

Non-Thermal Plasma Processing of TiN Nanoparticles for Plasmonic Catalysis

A. Alvarez Barragan¹, C. Berrospe Rodriguez¹, L. Mangolini^{1,2}

¹Department of Mechanical Engineering, University of California Riverside, Riverside, CA, USA

²Materials Science and Engineering Program, University of California Riverside, Riverside, CA, USA

Abstract: Titanium nitride (TiN) nanoparticles continue to gain interest as an alternative plasmonic material to gold and silver. In this work, we shed light on the potential of TiN in the field of plasmonic catalysis. The particles are synthesized by a non-thermal plasma method. The resulting powder was used to successfully drive the photoreduction of a platinum precursor from Pt⁴⁺ to Pt⁰. The reaction took place between 600 nm and 900 nm radiation.

Keywords: plasmonic nanoparticles, titanium nitride, non-thermal plasma, plasmonic catalysis

1. Introduction

The light-harvesting capacity of plasmonic nanoparticles has recently garnered attention in the synthesis of plasmon-driven photocatalysts.[1] Gold and silver have been used to successfully drive hydrogen dissociation and CO oxidation reactions by injecting hot electrons into molecules adsorbed to their surface.[2,3] However, the chemical instability of silver and the low thermal stability of both metals, in addition to their high cost, inspire the quest for alternative plasmonic materials that could potentially expand the field towards more ambitious and cost-effective applications.[4] Titanium nitride (TiN) is a conductive ceramic with high hardness and bulk melting point (2930 °C). Its plasmon resonance located in the visible-NIR region, low cost relative to gold and silver, and well-understood properties as a thin film in the semiconductor industry make it a strong alternative to mainstream plasmonic metals.[5–7] The present work encompasses a comprehensive study of the synthesis of TiN nanoparticles via a non-thermal plasma method and highlights the potential of this material as an alternative material in plasmonic catalysis. TiN particles are synthesized via a scalable, modular, non-thermal plasma method.[8–10] Titanium and nitrogen precursors are transported into a RF frequency plasma where TiN particles nucleate and grow. Platinum nanoparticles were subsequently deposited on the TiN by photo-induced reduction of an aqueous solution of chloroplatinic acid (H₂PtCl₆). The reduction of the precursor metal was driven by electron hole pair generation via plasmon decay. The addition of methanol as a hole scavenger increased the electron lifetime, leading to the obtention of metallic platinum. This reaction occurred at temperatures below 40°C under visible light illumination. The results were corroborated by X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) measurements. This work strengthens the case for alternative plasmonic materials in a field dominated by precious metals, and heavily driven by materials cost.

2. Experiment

Ammonia (NH₃) and titanium tetrachloride (TiCl₄) were used as precursor gases and transported independently into the upstream flange of a 25.4-cm long, 2.54-cm diameter quartz reactor, where a plasma discharge was initiated with a 5-cm long, 2.54-cm diameter cylindrical copper electrode wrapped around the reactor and connected to a 13.56 MHz (RF) power supply. The distance between the center of the electrode and the upstream flange was 4 cm. TiCl₄ was delivered using a bubbler kept at atmospheric pressure and in a water bath at 22 °C. Argon was used as a carrier gas and maintained at a flow rate of 70 sccm. Based on the vapor pressure of TiCl₄, we estimate that the net TiCl₄ flow rate is 1 sccm under these conditions. The NH₃ flow rate was maintained at 2.0 sccm. The pressure in the reactor was set to 3 Torr. The TiN particles were collected downstream of the reactor on a stainless-steel mesh filter. The TiN powder was added to a 90:10 (v/v) water-methanol solution at a concentration of 160 µM. An 8 wt. % H₂PtCl₆ aqueous solution was added at a concentration of 6.9 µM. The solution was then illuminated with a 500 W Hg-Xe Lamp and kept under constant stirring (**Figure 1**). The distance between the reactor and the light source was 23 cm. Two optical filters (600 nm longpass and 900 nm shortpass) were used to limit the incident light in between 600 nm and 900 nm. Control samples (under no illumination) were maintained under stirring at 40 °C to match the maximum temperature reached by the illuminated samples due to heating via light absorption of the nanoparticles. Different samples were illuminated at various reaction times. XPS and TEM characterization was performed to identify the presence of Pt⁰ at the particle surface.

