Supporting information

Preparation, Microstructure Characterization and Catalytic Performance of Cu/ZnO and ZnO/Cu Composite Nanoparticles for Liquid Phase Methanol Synthesis

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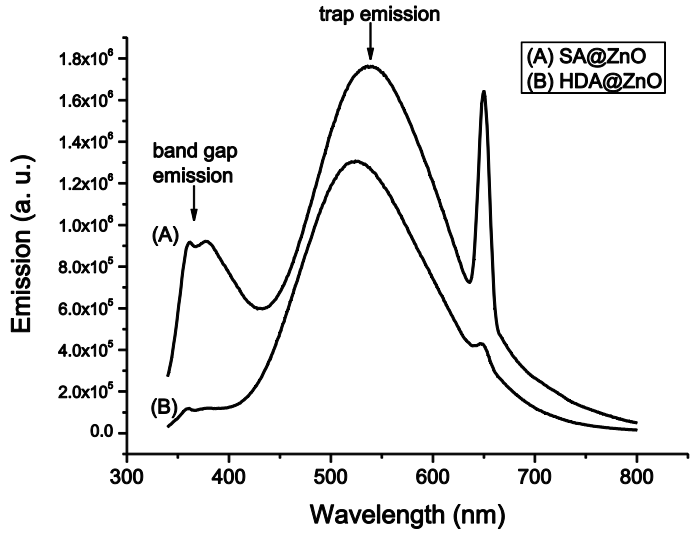

Figure S1. Optical properties of ZnO NPs with different stabilizing agents. (A) Represents the PL spectrum of stearate@ZnO NPs and (B) illustrates the PL spectrum of HDA@ZnO NPs (λex = 325 nm).

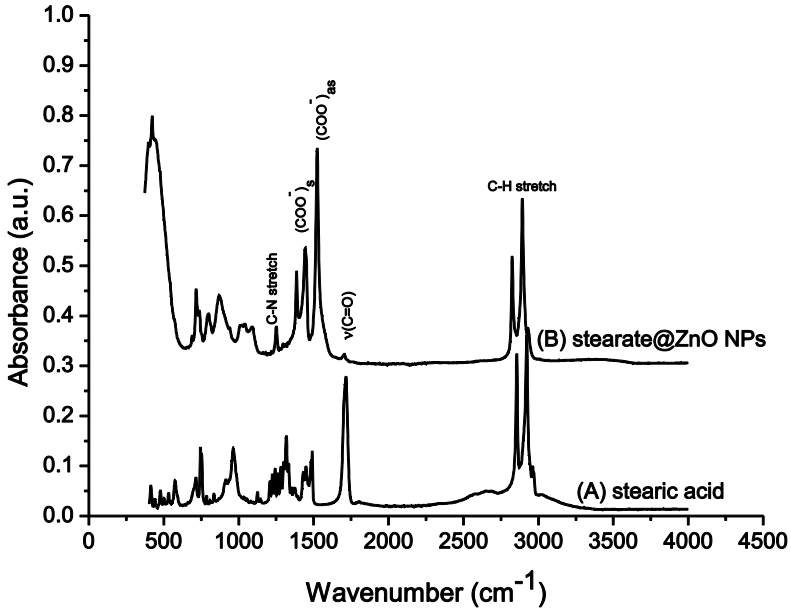

Figure S2. FTIR spectra of (A) stearic acid and (B) stearate@ZnO NPs. It's clearly shown that there are no N-H valence vibrations due to replacement with stearate groups.

