Role of UV Plasmonics in the Photocatalytic Performance of TiO2 Decorated with Aluminum Nanoparticles

Ghori, Muhammad Zubair; Veziroglu, Salih; Hinz, Alexander; Shurtleff, Bill Brook; Polonsky, Oleksandr; Strunskus, Thomas; Adam, Jost; Faupel, Franz; Aktas, Oral Cenk

Published in:
ACS Applied Nano Materials

DOI:
10.1021/acsanm.8b00853

Publication date:
2018

Document version:
Accepted manuscript

Citation for published version (APA):

Go to publication entry in University of Southern Denmark's Research Portal

Terms of use
This work is brought to you by the University of Southern Denmark. Unless otherwise specified it has been shared according to the terms for self-archiving. If no other license is stated, these terms apply:
• You may download this work for personal use only.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying this open access version

If you believe that this document breaches copyright please contact us providing details and we will investigate your claim. Please direct all enquiries to puresupport@bib.sdu.dk

Download date: 01. Nov. 2023
The Role of UV Plasmonics on Photocatalytic Performance of TiO₂ Decorated with Al Nanoparticles

Muhammad Zubair Ghori, Salih Veziroglu, Alexander Hinz, Bill Brook Shurtleff, Oleksandr Polonskyi, Jost Adam, Thomas Strunskus, Franz Faupel, and Oral Cenk Aktas

ACS Appl. Nano Mater., Just Accepted Manuscript • DOI: 10.1021/acsanm.8b00853 • Publication Date (Web): 26 Jun 2018

Downloaded from http://pubs.acs.org on June 28, 2018

Just Accepted

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.
The Role of UV Plasmonics on Photocatalytic Performance of TiO$_2$ Decorated with Al Nanoparticles

Muhammad Zubair Ghori$^{1,*}$, Salih Veziroglu$^{1,*}$, Alexander Hinz$^1$, Bill Brook Shurtleff$^1$, Oleksandr Polonskyi$^1$, Thomas Strunskus$^1$, Jost Adam$^2$, Franz Faupel$^{1,**}$, Oral Cenk Aktas$^{1,**}$

1. Institute for Materials Science - Multicomponent Materials, Faculty of Engineering, Christian-Albrechts-University of Kiel, Kaiserstraße 2, 24143 Kiel, Germany.
2. Mads Clausen Institute, NanoSYD, University of Southern Denmark, Alsion 2, DK6400 Sønderborg, Denmark.

* Both authors contributed equally.
** Corresponding authors’ email: ff@tf.uni-kiel.de; oca@tf.uni-kiel.de

Keywords: Aluminum, nanoparticles, plasmon, photocatalysis, titanium oxide, sputtering, gas aggregation source.

Abstract: We present a facile method, combining sputtering and gas aggregation techniques, to prepare a photocatalytic TiO$_2$ thin film decorated with stable Al plasmonic nanoparticles (NPs) to reveal the localized surface plasmon resonance (LSPR) effect on TiO$_2$ photocatalysis under UV irradiation. We demonstrate for the first time the negative and positive influences of LSPR on UV photocatalysis by irradiating Al NPs/TiO$_2$ hybrid structures at two different UV wavelengths: both at and above the plasmonic absorption of Al NPs. These findings open the door to designing low-cost Al-TiO$_2$ photocatalytic hybrid surfaces which function in a broad spectrum range from deep UV to VIS wavelengths.