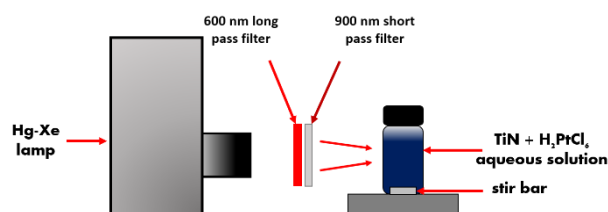


Figure 1. Experimental setup of the photoreduction of the platinum precursor. White light is filtered out in order to illuminate an aqueous/methanol solution of TiN and H_2PtCl_6 with visible radiation.

3. Results and Discussion

Figure 2a shows a TEM image of TiN nanoparticles after 6 hours of light exposure in the H_2O /methanol solution with the platinum precursor. The presence of ~ 2 nm clusters is observed. The maximum temperature during the reaction was 38°C . The control sample (**Figure 2b**), which was prepared under the same conditions, but not exposed to light, does not show the presence of such clusters, suggesting that the reaction is driven via plasmon decay and not by the thermal contribution of the vis-NIR radiation.

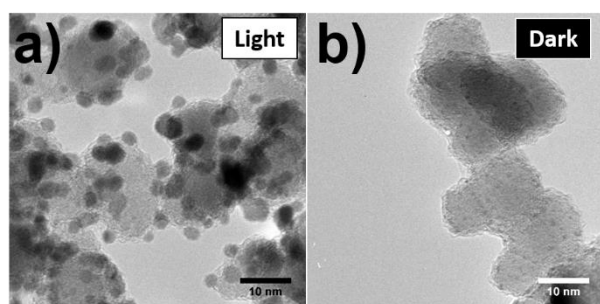


Figure 2. a) High magnification images of the illuminated samples show that large clusters (~ 2 nm) have been deposited at the TiN surface. These clusters were not observed in the control sample b) that remained unexposed to the light source. These data provide evidence on the role of methanol as a sacrificial electron donor upon the excitation of TiN with visible light.

Despite having evidence of the deposition of clusters at the TiN surface, it is still essential to confirm the presence of fully reduced platinum. Surface analysis with X-ray photoelectron spectroscopy (XPS) expands on the data presented above. **Figure 3a** shows the Pt 4f spectrum of a sample exposed to light but without the addition of methanol as an electron donor. The Pt^{4+} and Pt^{2+} primary doublets are observed at ~ 75 eV and ~ 72.7 eV.[11,12] No signal from Pt^0 was identified. We hypothesize that the signal corresponds to non-reduced aggregates at the nanoparticle surface that were adsorbed due to the attractive interaction of the hexachloroplatinate (PtCl_6^{2-}) anion and the positively charged particle surface, which remained in that state because of the high proton concentration in the acidic environment of the reaction.[13,14] **Figure 3b** shows the Pt 4f spectrum of a sample after adding 10 % methanol (v/v) into the aqueous solution. The spectrum confirms the signal of Pt^0 doublets at ~ 71.0 eV and ~ 74.3 eV.[11,12] This highlights the importance of methanol as a sacrificial hole scavenger and its role in extending the lifetimes of charge carriers so that they can reduce the platinum-containing adsorbates to metallic Pt. EDX mapping obtained by high-angular

annular dark-field scanning transmission electron microscopy (HAADF-STEM) imaging (**Figure 3c**) unequivocally confirms the deposition of Pt on the TiN nanoparticles, identified as the green clusters deposited onto the TiN nanoparticles (red signal).

