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Advances in Fundamental Materials Research

Plasmonic Cu Nanoparticles on Aerogel Supports for Thermal and Photodecomposition of CW Simulants and Live Agents

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Background: Most materials for CWA protection function by physically (and often reversibly) adsorbing target chemicals, but do not degrade CWAs to non-toxic products. Integrating visible-light–activated plasmonic sensitizers into CWA-degrading semiconductor materials can enhance their catalytic activity with plasmonically generated carriers (i.e., electrons and holes). Effective composite catalysts that feature plasmonic materials for CWA degradation should include: 1) high-surface area mesoporous supports that adsorb target chemicals; 2) plasmonic nanostructures with a surface plasmon resonance (SPR) that overlaps the solar spectrum; and 3) components made of relatively cheap, abundant, and non-toxic materials. Detailed knowledge about the mechanisms of plasmonic enhancement, how CWAs adsorb to composite materials, and the degradation pathways of CWAs via plasmon-mediated photochemistry are critical to developing a fundamental understanding of materials design parameters that influence the effectiveness of plasmon-enhanced decontamination.

Rationale and methods: We couple the plasmonic activity of Cu nanoparticles, a low-cost alternative to typical plasmonic metals, with chemical warfare agent (CWA)-adsorbing TiO_2 supports, creating Cu–TiO_2 aerogels that serve as a platform with which to elucidate the effects visible-light plasmonic sensitization has on the rates and pathways of CWA degradation. The Cu/TiO_2 composite aerogel design stabilizes Cu against oxidation, and maintains the metallic character necessary for plasmonic activity. Using state-of-the-art in-situ IR surface spectroscopy, we identify adsorption sites and degradation pathways for agents/simulants on Cu–TiO_2 aerogels. The insights gained from this work will lead to the development of new strategies for mitigating the threat of CWAs and the development of new plasmonic materials free of expensive precious metals.

Preliminary Results: Unprecedented stabilization of SPR active TiO_2 aerogel-supported Cu nanoparticles against oxidation has been demonstrated. The Cu/TiO_2 aerogel composite oxidizes small molecules such as methanol when illuminated with visible light. Initial in-situ FTIR studies demonstrate that simulants and CW agents (GB and GD) oxidize to completion under broad-spectrum illumination under UHV conditions. Effects of admitting oxygen to the reactor on adsorbed agents under dark conditions and visible-light illumination are underway.

Impact to the mission: The fundamental experimental and theoretical insights gained from this work can lead to the development of new strategies for decontaminating CWAs using sunlight. This work will also improve the fundamental understanding of plasmonic applications for Cu as a cheaper more abundant substitute for traditional plasmonic materials.

This work is supported by the Office of Naval Research.