Various methods have been proposed to enhance the photocatalytic performance of TiO$_2$, such as doping, preparing TiO$_2$ composite structures (incorporating metals or oxides) or
decorating TiO$_2$ with plasmonic metal nanoparticles (NPs). Among others, plasmonic photocatalysis has been garnering enormous interest.$^{1-4}$ Basically, plasmonic photocatalysis utilizes localized surface plasmon resonance (LSPR) of metallic NPs, mainly gold (Au) and silver (Ag), to enhance the photocatalytic performance of TiO$_2$.\textsuperscript{5} Recently, aluminum (Al) has attracted considerable attention in plasmonic photocatalysis research as an alternative plasmonic material with an extended response into the deep UV.$^{6,7}$

Besides various successful studies demonstrating the enhancement of the photocatalytic performance of TiO$_2$ by LSPR, recent studies have shown simultaneous existence of both pros and cons of LSPR in photocatalysis.$^8$ It has been shown that for TiO$_2$ decorated with Au NPs, hot electrons injected from Au to TiO$_2$ by LSPR may overcome the Schottky barrier (SB) and flow back into the TiO$_2$ under mixed ultraviolet (UV) and visible (Vis) irradiation. These electrons may compensate for those transferred from TiO$_2$ to Au NPs and promote the recombination of electron–hole pairs.$^8$ This can be considered the negative effect of LSPR on the photocatalysis. Since Au and Ag exhibit plasmonic properties in the Vis region of the spectrum, which is significantly far away from the absorption edge of TiO$_2$, a selective activation of such noble metal NPs by Vis or TiO$_2$ by UV irradiation appears to be useful to reveal the pros and cons of LSPR in photocatalysis. On the other hand, such a systematic study is not trivial in the case of Al NPs, since both Al NPs and TiO$_2$ are active in the UV range. In addition, with respect to noble metallic NPs, it is challenging to get reproducible plasmonic properties in the case of Al NPs due to the difficulty in controlling the thickness of the surrounding oxide cover.$^9$

Here, we present a facile method to prepare a photocatalytic TiO$_2$ thin film decorated with stable plasmonic Al NPs to reveal the LSPR effect on photocatalysis under UV irradiation. We demonstrate for the first time the negative and positive influences of LSPR on Al/TiO$_2$ photocatalysis by irradiating Al NPs/TiO$_2$ hybrid structures at two different UV wavelengths (both at and above the plasmonic absorption of Al NPs). The wavelength
dependence of photocatalysis reveals two different mechanisms contributing to TiO$_2$
photocatalysis. Understanding of these both mechanisms is crucial for designing cost-
effective and broad-band (deep UV to VIS) efficient photocatalytic surfaces.

Following sputter deposition of a TiO$_2$ thin film, a gas aggregation source (GAS as
shown schematically in Figure 1a)\textsuperscript{10,11} was used to decorate the deposited film with Al NPs.
In addition to argon (Ar), we introduced an extremely low amount of oxygen (O$_2$) during
sputtering to promote Al cluster nucleation by binding oxygen to sputtered Al atoms.\textsuperscript{11–13} It is
known that Al-O binding is quite stable in comparison to the low dimer binding energy of Al–
Al.\textsuperscript{14} While at 0.001-0.400 SCCM O$_2$ flow range we were able to produce Al clusters
(confirmed by both in-situ quartz-crystal-microbalance monitoring (Figure S1) and SEM
analysis (Figure 1b, Figure S2 and Figure S3)), at higher O$_2$ flow rates (>0.400 SCCM) we
did not observe any cluster formation (Figure 1b), which might be attributed to target
poisoning (oxidation). The proposed method allows synthesis of stable Al NPs of well-
controlled size (Figure 1c) and surface coverage (Figure 1d) over a wide range of O$_2$ flow
rates.
Figure 1. (a) Schematic representation of the gas aggregation source (GAS) used to produce Al NPs, (b) Schematic representation of the influence of O$_2$ flow rate on the shape and size of Al NPs (images of single NPs are implemented from SEM images given in Figure S2 and Figure S3), (c) primary particle size of Al NPs as a function of the magnetron power and (d) surface coverage of Al NPs as a function of deposition time (details are provided in Figure S4).