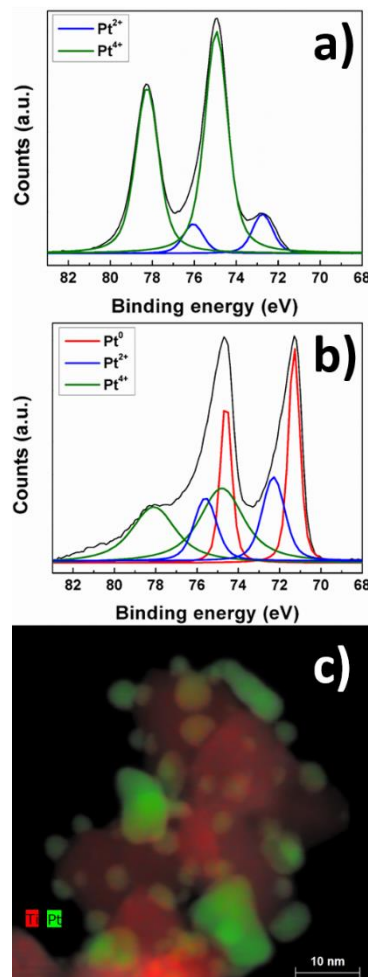


Figure 3. a) Pt 4f XPS analysis of a sample without the addition of methanol. Pt^{4+} and Pt^{2+} doublets are prevalent, whereas no Pt^0 peaks are observed. b) XPS spectrum of a sample under illumination with methanol show the appearance of Pt^0 peaks signifying a full reduction of Pt under visible light irradiation. c) EDX mapping of HAADF-STEM image shows a clear signal from Pt atoms deposited at the TiN surface.

The data presented in this contribution demonstrate the plasmonic capabilities of TiN nanoparticles, which were used for the low-temperature reduction of a platinum precursor from Pt^{4+} to Pt^0 . The reaction fully driven with the generation of electron-hole pairs through plasmon decay, and sets a baseline for future work on TiN in plasmonic catalysis.

4. Conclusion

In summary, we have used TiN nanoparticles to drive the photoreduction of Pt to the 0 state via plasmon excitation with vis-NIR radiation. TEM, HAADF-STEM, EDX, and XPS analyses conclusively show that, after illumination, Pt⁰ nanoparticles are deposited at the TiN surface. This work shows, for the first time, a comprehensive study on a plasmon-induced reaction directly driven by TiN, expanding the prospects of this material as an alternative to gold and silver.

5. References

- [1] L. Zhou, D.F. Swearer, C. Zhang, H. Robotjazi, H. Zhao, L. Henderson, et al., *Science*, 362 (2018), 69–72.
- [2] U. Guler, J.C. Ndukaife, G. V. Naik, a. G.A. Nnanna, A. Kildishev, V.M. Shalaev, A. Boltasseva, *Nano Lett.* 13 (2013) 6078–6083.
- [3] K. Li, N.J. Hogan, M.J. Kale, N.J. Halas, P. Nordlander, P. Christopher, *Nano Lett.* 17 (2017) 3710–3717.
- [4] G. V. Naik, V.M. Shalaev, A. Boltasseva, *Adv. Mater.* 25 (2013) 3264–3294.
- [5] G. V Naik, J.L. Schroeder, X. Ni, V. Alexander, T.D. Sands, A. Boltasseva, *Opt. Mater. Express.* 2 (2012) 534–537.
- [6] U. Guler, S. Suslov, A. V. Kildishev, A. Boltasseva, V.M. Shalaev, *Nanophotonics.* 4 (2015) 269–276.
- [7] S. Saha, A. Dutta, N. Kinsey, A. V. Kildishev, V.M. Shalaev, A. Boltasseva, *ACS Photonics.* 5 (2018) 4423–4431.
- [8] A. Woodard, L. Xu, A.A. Barragan, G. Nava, B.M. Wong, L. Mangolini, *Plasma Process. Polym.* 15 (2018) 1–7.
- [9] S. Exarhos, A. Alvarez-Barragan, E. Aytan, A.A. Balandin, L. Mangolini, *ACS Energy Lett.* 3 (2018) 2349–2356.
- [10] A. Alvarez Barragan, N. V. Ilawe, L. Zhong, B.M. Wong, L. Mangolini, *J. Phys. Chem. C.* 121 (2017) 2316–2322.
- [11] C. Sungbom, M. Kawai, K. Tanaka, *Chem. Soc. Japan.* 57 (1984) 871–872.
- [12] J. Lee, W. Choi, *J. Phys. Chem. B.* 109 (2005) 7399–7406.
- [13] L. Jiao, J.R. Regalbuto, *J. Catal.* 260 (2008) 342–350.
- [14] M. Schreier, J.R. Regalbuto, *J. Catal.* 225 (2004) 190–202.