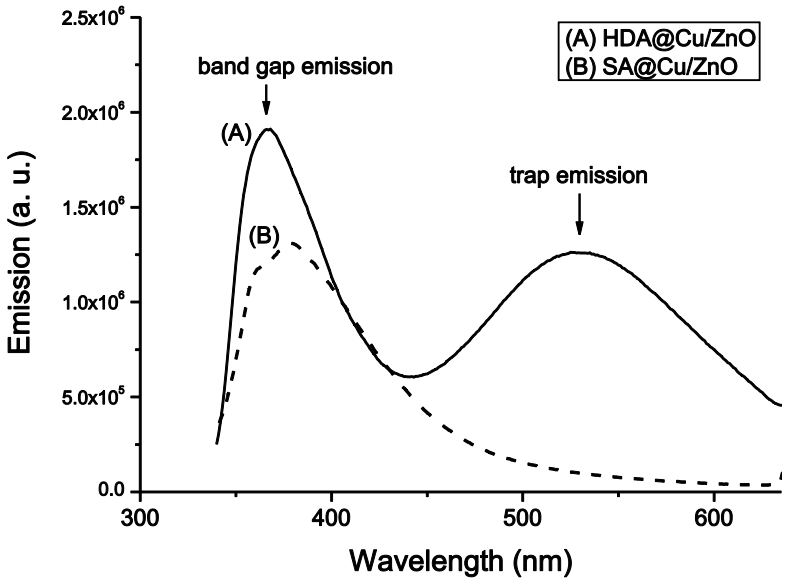

Figure S3. (A) PL spectrum of HDA@Cu/ZnO NPs and (B) PL spectrum of stearate@Cu/ZnO NPs (λex = 325 nm).

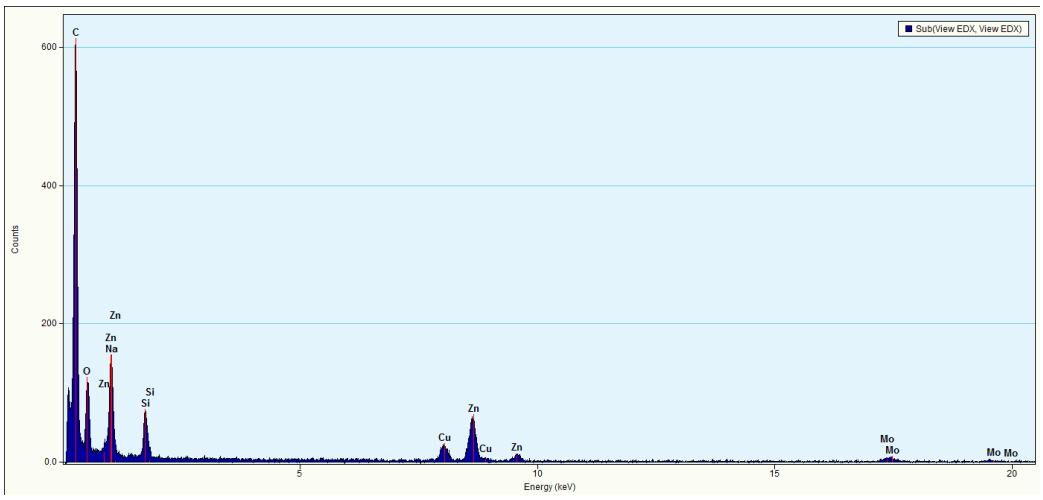

Figure S4. Energy dispersive X-ray (EDX) spectrum of sample (**1**) after photodeposition of Cu at the surface of stearate@ZnO nanoparticles. The spectrum was taken through EELS measurements.

