

## Controllable Growth of Copper on TiO<sub>2</sub> Nanoparticles Through Coupled Effects of Solution Viscosity and Photoreduction Rate

Peter Tieu<sup>1</sup>, Djawhar Ferrah<sup>2</sup> and Xiaoqing Pan<sup>3</sup>

<sup>1</sup>University of California, Irvine, California, United States, <sup>2</sup>University of California, Irvine, United States, <sup>3</sup>Department of Physics and Astronomy, University of California, Irvine, CA 92697, Irvine, California, United States

Wet chemical techniques for nanomaterials synthesis is an attractive method compared to high-vacuum synthesis approaches due to ease of synthesis and lower temperature formation. Others have reported upon the effect of different aspects of the solution, including the choice of reducing agent on the size, composition, and morphology of the resultant nanoparticles.[1] However, experimental studies about the impact of the viscosity on the nanomaterial formation have not been performed. Here, we report the impact of solution viscosity on the formation of nanomaterials at the solid-liquid interface through an investigation of photocatalytic growth of copper on TiO<sub>2</sub> nanoparticles supported on graphite.[2] The nanostructures were characterized by transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS). Together, the observations demonstrate the growth of copper on TiO<sub>2</sub> proceeded through different mechanisms depending on the combination of photoreduction rate and solution viscosity, illuminating further methods to control nanomaterial synthesis (Figure 1).

Copper was photoreduced with water and methanol (viscosity= 0.89 Pa·s and 0.59 Pa·s, respectively) as solvents at different photoreduction rates. Cu 2p<sub>3/2</sub> XPS signal, normalized to the Ti 2p signal, was used to compare the total deposition of copper onto the TiO<sub>2</sub>. The photoreduction rates are referred to as N1 and NM1 (N2 and NM2) for low value (high value) within water and methanol, respectively. A comparison of N1, N2, and NM2 integrated Cu 2p intensity showed the expected behavior based on solvent choice and photoreduction rate. However, the integrated intensity of NM2 showed an attenuation of 3 orders of magnitude compared to NM1 which did not conform to our expectations for the synthesis and warranted investigation of the reaction products.

Low magnification TEM imaging of N2 and NM2 showed distinct species formation. For N1, NM1, and N2, small nanoparticles of copper formed on the TiO<sub>2</sub> surface as expected (Figure 2a). On the other hand, for NM2, copper oxide the form of flakes up to 5 times larger than the TiO<sub>2</sub> nanoparticles were observed (Figure 2b). Closer examination of N2 with STEM imaging showed no noticeable difference in the TiO<sub>2</sub> nanoparticles compared to before photoreduction (Figure 2c). However, examination of NM2 to reveal the composition of the flakes caused the reduction of the copper oxide to small metallic copper nanoparticle over the course of a few minutes (Figure 2d, e). The formation of the small copper and copper oxide nanoparticles seen in N1, NM1, and N2 follow Lamer's nucleation theory wherein growth occurs gradually and locally. However, the non-classical growth theory is needed to explain the formation of the copper oxide flake in NM2.[3] Here, viscosity is considered inversely related to the diffusion of copper clusters along the TiO<sub>2</sub> surface and displays an anisotropic effect. A high in-plane and a high out-of-plane diffusion causes the formation of the flake instead of the small nanoparticles seen in N2.

Understanding the dynamics of nanomaterial formation at solid surfaces in a liquid environment is important for the controlled synthesis of material with desired shape, size, and function. We observed growth of copper from precursor onto a TiO<sub>2</sub> nanoparticle on graphite and analyzed the results with TEM,

EDS, and XPS to reveal the influence of viscosity which led to a non-classical growth mechanism and a distinct shape from classical growth. The viscosity at the surface of a solid-liquid interface must be considered along with other factors such as reduction rate and temperature when designing a synthesis process for future nanomaterials.[4]

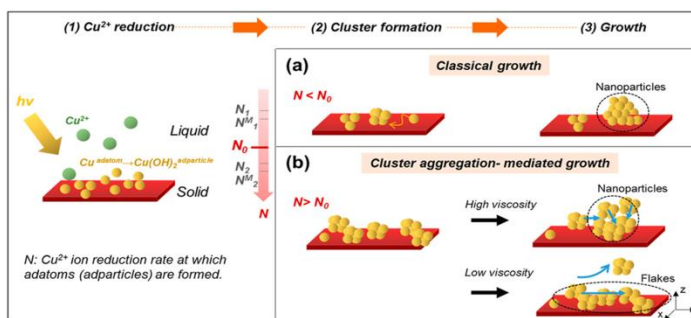


Figure 1. Schematic of the mechanism of copper cluster formation and growth at the solid-liquid interface under (a) low and (b) high photoreduction rate. The growth of the copper cluster into a final shape can be influenced by viscosity at the interface.

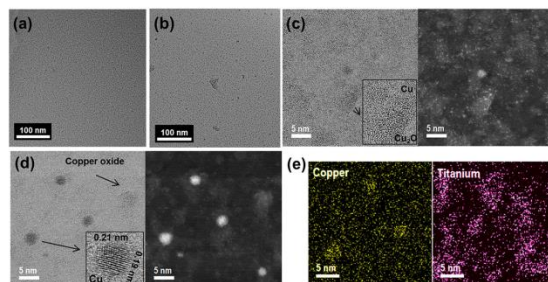


Figure 2. Copper nanomaterials synthesized at a high photoreduction rate onto TiO<sub>2</sub> nanoparticles supported on graphite. Low magnification TEM images of the copper nanostructure synthesized in (a) water and (b) methanol. High magnification STEM bright field (left) and high angle annular dark field (right) images of the nanostructure in (c) water and (d) methanol. Insets show magnified copper species. (e) EDS maps of copper and titanium from (d).

#### References

- [1] M.A. Boles, *et al. Chem. Rev.* 2016, 116 (18), 11220–11289.
- [2] D. Ferrah & P. Tieu. *ACS Appl. Nano Mat.* 2020, 3(6), 5855–5861.
- [3] J.J De Yoreo, *et al. Science* 2015, 349, 6247.
- [4] This work was supported by the National Science Foundation (NSF) awards under grant No. CBET-2031494, CBET-2031512, and CHE-1955786. The authors acknowledge the use of facilities and instrumentation at the UC Irvine Materials Research Institute (IMRI) supported in part by the National Science Foundation through the Materials Research Science and Engineering Center program (DMR-2011967).