanol is a feedstock for the plastics industry and an important intermediate for fuels and bulk chemicals. Methanol steam reforming (MSR) is a promising technology for producing hydrogen for onboard fuel cell applications. Copper-based catalysts, especially when enhanced by the use of promoters (e.g., ZnO, CeO_2, etc.), can effectively convert methanol into hydrogen and carbon dioxide or for synthesis of methanol from syngas. The reaction rate for MSR and methanol synthesis is proposed to depend on the interactions between the promoters and the Cu surfaces as well as the number of the available interfacial active sites. In our last reporting period, we synthesized ZnO nanowires and investigated the performance of ZnO nanowire supported Pd and Cu nanoparticle catalysts for MSR. During this reporting period, we scaled up the synthesis and purification processes of pentagonal Cu nanowires and utilized these Cu nanowires as templates to fabricate Cu_2O and CuO nanotubes with ultrathin walls. Such copper oxides possess high surface area and can be used to synthesize catalysts for methanol synthesis and reforming. The stability of the synthesized Cu nanowires, Cu_2O and CuO nanotubes under different gas environment was evaluated. By dispersing ZnO and CeO_2 nanoparticles onto the synthesized Cu nanowires and Cu_2O nanotubes we fabricated ZnO/Cu nanowire and CeO_2/Cu_2O nanotube reverse catalysts and evaluated their performance for MSR. The goal is to identify the catalytically active sites and to explore the key parameters that control the catalytic properties of the active sites for both methanol synthesis and reforming.

Figure 1 shows the schematic diagrams for synthesizing ultrathin wall Cu nanotubes. The pentagonal shaped Cu nanowires were synthesized by a solution process with the use of hexadecylamine (HDA) as capping agent. A rapid thermal annealing of the synthesized Cu nanowires was conducted to eliminate the HAD capping molecules and to produce a thin layer of Cu_2O on the surfaces of the Cu nanowires. The thickness of the Cu_2O shell is determined by the annealing temperature and period. After the rapid thermal annealing, the produced Cu_2O@Cu shell-core nanowires were soaked into a solution containing hexadecyltrimethylammonium bromide (CTAB) for preferential etching of Cu^0 (to form $CuBr_2^-$) from the inner Cu nanowire and redeposit it on the external surfaces of the Cu_2O shells. Such a local corrosion process continues until all the Cu^0 were transported out to the external surfaces of the Cu_2O shells and redeposit as amorphous-like $CuO_x/Cu(OH)_2$ nanoparticles. The redeposited, amorphous-like $CuO_x/Cu(OH)_2$ nanoparticles can be dissolved into the aqueous solution by lowering the solution pH to about 6.0. We found that prolonged soaking time and use of more acidic aqueous solutions can degrade or destroy the crystalline Cu_2O thin shells. The wall thicknesses of the fabricated Cu2O nanotubes are controlled by the rapid thermal annealing process and influenced by the electrochemical corrosion process. Porous Cu_2O nanotubes can be produced as well although these porous nanotubes become fragile. The fabrication of CuO nanotubes can be easily accomplished by a mild calcination of the Cu_2O nanotubes.
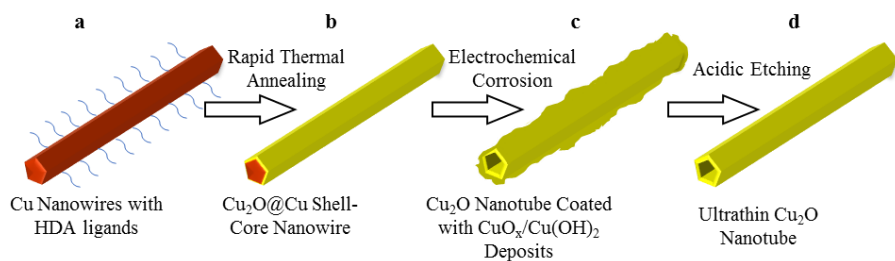