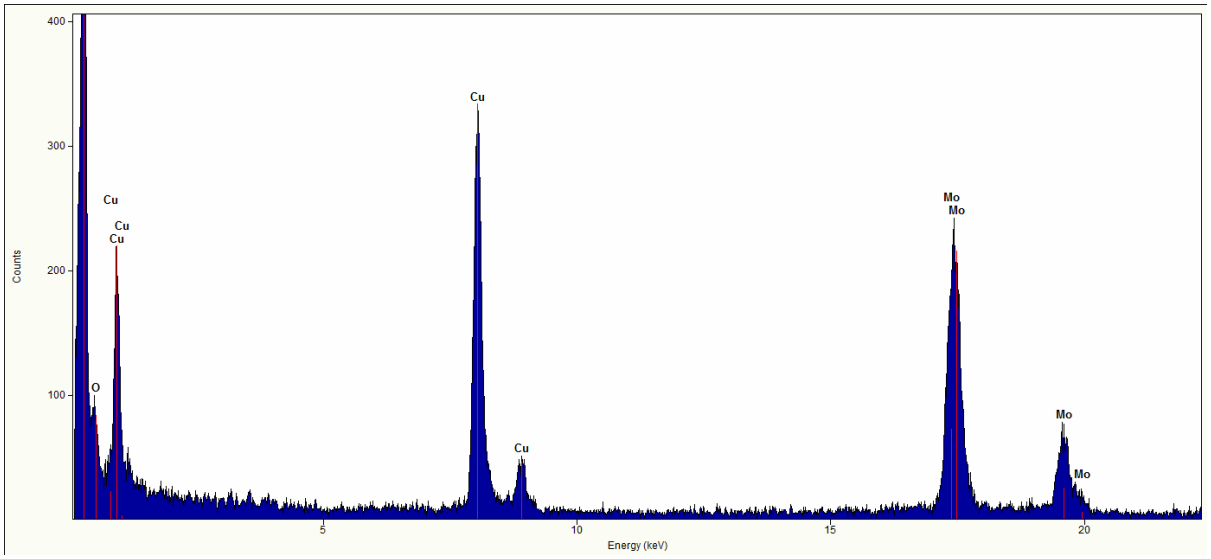

Figure S5. Energy dispersive X-ray (EDX) spectrum of sample (**1**) after ATR measurements taken from a group of larger particles in the TEM image (Figure 2b). The particles are clearly Cu nanoparticles as a result of reduction of the rest of Cu precursor with CO at 8 bar and 180 °C.

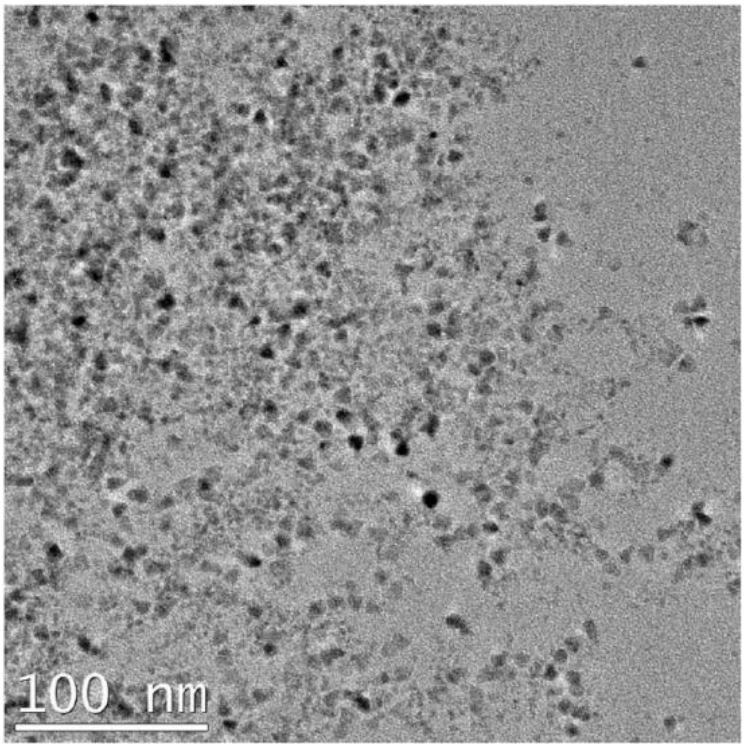

Figure S6. TEM image of stearate@Cu-ZnO colloid (1:2 molar ratio) after catalysis at 220 °C for 72 h (sample **2**).

