PROTECTION - SCIENCE AND TECHNOLOGY ADVANCES FOR CHEMICAL AND BIOLOGICAL PROTECTION

Oxide Aerogels With Enhanced Sorptive And Degradative Activity For Acute Chemical Threats

Paul DeSario U.S. Naval Research Laboratory **Robert Balow** U.S. Naval Research Laboratory **Travis Novak** NRC Postdoctoral Associate, U.S. Naval Research Laboratory **Alex Balboa** U.S. Army DEVCOM Chemical Biological Center **Wesley Gordon** U.S. Army DEVCOM Chemical Biological Center

Reactive sorbents that both sequester and decontaminate toxic compounds are of great interest for protecting warfighters and civilians. Current strategies for personal protection rely on passive sorbents that do not degrade toxic threats whereas materials that possess dual adsorptive and degradative functionality offer the prospect of more complete protection and prolonged use. Of particular interest are the development of materials that utilize passive energy sources and ambient reactants to drive degradation chemistry. While the most operationally relevant and abundant stimulus for driving decontamination is sunlight, sunlight-driven processes face intermittency challenges. In this presentation, we summarize strategies to develop oxide-based composites that possess both dark and photo-initiated degradation pathways in order fulfill the need for continual threat mitigation.

Whereas many metal oxides are good adsorbents for organophosphorus or organosulfur compounds, oxide aerogels offer multiple avenues to add oxidative power and photo-initiated degradation pathways. Oxide aerogels are pore–solid networks notable for their mesoporosity and high surface area. We describe strategies to maximize sorptive capacity and degradation rates in oxide aerogels that include: 1) creating a high density of surface hydroxyls or oxygen vacancies; 2) exploiting semiconducting photocatalytic oxides; 3) leveraging synergistic interactions with supported metal nanoparticles; and 4) incorporating defects that stabilize reactive oxygen species. We use in-situ infrared spectroscopy to probe the interactions of the chemical warfare simulants and agents with TiO2 and CeO2 aerogel composites. We characterize differences in degradation rates under dark and photo-illuminated conditions at semiconducting TiO2 aerogels and reveal how supported metal nanoparticles help sensitize the bandgap of TiO2 and modify the surface-hydroxyl sites on the TiO2 surface. We reveal how oxygen vacancy defects in CeO2 assist in the formation and stabilization of reactive oxygen species that initiate degradation chemistry.