TEM analysis showed that most of the deposited Al NPs (>95 %) had a projected rhombus shape (Figure 2a) and size of about 20 nm. The selected area electron diffraction
(SAED) rings could be indexed as FCC Al. Further investigation by SEM showed that a majority of Al NPs have octahedral morphology (exhibiting projected rhombus shape in TEM micrographs in Figure 2c) as shown in Figure S3 (the mechanism behind the co-existence of different particle morphologies is discussed in Supporting Information section 1) and the rest exhibited truncated triangular pyramidal structure (exhibiting projected triangular shape in TEM micrographs, Figure 2b). Figure 2c shows the HRTEM image of a single Al NP with an octahedral structure exhibiting a metallic core (proven by the lattice fringes) and the surrounding shell of stable oxide about 2 nm thick. This oxide shell protects Al NPs from further oxidation and agglomeration. An XPS spectrum (Figure 2d) verified the co-existence of an ultra-thin oxide shell and the metallic Al core (more details are given in Supporting Information section 2).  

![Figure 2](image-url)

**Figure 2.** TEM images of (a) Al NPs deposited at a magnetron power of 150W for 2 min (SAED analysis is given as inset), (b) octahedral and truncated triangular bi-pyramidal Al NPs, (c) HRTEM image of an octahedral Al NP (arrows indicate the oxide shell) and (d) XPS spectrum of Al NPs.

The spectral response of Al NPs deposited on quartz substrates (three different types of surfaces composed of 20±3 nm, 40±3 nm and 80±5 nm Al NPs) was calculated (as shown in detail, Figure S5) and measured as a function of increasing particle size. As clearly seen in
the calculated spectra, the presence of a 2 nm surface oxide redshifts the plasmon resonance significantly. While 20 nm Al NPs exhibited a sharp plasmon peak, the increase in the particle size led to redshift and broader absorption spectra (Figure 3c and 3d). The difference between the calculated and experimental spectra may arise due to particle-particle interactions. For instance, in SEM images (given as insets in Figure 3b-d) Al NPs are seen in the form of self-assembled aggregates rather than isolated NPs (details on plasmonic properties of deposited Al NPs are further discussed in Supporting Information section 3).

![Figure 3](image_url)

**Figure 3.** (a) Simulated (with and without 2 nm oxide cover) and (b-d) experimental absorption spectra of Al NPs with primary sizes of 20±3 nm, 40±3 nm and 80±5 nm, respectively (insets show SEM images of corresponding Al NPs with a scale bar of 200 nm).

We deposited Al NPs on sputter-deposited TiO$_2$ films to reveal the NP influence on photocatalysis (while keeping the surface coverage of Al NPs as comparable as possible at 30-35 %, the particle size was systematically altered as presented in Figure S6). A diluted aqueous solution of methylene blue (MB) was spin coated on prepared surfaces and the
photocatalytic reaction was monitored by the change of the MB absorbance at 580 nm under UV irradiation (using UV LEDs operating at wavelengths of 280 nm and 365 nm).\textsuperscript{15} Figure 4a and b show the photocatalytic bleaching of MB on bare and Al NPs decorated TiO\textsubscript{2} layers at two different wavelengths, respectively.