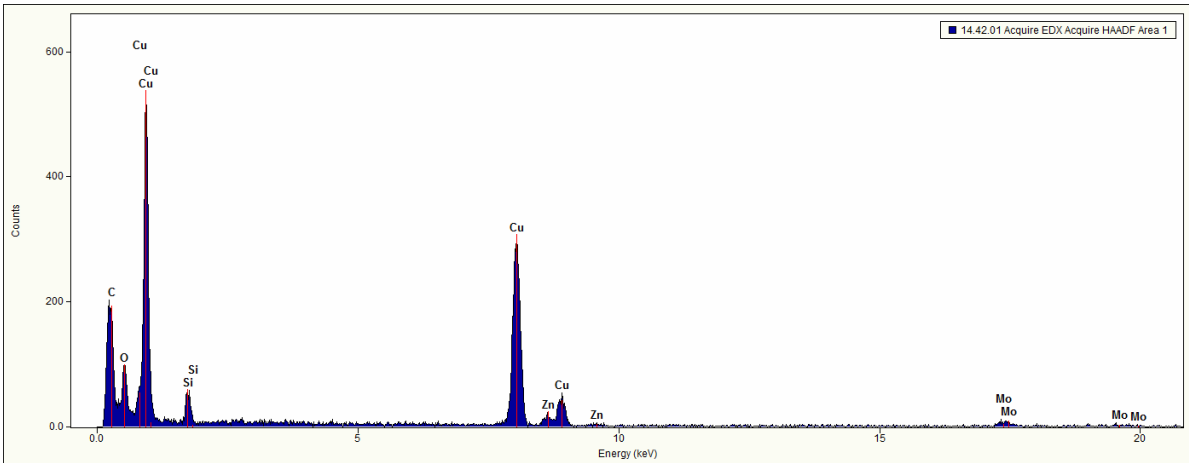

Figure S7. EDX spectrum taken from the large nanoparticles region indicated in the figure 4a. The large particles are Cu nanoparticles; some ZnO is also detected, probably at the surface of the larger Cu nanoparticles.

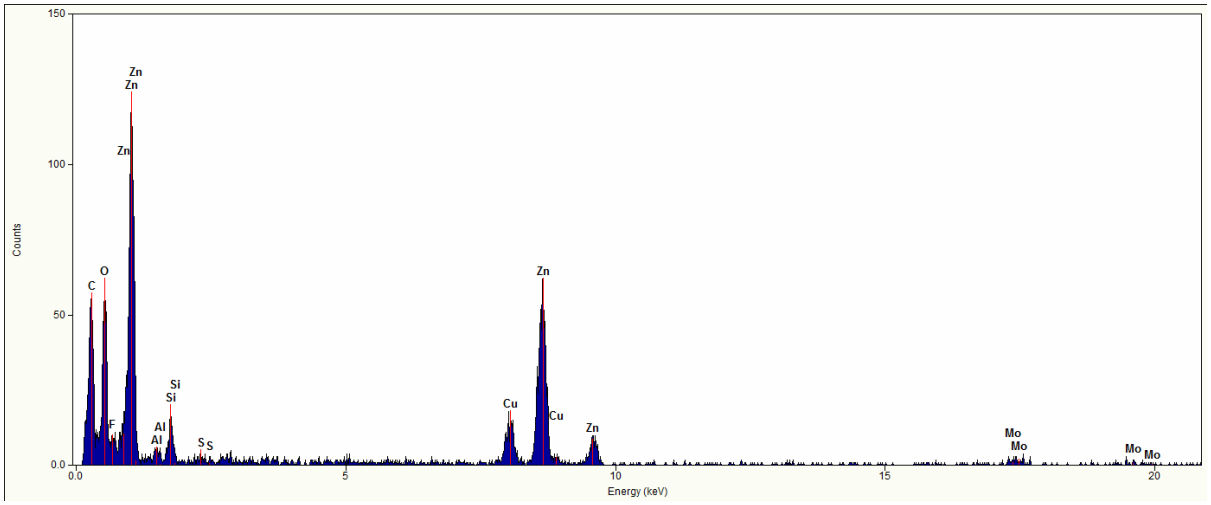

Figure S8. EDX spectrum taken from the region surrounding the large nanoparticles of figure 4b and donated by square, showing that the smaller material is ZnO. Some Cu is still detected.

