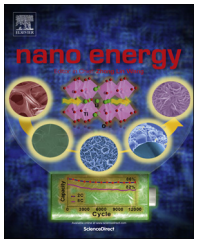
Nano Energy (2016) 21, 115–122

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/nanoenergy



COMMUNICATION

# Two-dimensional metal-dielectric hybrid-structured film with titanium oxide for enhanced visible light absorption and photo-catalytic application

Joonmo Park[a], Hee Jun Kim[a], SangHyeon Nam[b], Hyowook Kim[b], Hak-Jong Choi[c], Youn Jeong Jang[e], Jae Sung Lee[d], Jonghwa Shin[b], Heon Lee[c,*], Jeong Min Baik[a,*]

[a]*School of Materials Science and Engineering, KIST-UNIST-Ulsan Center for Convergent Materials, Ulsan National Institute of Science and Technology (UNIST), Ulsan, Republic of Korea*
[b]*Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon, Republic of Korea*
[c]*Department of Materials Science and Engineering, Korea University, Anam-dong 5-ga, Seongbuk-gu, Seoul 136-713, Republic of Korea*
[d]*Department of Energy and Chemical Engineering, Ulsan National Institute of Science and Technology (UNIST), 50 UNIST-gil, Ulsan 689-798, Republic of Korea*
[e]*Department of Chemical Engineering, Pohang University of Science and Technology (POSTECH), San 31 Hyoja-Dong, Pohang 790-784, Republic of Korea*

Received 11 August 2015; received in revised form 30 December 2015; accepted 8 January 2016
Available online 14 January 2016

**KEYWORDS**
2-dimensional Design;
$TiO_2$;
Visible Light Absorption;
Photocatalyst;
Water-splitting

**Abstract**
Two-dimensional design based on ultrathin $TiO_2$ film for enhanced visible light absorption and photo-catalytic applications is reported, which mainly consists of three layers of gold film, $TiO_2$ film, and gold nanoparticles (Au NPs). The Au and $TiO_2$ films are produced by e-beam evaporation and atomic layer deposition, respectively, in a carefully controlled way to minimize surface roughness. As compared with bare $TiO_2$ film, the Au NPs/$TiO_2$/Au film significantly increased the photoactivity over the entire UV and visible wavelength range. The Au film increases the light absorption in the UV region with $TiO_2$ acting as an impedance-matching layer, while the Au NPs increase the light absorption in the visible region due to the plasmonic resonance effects, increasing the photocurrent under visible light. 3D numerical simulation results suggest that the Au film also plays an important role in enhancing the electrical field

*Corresponding authors.
*E-mail addresses:* heon.lee@gmail.com (H. Lee), jbaik@unist.ac.kr (J.M. Baik).

http://dx.doi.org/10.1016/j.nanoen.2016.01.004

intensity at the $TiO_2$ film in contact with Au NPs, by efficient excitation of localized surface plasmon resonances, thereby, contributing to the enhanced photoactivity of the film in the visible range. This simple system may serve as an efficient platform for solar energy conversion utilizing the whole UV-visible range of solar spectrum based on two-dimensional plasmonic photoelectrodes.


## Introduction

Photocatalytic water splitting to produce molecular hydrogens and oxygen in artificial photosynthetic system has been practiced in laboratories for decades. So far, many materials have been suggested until now, however, titanium dioxide ($TiO_2$) is still one of attractive photoelectrodes due to its strong optical absorption, high chemical stability, environmental benignity, and low cost [1]. There have been many reports which show the photoconversion efficiencies to enable the development and commercialization of $TiO_2$-related materials [2-4]. However, the $TiO_2$-based photoelectrodes still suffer from many drawbacks that limit the successful commercialization such as the predominant absorption in the UV region due to the wide bandgap ($\sim$3.4 eV) and the slow water oxidation kinetics due to the valence band far away ($\sim$1.17 eV) below the water oxidation level. These resulted in a dramatic decrease in the energy conversion efficiency.