Plasmonic Al NPs/TiO\textsubscript{2} hybrid layers exhibited lower photocatalytic activity at 365 nm UV irradiation in comparison to the bare TiO\textsubscript{2} layer (Figure 4a). In contrast, the photocatalytic performance of plasmonic Al NPs/TiO\textsubscript{2} hybrid layers significantly increased at 280 nm UV irradiation (Figure 4b). A TiO\textsubscript{2} layer decorated with 20 nm Al NPs exhibited the highest photocatalytic activity. Honda et al. similarly demonstrated a significant enhancement of TiO\textsubscript{2} photocatalysis by incorporating Al NPs.\textsuperscript{16} On the other hand, they reported a recovery in the MB absorbance after switching off the UV irradiation. We also observed a similar recovery (Figure 4b, indicated with the dashed line) and this may be attributed to the conversion of MB to its colorless form leuco-MB (LMB). Recently, we showed a detailed analysis of such a phenomenon\textsuperscript{6}, where the decomposition of a 60-80 nm thick MB layer even took several minutes rather than seconds as Honda et al. claimed.\textsuperscript{17} Therefore, the sudden change in the MB absorbance (within seconds) cannot be described as photocatalytic bleaching. As shown in Figure 4c, the absorption went down drastically within 20 seconds on TiO\textsubscript{2} layer decorated with 20 nm Al NPs (in-situ UV-Vis analysis), which is even much faster than the time interval reported by Honda et al.\textsuperscript{17} Thus, to monitor irreversible photocatalytic mineralization of MB, longer irradiation and observation time periods are mandatory.
Figure 4. (a) Photocatalytic bleaching of MB at 365±10 nm UV irradiation by Al/TiO$_2$ hybrid structures. Photocatalytic bleaching of MB at 280±10 nm UV irradiation (b) at-long term (c) at short-term by Al/TiO$_2$ hybrid structures. Main mechanisms observed in photocatalytic bleaching of MB by Al/TiO$_2$ hybrid structures upon (d) 280±10 nm and (e) 365±10 nm: 1: Electron-hole generation, 2: Reduction of Ti$^{4+}$ cations to Ti$^{3+}$ state, 3: Recombination, 4: Trapping of electrons by Al NPs and 5: Injection of electrons by Al NPs. (4 and 5 coexist, but depending on the corresponding wavelength, one of them dominates. Schematics only show the dominating mechanism by considering an effective electron transfer through the thin oxide shell surrounding Al NPs as discussed in Supporting Information section 4).
The difference between photocatalytic performance at 365 nm and 280 nm UV irradiation can be explained by two different mechanisms as depicted schematically in Figure 4d. At both wavelengths, electron-hole pairs are generated (Mechanism 1, Figure 4d and 4e) since in both cases bare TiO$_2$ exhibit photocatalytic activity (Figure 4a and b). The low photocatalytic activity of the deposited TiO$_2$ layer can be explained by the limited thickness and the lack of a high surface area (due to the lack of dense crack networks in such thin layers, as we presented recently$^{18}$). Photogenerated electrons can reduce Ti$^{4+}$ cations to the Ti$^{3+}$ state and this may be followed by the degradation of MB (by directly attacking acceptors, as shown by Mechanism 2, Figure 4d and 4e)$^{19}$ On the one hand, some photogenerated electrons from TiO$_2$ may overcome the SB and be trapped and localized in adjacent Al NPs (Mechanism 4, Figure 4d)$^8$ These electrons may have the chance to gather on the surface of Al NPs (LSPR induced movement to the surface) and enhance the degradation of MB by promoting interaction with surrounding acceptors (Figure 4d). On the other hand, some of trapped electrons can be injected back to TiO$_2$ (Mechanism 5, Figure 4e) which significantly triggers electron-hole recombination$^8$ thus negatively influencing the photocatalytic effect. At 280 nm UV irradiation, Mechanism 4 seems to dominate since the irradiation wavelength matches well with the plasmon absorption of Al NPs. But at 365 nm UV irradiation, the effect of LSPR is not strong enough to trigger the movement of trapped electrons to the surface of Al NPs. Rather, the Mechanism 5 (injection of electrons back to TiO$_2$) possibly dominates and reduces the overall photocatalytic activity. It should be kept in mind that in both cases (280 nm and 365 nm irradiation) Mechanism 4 and Mechanism 5 coexist, but depending on the corresponding wavelength, one of them dominates.

One can think about the shading effect of Al NPs on the TiO$_2$ surface, thus reducing the UV light-irradiated area during 365 nm UV irradiation. But then 80 nm Al NPs should have exhibited the lowest photocatalytic effect; conversely, at 365 nm UV irradiation 80 nm Al NPs exhibited slightly higher photocatalytic performance in comparison to 20 nm and 40
nm Al NPs. This may be explained by the injection of some electrons to Al NPs (Mechanism 4, Figure 4d) since the redshifted plasmon peak of 80 nm Al NPs provides relatively higher absorption (in comparison to 20 nm and 40 nm Al NPs) at 365 nm. But in all cases, the second mechanism seems to dominate under UV irradiation at a wavelength slightly further from the plasmonic absorption peak of Al NPs. These findings are in accordance with those of Lin et al. who similarly presented two mechanisms by selectively activating Au NPs and TiO$_2$ using two different wavelengths of 525 nm and 365 nm, respectively.\textsuperscript{8}

