

Plasmon-Induced Chemical Bond Cleavage by Refractory Transition Metal Nitrides

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October 14, 2021

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

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1. REPORT DATE (DD-MM-YYYY) 14-10-2021		2. REPORT TYPE NRL Memorandum Report		3. DATES COVERED (From - To) 10-01-2016 – 10-01-2021	
4. TITLE AND SUBTITLE Plasmon-Induced Chemical Bond Cleavage by Refractory Transition Metal Nitrides				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER 61153N	
6. AUTHOR(S) Olga A. Baturina, Albert Epshteyn, Spencer Giles, Andrew Purdy, and Blake Simpkins				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER 1G40	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Naval Research Laboratory 4555 Overlook Avenue, SW Washington, DC 20375-5320				8. PERFORMING ORGANIZATION REPORT NUMBER NRL/6130/MR--2021/7	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Naval Research Laboratory 4555 Overlook Avenue, SW Washington, DC 20375-532				10. SPONSOR / MONITOR'S ACRONYM(S) NRL Base Program	
				11. SPONSOR / MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION / AVAILABILITY STATEMENT DISTRIBUTION STATEMENT A: Approved for public release; distribution is unlimited.					
13. SUPPLEMENTARY NOTES This is an executive summary of the base program that ends 09/30/2021. The full report will be submitted in November.					
14. ABSTRACT This report presents research conducted by NRL Chemistry Division on plasmon-mediated photocatalysis by refractory transition metal nitrides (RTMNs). RTMN materials are synthesized, characterized by a variety of physico-chemical methods and utilized for evaluation of their photocatalytic activity in two reactions: (1) methanol photoelectrochemical oxidation at the electrode/solution interface and (2) oxidation of 2-chloro ethyl sulfide at the photocatalyst/air interface. The mechanisms of promotions are proposed.					
15. SUBJECT TERMS Refractory transition metal nitride Localized surface plasmon resonance Photocatalytic activity Methanol photoelectrochemical oxidation 2-chloro ethyl ethyl sulfide					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Olga Baturina
U	U	U	U	5	19b. TELEPHONE NUMBER (include area code) (202) 767-6345

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EXECUTIVE SUMMARY

This report presents research conducted by NRL Chemistry Division on plasmon-mediated photocatalysis by refractory transition metal nitrides (RTMNs). Plasmonic photocatalysis is promising way to harvest energy of visible light and drive chemical reactions on the surface of photocatalysts. Interaction of plasmonic nanostructures with light at certain frequencies leads to the generation of hot electrons that can directly or indirectly break chemical bonds on the surface of the photocatalysts. The current state-of-the-art material used in the majority of plasmonic systems, and in particular in photocatalysis is gold, typically supported on a semiconductor support. Although gold is one of the best plasmonic materials, its real-life application is hindered by its high cost. RTMNs represent an attractive low-cost alternative to gold. Because of large concentrations of free carriers in some of these materials ($\sim 10^{22} \text{ cm}^{-3}$), they establish metallic optical properties which support localized surface plasmon resonances (LSPRs) in the visible and near-infrared (IR) regions. Unlike Au, the optical properties of RTMN can be tuned by changing their processing conditions and composition thus making them more versatile than metals in terms of system design. Furthermore, the high-temperature stability of RTMN materials suit them well for catalytic processes, which are often carried out at higher temperatures due to reaction acceleration. While the photocatalytic activity of Au/TiO₂ NPs has been demonstrated before, very little work exists on plasmon-induced photocatalytic reactions by RTMN nanoparticles. The objective of this program was (1) to demonstrate that gold nanoparticles can be replaced by low-cost groups IV-VI refractory RTMN nanoparticles that possess similar plasmonic, but different catalytic, adsorptive and structural properties and (2) elucidate the mechanisms of photo-induced bond cleavage by RTMN-based nanoparticles for two Navy-relevant reactions: methanol (CH₃OH) oxidation and the decomposition of 2-chloroethyl ethyl sulfide (CEES, chemical warfare agent simulant). Our hypothesis is that for photocatalytic reactions in which the Au surface character (i.e. its chemical, adsorptive, and structural properties) is not essential, RTMN NPs can successfully replace Au NPs providing inexpensive, tunable, chemically robust plasmonic activation. For photocatalytic reactions, in which the gold surface structure is essential, the amount of gold in NPs can be minimized by implementing core-shell nanostructures. Core-shell NPs with RTMN cores and Au shells are expected to combine catalytic activity of gold with plasmonic properties of refractory metal nitride core.

Prior to utilizing RTMN nanoparticles in plasmon-mediated photocatalytic reactions, they were synthesized, characterized by a variety of physical and microscopic techniques, and compared to commercially available materials. RTMN nanoparticles were synthesized by ammonolysis of MCl₃(THF)₃ (M=Ti, V, Cr) and Zr(NMe₂)₄ precursors [1]. A novel method has been developed for growing well-dispersed TiN nanoparticles inside a non-reactive porous Al₂O₃ (TiN/Al₂O₃). In-house made TiN, VN and CrN nanoparticles exhibited weak LSPR in comparison to commercial TiN (Plasma Chem) most likely due to NPs' oxidation and agglomeration. On the contrary, in-house made ZrN nanoparticles outperformed commercial material produced by American Elements. A method has been proposed for synthesis of TiN-Au core-shell nanoparticles with an ultra-thin (monolayer or less) Au shell.