Figure 1. Schematic diagrams illustrate the synthesis processes of fabricating ultrathin-wall Cu_2O nanotubes: a) pentagonal Cu nanowire coated hexadecylamine (HDA) capping molecules, b) rapid thermal annealing to produce a thin layer of Cu_2O on the Cu nanowire and to eliminate the HDA capping molecules, c) hexadecyltrimethylammonium bromide (CTAB) electrochemical corrosion process to oxidize Cu^0 from the Cu nanowire and redeposit it as $CuO_x/Cu(OH)_2$ particles on the external surface of the original Cu_2O shell, and d) short period of acidic etching to dissolve the amorphous-like $CuO_x/Cu(OH)_2$ particles while maintaining the integrity of the Cu_2O nanotubes.

Figure 2 shows SEM images of a) the as-synthesized Cu nanowires and b) the as-synthesized Cu_2O nanotubes decorated with a thick layer of amorphous-like $CuO_x/Cu(OH)_2$ particles prior to the acidic etching of the amorphous deposits. Figure 2c shows a high resolution backscattered electron image clearly demonstrating the hollow nature of the Cu_2O nanotubes with ultrathin walls. Some of the nanowires/nanotubes may have been broken during the repeated washing processes but the majority of the Cu_2O nanotubes resemble those of the original Cu nanowires except that the outer diameters increased. Some of the residue Cu nanoparticles mixed with the Cu nanowires and the electrochemical corrosion and acidic etching processes also produced hollow Cu_2O particles. Therefore, our synthesis process is general and can be used to produce various types of Cu_2O hollow structures. In order to understand the

detailed structure and morphology of the fabricated Cu_2O nanotubes Figure 3 shows a series of high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images clearly revealing the morphology of the rapidly calcined Cu nanowires (a), the formation of thick layers of amorphous-like $CuO_x/Cu(OH)_2$ particles attached to the crystalline Cu_2O ultrathin shells (b), and the final ultrathin wall and clean Cu_2O nanotubes after the acidic etching process (c). The thickness of the nanotube walls ranges from about 4 nm to 9 nm with an average wall thickness of ~ 6 nm.

The stability of the fabricated Cu_2O nanotubes was evaluated. Under ambient air, the Cu_2O nanotubes were not stable and they slowly changed to the more stable CuO phase. The tube morphology, however, was maintained. Under calcination condition, the tube morphology of the Cu_2O was stable up to about 300°C. However, they chemically changed to CuO. Under reducing environment, for example H_2 gas, the tube morphology of both the Cu_2O and CuO was stable up to 200°C. At temperatures above 200°C the both the CuO and Cu_2O nanotubes can collapse to form large Cu particles. Therefore, these delicate CuO and Cu_2O nanotubes cannot be used for high temperature catalytic reactions.

We dispersed ZnO and CeO_2 nanoparticles onto the synthesized Cu (with a thin layer of Cu_2O) and CuO nanowires and evaluated their catalytic performance for MSR. Figure 4a clearly shows that both the Cu and CuO nanowires did not have much activity for low temperature MSR. The CuO nanowire supported ZnO catalyst, however,

Figure 2. SEM images of a) Cu nanowires and b) Cu_2O nanotubes coated with thick layers of amorphous-like CuO_x particles, and c) backscattered electron image of ultrathin wall Cu_2O nanotubes.

Figure 3. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images of a) Cu nanowires after rapid calcination, b) Cu_2O nanotubes decorated with amorphous-like $CuO_x/Cu(OH)_2$ nanoparticles and c) ultrathin wall Cu_2O nanotubes.

demonstrated appreciable methanol conversion even at temperatures as low as 180°C, unambiguously revealing the effect of the addition of the ZnO nanoparticles. The addition of CeO_2 nanoparticles to the CuO nanowires and nanotubes showed similar effects. Figure 4b shows the low temperature CO oxidation on the as-synthesized Cu_2O nanotubes. After the first cycle run the Cu_2O nanotubes were stabilized and the CO conversion was increased significantly during the second and third cycle run. Complete CO conversion was achieved at temperatures below 150°C. It is expected that during the CO oxidation reaction the Cu_2O may have converted to CuO and at low temperatures (e.g., < 200°C) the nanotube morphology was maintained even after prolonged CO oxidation reaction.