Among the challenges of overcoming the issues is the development of photoelectrodes with various nanostructures such as 0-D nanodots, 1-D nanowires, 2-D ultrathin films and 3-D nanostructures [5-8]. Recently, several structural designs such as hierarchical [9], branched [10] assemblies of nanoscale materials are effective in increasing the UV-vis absorption, consequently, enhancing water-splitting efficiency. Several methods of dopant incorporation into $TiO_2$ such as metals [11,12] or non-metals [13-15] were highly spotlighted in a semiconductor viewpoint, which provides suitable energy levels for maximizing the light absorption, carrier lifetime (by decreasing the diffusion length), and water redox kinetics [16]. However with these doping strategies, it may occur undesired recombination of photo-generated carriers, which dramatically reduces the efficiency of photoelectrochemical (PEC) cells.

Not only this strategies, but the incorporations of plasmonic metal nanoparticles (i.e. Au) to $TiO_2$ structures have been shown to enhance the water-splitting efficiency especially in the visible region due to strong localized surface plasmon resonance (LSPR) excitation from collective oscillations of the surface electrons on metal nanoparticles [17-22]. The plasmonic metal nanoparticles sensitize $TiO_2$ to visible light and increase the light absorption, injecting additional hot electrons to $TiO_2$ and leaving behind holes for water oxidation. This approach was found to be much effective in semiconductor with very confined dimension than the doping sensitization. The LSPR can be intensified by the electromagnetic interaction between adjacent metal nanoparticles, in which the resonance excitation is tuned by changing the size and distance between each nanoparticles, as well as the kinds of metal; as the distance decreases, the resonant peaks get bigger and in Au nanoparticles, the peaks are observed in the higher wavelength than Ag nanoparticles [23]. According to the theoretical calculation, the spectral modulation in the excitation and the light absorption amplification can enhance the injection of the hot carriers toward the conduction band of the semiconductor [24]. However, in this approach, it is still unsatisfactory as only a few hot-carriers are transferred to surface via this localized SPR property, resulting in a low plasmonic conversion efficiency ($\sim$1%) to water splitting [25].

Here, we demonstrate a simple approach for maximizing the light absorption in the entire UV-visible region, in which the photoelectrode consists of three layers of Au film, $TiO_2$ film, and Au nanoparticles (NPs). The layers are carefully produced using thin-film deposition technique, followed by the post annealing process. Although the electrode does not have a large surface-area-to-volume ratio, compared with previous nanostructures, we will show that a significant increase of the photoelectrochemical water oxidation rate can be achieved by optimal design of the three-layered photoelectrodes for broadband enhancement over the UV and visible part of solar spectrum. This ascribes to the increase of the light absorption in UV region due to the light reflected at $TiO_2$/Au thin film and in visible region due to the electric field enhancement at the $TiO_2$ film resulting from LSPR of Au NPs.

## Experimental

### Fabrication of 2-dimensional metastructured films

A glass substrate was used as the starting substrate. Before the fabrication of the photoelectrode, the substrate was cleaned with acetone, isopropanol, and de-ionized water. A thin layer of 100-nm-thick Au was deposited on the glass substrate using e-beam evaporation at a very slow deposition rate of less than 0.2 A/s. A 20 nm $TiO_2$ thin film was then coated onto the Au layer by using an atomic layer deposition (ALD) system (LUCIDA D100, NCD Technology, Korea). It was conducted with alternating exposure of titanium tetraisopropoxide (TTIP) and de-ionized water vapor at temperature of 200 °C with nitrogen as the carrier gas and purge gas at a pressure of 6.5 Pa. The pulse/purge times are 0.1 s/20 s for the precursors. The deposition rate of the $TiO_2$ layer is approximately 0.23 Å per cycle. The thickness of the $TiO_2$ film was measured from ellipsometer (M2000V, J. A. Woolam Co.). Finally, an Au film with the thickness ranging 3 to 7 nm was deposited over the film at a