Comparison of optical response of the best performing TiN nanoparticles to that of Au showed that TiN NPs exhibited a broader red-shifted LSPR in comparison to Au which was assigned mostly to quasi-metallic character of TiN NPs. Comparison of activity of TiN/TiO₂ photocatalyst towards photocatalytic methanol oxidation to that of Au/TiO₂ demonstrated that both TiN and Au nanoparticles acted as photosensitizers extending TiO₂ activity into the visible spectral region. Further analysis highlighted two major differences between the TiN/TiO₂ and Au/TiO₂ photocatalysts. First, potential bias was required to initiate visible light-induced CH₃OH oxidation at the TiN/TiO₂ interface since it formed an Ohmic junction. Second, the reaction at the TiN/TiO₂ interface was most likely driven by the highly reactive holes generated by interband transitions in TiN NPs at wavelengths shorter than 630 nm, while the plasmonic effect, peaking at 580 nm was thought to be a major driving force for the CH₃OH oxidation on the Au/TiO₂ material. The

differences between the effects of TiN and Au NPs were assigned to the differences in their electronic structure, morphology, plasmonic nanoparticle/TiO₂ interface, optical properties, and electrocatalytic activity [2].

In a separate effort, we embedded commercial and in-house synthesized TiN nanoparticles into matrixes of TiO₂ and compared their ability to enhance electrochemical oxidation reactions to that of conventional Au nanoparticles. Although the photon-to-carrier conversion efficiencies were low ($\sim 10^{-4}$ %), the reaction rates were enhanced by a factor of 4 in the visible and near-infrared for both Au and TiN compared to a pure TiO₂ control, with TiN showing an order of magnitude improvement over Au in the near IR region. The spectral dependence of reaction rate enhancement followed the nanoparticle extinction spectra, and a linear power-dependence identifies a photo-excited carrier mechanism (i.e., decaying plasmons excite carriers that participate in chemistry rather than heating of the system). Lastly, photo-induced transients of the electrochemical signal are consistent with interfacial defect charging in these heterosystems. Consistent with our previous results, the TiN/TiO₂ system, which has no Schottky barriers, exhibited a bias-dependent and transient photoelectrochemical response, while the Au/TiO₂ system, which naturally forms a Schottky barrier that immediately separates charged carriers, exhibited a near-instantaneous response [3].

ZrN is expected to have a sharper blue-shifted LSPR response in comparison to TiN. However, ZrN NPs appear to be less chemically inert than TiN, owing to zirconium's strong affinity for oxygen. A layer of dielectric ZrO₂ readily forms on the surface of ZrN NPs even in the presence of only trace oxygen. The oxide layer has a detrimental effect on the LSPR, leading to its broadening and red-shifting. Photocatalytic activities of TiO₂-supported ZrN NPs were compared to those of TiN/TiO₂ in a series of experiments utilizing in-house made ZrN NPs. Our results indicate that optical properties and photocatalytic activity of ZrN/TiO₂ are strongly affected by ZrN surface oxidation and agglomeration. We found that under visible illumination, both in-house synthesized 17 nm ZrN and commercial 30 nm TiN NPs promote TiO₂ activity for CH₃OH oxidation, but the mechanism of enhancement appears to be different for the two nitrides. The photocurrent enhancement observed for ZrN NP is assigned to a photothermal effect, since charge transport from the NPs is expected to be drastically inhibited due to the dielectric ZrO₂ shell, while interband transitions in TiN NPs are likely the major contributor to an increase in photocurrent at the TiN/TiO₂ interface [4].

In spite of the promising plasmonic properties of TiN NPs, application of TiN/TiO₂ photocatalyst is limited to electrochemical interfaces (i.e. photocatalyst/electrolyte interface) due to the absence of Schottky barrier at the TiN/TiO₂ interface. In order to utilize this photocatalyst at the interface with air, the TiN/TiO₂ interface needs to be re-designed. Two strategies were explored in order to create a Schottky barrier: (1) modification of plasmonic TiN NPs by decorating them with the gold shell, and (2) using semiconductor with the different band alignment in comparison to TiO₂. To implement the second strategy, GaN was selected as an alternative to TiO₂. Measurements of a Schottky barrier at the interface of TiN and *n*- and *p*-type GaN films showed that only *p*-type GaN formed an electronic barrier with TiN.

Unlike TiN, Au forms a Schottky barrier with TiO₂, and Au/TiO₂ photocatalyst is capable of promoting photocatalytic reactions at the photocatalyst/air interface. This material was used to determine the mechanism of the effect of visible light on photooxidation of the Navy-relevant organic molecule CEES. We (in collaboration with co-authors from US Army DEVCOM CBC) demonstrated that under anaerobic conditions, 2-CEES partially desorbs from the Au/TiO₂ surface likely due to a photothermal effect, induced by photo-excited plasmonic Au nanoparticles [5].

To optimize photocatalytic activity of the semiconducting TiO₂ support, materials with different morphology have been synthesized and investigated [6, 7]. Addition of long-chain alkyl phosphonic acids to the synthesis led to formation of hierarchical TiO₂ structures, comprising (1) assemblies of nanorods, and (2) nanoflowers that appear roughly spherical and made up of fine 8-10 nm diameter nanowires radiating out from a central point. These materials exhibited high photocatalytic activity towards CEES

photooxidation which was assigned to (1) better light absorption by assemblies of nanowires and nanorods in comparison to individual nanorods, (2) improved separation of photogenerated carriers in thinner nanorods and nanowires and at Anatase/Rutile junctions, (3) high surface area, and (4) the exclusion of surface OH groups due to the formation surface functionalization with alkyl phosphonic acids via Ti-O-P bonds on the TiO₂. These materials can be used as a platform for modification by plasmonic nanoparticles in the future.

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