The research on plasmonic photocatalysis has progressed steadily, but still the underlying mechanism has not yet been fully understood. Here, we could demonstrate for the first time the coexistence of effects both negative (injection of electron from Al NPs) and positive (trapping of electrons by Al NPs) of UV plasmonics on the photocatalytic activity of TiO$_2$. We are aware that LSPR can influence the photocatalysis by various mechanisms, including sensitization (shifting absorption of TiO$_2$), tuning bandgap energy (e.g. SB barrier formation), radiative and non-radiative decays and most of the time these mechanisms can co-exist. Therefore, the current study assists in understanding the mechanism of UV plasmonic photocatalysis under UV irradiation, which may help in designing cheaper and high efficient photocatalysts functioning at a broad spectral range.

**Associated Content**

**Supporting Information**

In-situ deposition rate analysis, SEM images of Al NPs, surface coverage analysis, simulated absorption spectra of Al NPs and explanation of corresponding numerical methods using COMSOL software. Additional information about the particle formation mechanism, structural properties of the oxide shell, plasmonic properties of Al NPs, and Al/TiO$_2$ interface and electron transfer mechanism though oxide shell.
ORCID
Franz Faupel: 0000-0003-3367-1655
O. Cenk Aktas: 0000-0003-1328-9854
M. Zubair Ghori: 0000-0001-8633-4316

Notes
The authors declare no competing financial interest

Acknowledgements
Simulation for the work described in this paper was supported by the DeiC National HPC Centre, SDU. M. Z. Ghori acknowledge Graduate Center and Federal State Funding CAU Kiel for providing funding for his PhD study. Authors would like to thank Stefan Rehders for his continuous support for sputtering setup.

References


Graphical Abstract
Figure 1. (a) Schematic representation of the gas aggregation source (GAS) used to produce Al NPs, (b) Schematic representation of the influence of O2 flow rate on the shape and size of Al NPs (images of single NPs are implemented from SEM images given in Figure S2 and Figure S3), (c) primary particle size of Al NPs as a function of the magnetron power and (d) surface coverage of Al NPs as a function of deposition time (details are provided in Figure S4).
Figure 2. TEM images of (a) Al NPs deposited at a magnetron power of 150W for 2 min (SAED analysis is given as inset), (b) octahedral and truncated triangular bi-pyramidal Al NPs, (c) HRTEM image of an octahedral Al NP (arrows indicate the oxide shell) and (d) XPS spectrum of Al NPs.

150x72mm (300 x 300 DPI)
Figure 3. (a) Simulated (with and without 2 nm oxide cover) and (b-d) experimental absorption spectra of Al NPs with primary sizes of 20±3 nm, 40±3 nm and 80±5 nm, respectively (insets show SEM images of corresponding Al NPs with a scale bar of 200 nm).
Figure 4. (a) Photocatalytic bleaching of MB at 365±10 nm UV irradiation by Al/TiO2 hybrid structures. Photocatalytic bleaching of MB at 280±10 nm UV irradiation (b) at long-term (c) at short-term by Al/TiO2 hybrid structures. Main mechanisms observed in photocatalytic bleaching of MB by Al/TiO2 hybrid structures upon (d) 280±10 nm and (e) 365±10 nm: ❶ Electron-hole generation, ❷ Reduction of Ti4+ cations to Ti3+ state, ❸ Recombination, ❹ Trapping of electrons by Al NPs and ❺ Injection of electrons by Al NPs. (❹ and ❺ coexist, but depending on the corresponding wavelength, one of them dominates. Schematics only show the dominating mechanism by considering an effective electron transfer through the thin oxide shell surrounding Al NPs as discussed in Supporting Information section 4).

150x151mm (300 x 300 DPI)