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Metal-Oxide Nanostructures Fabricated from Laser-Assisted Synthesis Technique

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Controlling the Morphology of Silica-Copper Oxide Nanostructures from Laser Ablation in Liquid

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Motivation

Green and sustainable way of synthesizing oxide-metal composite nanomaterials: use photons to initiate chemical reactions rather than wet chemicals as reducing and stabilizing agents.

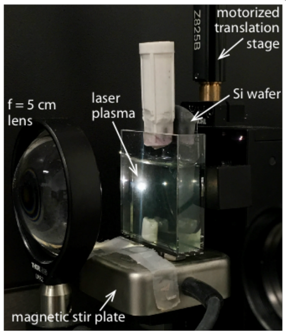
Pulsed Laser ablation in liquid (PLAL) is a common method for generating bare-surface metal nanoparticles by focusing intense laser pulses onto the surface of a solid target immersed in liquid.[1]

When the liquid contains metal ions, they may interact with the ablated clusters from the target, forming supported metal nanoparticles. This is referred to as femtosecond-Reactive Laser Ablation in Liquid (fs-RLAL), when femtosecond laser pulses are used.[2]

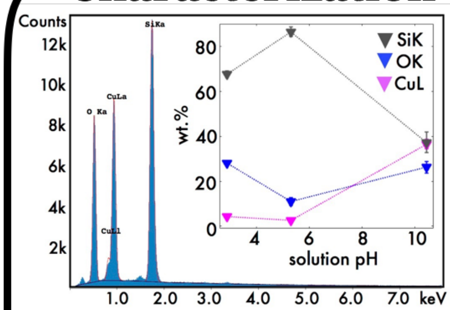
Silica-supported copper nanoparticles are valued for their catalytic activity toward various reactions such as CO_2 hydrogenation to form methane and methanol.

fs-RLAL Setup

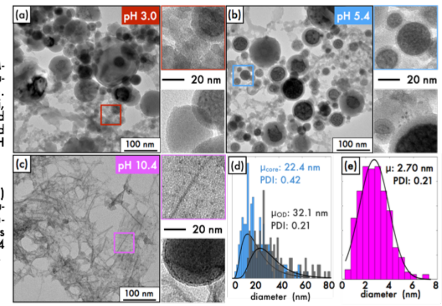
Ablated silicon wafer immersed in aqueous $Cu(NO_3)_2$ solutions (2 mM) with:
HNO_3 (pH 3.0, Cu-silica-3.0),
no additives (pH 5.4, Cu-silica-5.4), or
KOH (pH 10.4, Cu-silica-10.4)
to see effect of pH on final morphology.



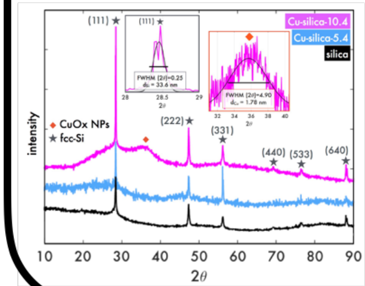
Characterization



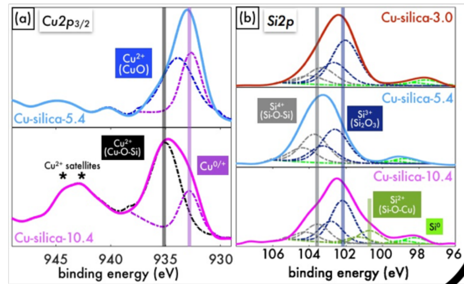
Left: Representative SEM-EDS spectrum of Cu-silica-10.4 sample. Inset shows wt.% Si, O, and Cu quantified in samples fabricated from different pH solutions



Right: TEM images of (a) Cu-silica-3.0, (b) Cu-silica-5.4, (c) Cu-silica-10.4, histograms of (d) Cu-silica-5.4 and (e) Cu-silica-10.4

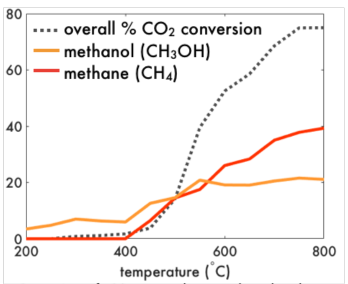


Left: XRD patterns of Cu-silica-10.4, Cu-silica-5.4, and silica generated from ablating a silicon wafer immersed in water. Inset shows FWHM fitting of peaks, with the particle diameter determined using the Scherrer equation.[3]



Right: XPS spectra of (a) $Cu2p_{3/2}$ of Cu-silica-5.4 (top) and Cu-silica-10.4 (bottom), and (b) Si2p of Cu-silica-3.0 (top), Cu-silica-5.4 (middle), and Cu-silica-10.4 (bottom).

CO_2 Hydrogenation

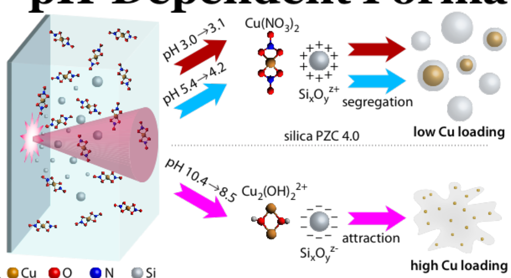


Conversion of CO_2 to methane and methanol over different reaction temperatures when testing Cu-silica-10.4 sample for catalytic activity.

> Conversion increases from 4% at 450°C to 75% at 800°C

> Selectivity toward methanol below 600°C, and selective toward methane above 600°C

pH-Dependent Formation



Low and *medium* *solution pH:* ablated silica clusters (oxidized silicon atoms upon interaction with water) are protonated, repel nearby Cu^{2+} ions, resulting in low wt.% loading of Cu, and Cu-core/silica-shell morphology

High solution pH: ablated silica clusters are deprotonated, attracting nearby $Cu_2(OH)_2^{2+}$ clusters, generating high wt.% loading copper on silica

References

[1] D. Zhang, B. Gökce, and S. Barcikowski. Chem. Rev., 117(5): 3990–4103, 2017
[2] M. G. John and K. M. Tibbetts. Appl. Surf. Sci., 475:1048 – 1057, 2019
[3] A. Monshi, M. R. Foroughi, M. Monshi. World Journal of Nano Science and Engineering 2, 154-160, 2012