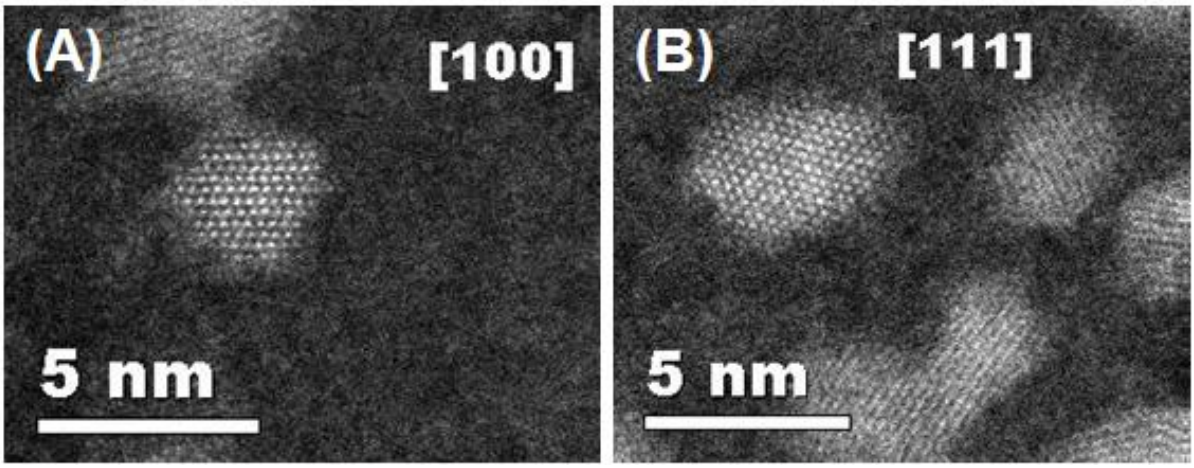

Figure S9. High resolution HAADF-STEM image of Cu/ZnO particles with different crystalline planes (A) [100] and (B) [100] on the carbon support film.

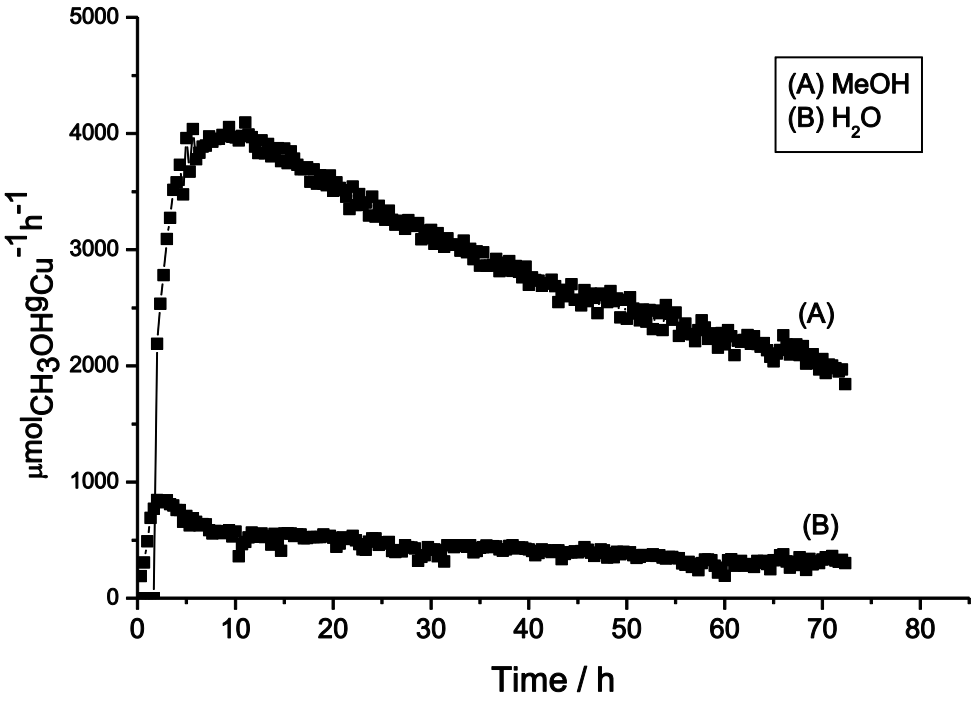

Figure S10. Rate of methanol and water formation over the stearate@ZnO/Cu (with Cu:ZnO 1:2 molar ratio) colloid versus time on stream applying the optimized reduction conditions. Reaction conditions: 220 °C, 26 bar, synthesis gas composition: 64 vol% H_2, 32 vol% CO, 2 vol% CO_2 and 2 vol% N_2.