Our work demonstrates that ultrathin wall Cu_2O and CuO nanotubes provide high surface area but they can only be utilized for catalytic reactions at relatively low temperatures. Under reducing environments, these delicate nanowires and nanotubes are especially fragile and can collapse at temperatures > 200°C. Structural stabilization may be needed for high temperature

Figure 4. Methanol steam reforming over ZnO/CuO nanowires, Cu_xO/Cu nanowires and bare CuO nanowires (a); CO oxidation over Cu_2O nanotubes for three cycles (b).

applications. Through this work, the student gained deep insights into how to effectively utilize nanoscale structures to develop desirable catalysts for selected reactions. The PI learned that development of new catalysts for targeted reactions require extensive interdisciplinary knowledge of materi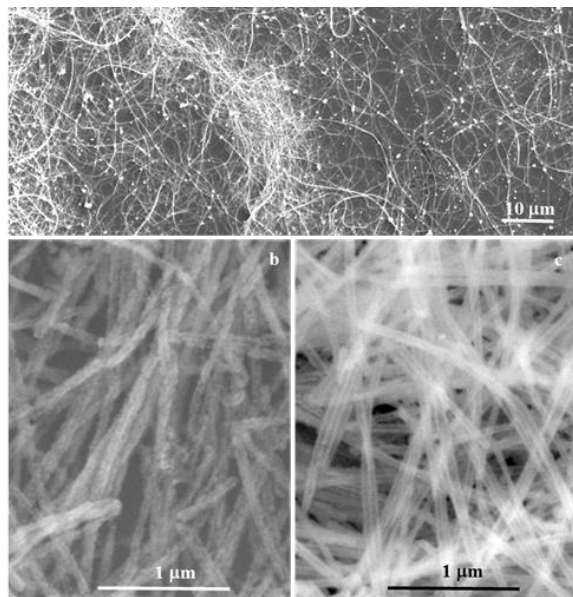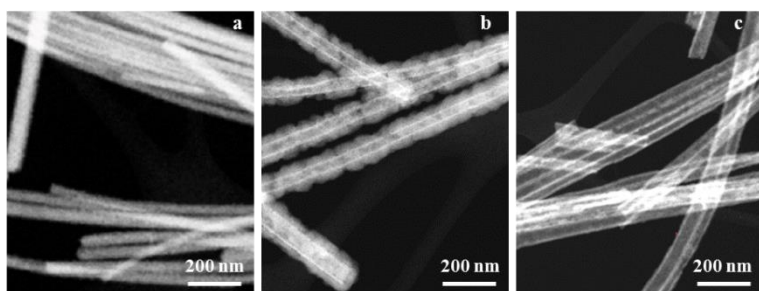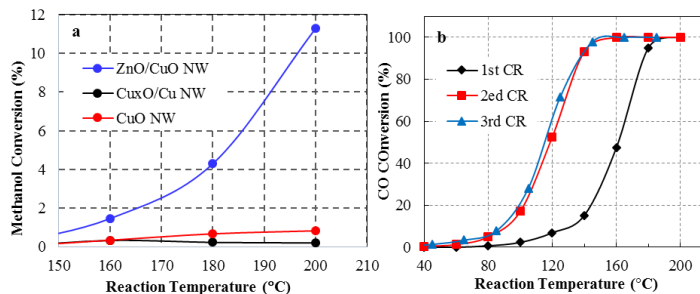als properties and dynamic structural evolutions.