INVESTIGATION OF PHONON-ASSISTED OPTICAL NEAR-FIELD EXCITATION ON NANOSTRUCTURED TiO_2 TOWARDS ON-CHIP FUEL CELL APPLICATION

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ABSTRACT

We report herein the investigation of a novel non-adiabatic optical near-field (ONF) excitation on nanostructured TiO_2 photo-anode. The usage of ONF allows the transition to the dipole forbidden phonon states, which is called the phonon-assisted ONF transition, and hence allows us to excite TiO_2 by sub-bandgap photon. Here, we investigated the usage of ONF to induce the photocatalytic activity of TiO_2 with visible light instead of conventional UV light. By introducing nanostructure into TiO_2 photo-anode to generate optical near-field at the surface of electrode, we confirmed the enhancement of photo current in the visible range, and this current is attributed to the phonon-assisted ONF excitation. This study should lead to a novel approach to excite TiO_2 by sub-bandgap photon, consequently improve its visible-light response photocatalytic performance. It also suggest that this kind of nanostructured semiconductor photocatalyst have promising properties for hydrogen production from water splitting.

KEYWORDS: Nanostructured titaninum dioxide, visible-light response photocatalyst, optical near-field(ONF), phonon-assisted excitation, overall water splitting.

INTRODUCTION

Over the past decades, due to the increasing need for clean energy, significant effort has been made to investigate semiconductor photocatalysts such as TiO_2, ZnO, and WO_3 that can efficiently produce hydrogen from water splitting. Yet the large bandgaps of those materials and the lack of absorption in visible range of solar spectrum is the major limitation so far. To overcome this, there have been approaches to manipulate the bandgaps of metal oxides by doping both transition metals as well as nitrogen, or carbon. The doping enhances the visible absorption whereas it makes recombination centers for photogenerated holes and electrons that conversely reduce the photocatalytic performance[1-2]. The visible-light response photocatalyst still remains a big issue. In this study, we report a novel approach to excite TiO_2 with visible light by using optical near-field without changing the electronic band structure of material. Thus unlike in the case of doping, it is expected to hav1e no influence on the photocatalytic performance of TiO_2.

Recently it has been reported by Ohtsu et al. that the optical near-field generated at nanomeric surface of material allows the transition of electric dipole forbidden states, together with the conventional excitation of electronic levels. This novel excitation has been confirmed to be able to excite the carriers by sub-bandgap photons in many kinds of materials and has already been applied in the development of novel photochemical vapor deposition [3], photolithography [4], self-organized photochemical etching [5], etc. Herein, we studied for the first time the usage of this novel property of optical near-field to excite photocatalyst TiO_2 by visible light. Besides, the enhancement of proton conductivity in nanochannels suggested us the usage of nanochannel-array as a novel class of proton exchange membrane for micro fuel cell application[6]. In the future, taking the advantages of these two effects, we are also simultaneously developing the integration of the investigated visible-light response photocatalyst into micro device and realizing the overall water splitting reactor and fuel cell in micro/nanofluidic device.

CONCEPT

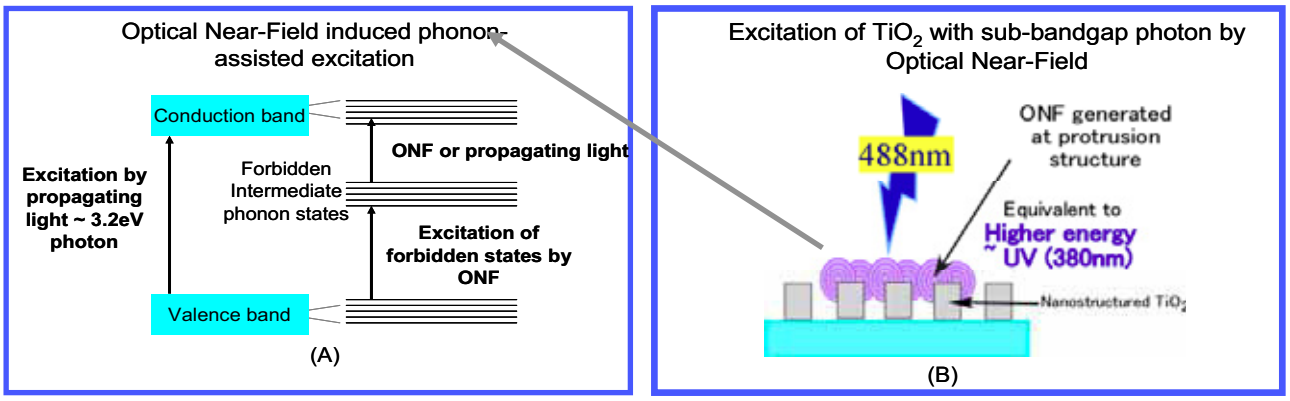

Fig 1. (A) Schematic diagram of ONF-induced phonon-assisted excitation (B) In case of TiO_2

Fig. 1 shows the schematic diagram of the excitation of titanium dioxide with sub-bandgap photon by two-step phonon-assisted process. The first step is the excitation of electrons from valence band to intermediate phonon states by optical near-field. The intermediate phonon states exist in the bandgap are dipole-forbidden levels that can not be excited by conventional propagating light, and hence optical near-field is indispensable for the transition to such levels. In the second step, electrons can be excited from phonon states to conduction band by both optical near-field and propagating light, since this is a dipole-allowed transition[3]. We have studied this multi-step phonon assisted excitation on TiO_2 thin film by introducing nanostructures into TiO_2 film and evaluating the visible light response of TiO_2 thin film in photocatalytic water splitting reaction based on photo electro chemical (PEC) cell.

EXPERIMENTAL

Since the nanostructure and morphology of materials play important roles in the generation of ONF, especially the protrusion surface structure[3], we introduced nanostructures into TiO_2 thin film by both (1)Top-down and (2) bottom-up approach. For the top-down method, the nano-pillar pattern was fabricated onto quartz substrate by EB lithography and dry etching process. We have reached the limitation of pillar sizes as 200nm, and pitch between pillars and depth as 200nm and 300nm. Two layers of Ti (50nm) (conducting layer) and TiO_2 (100nm) were deposited onto the quartz substrate to form a TiO_2 electrode. For the bottom-up approach, TiO_2 thin films were grown directly onto transparent conducting substrate SnO_2:F by CVD method with the thickness of 1.0, 0.5, 0.3, 0.1 μm, respectively. The morphology of films were controlled by film thickness. The morphology and the surface average roughness(Ra) of the films were characterized by scanning electron microscope (SEM) and atomic force microscope (AFM). The photocatalytic performance of TiO_2 photo anode was evaluated by PEC measurement with a 3-electrode cell setup, as shown in Fig. 2A. For comparison, the photo anode were irradiated by UV (SP-9 Spot Cure UV source) and 488nm laser. The electrolyte used in all measurement was 0.5M $NaClO_4$. A bias voltage of 0.5V vs Ag/AgCl was applied to all measurements.

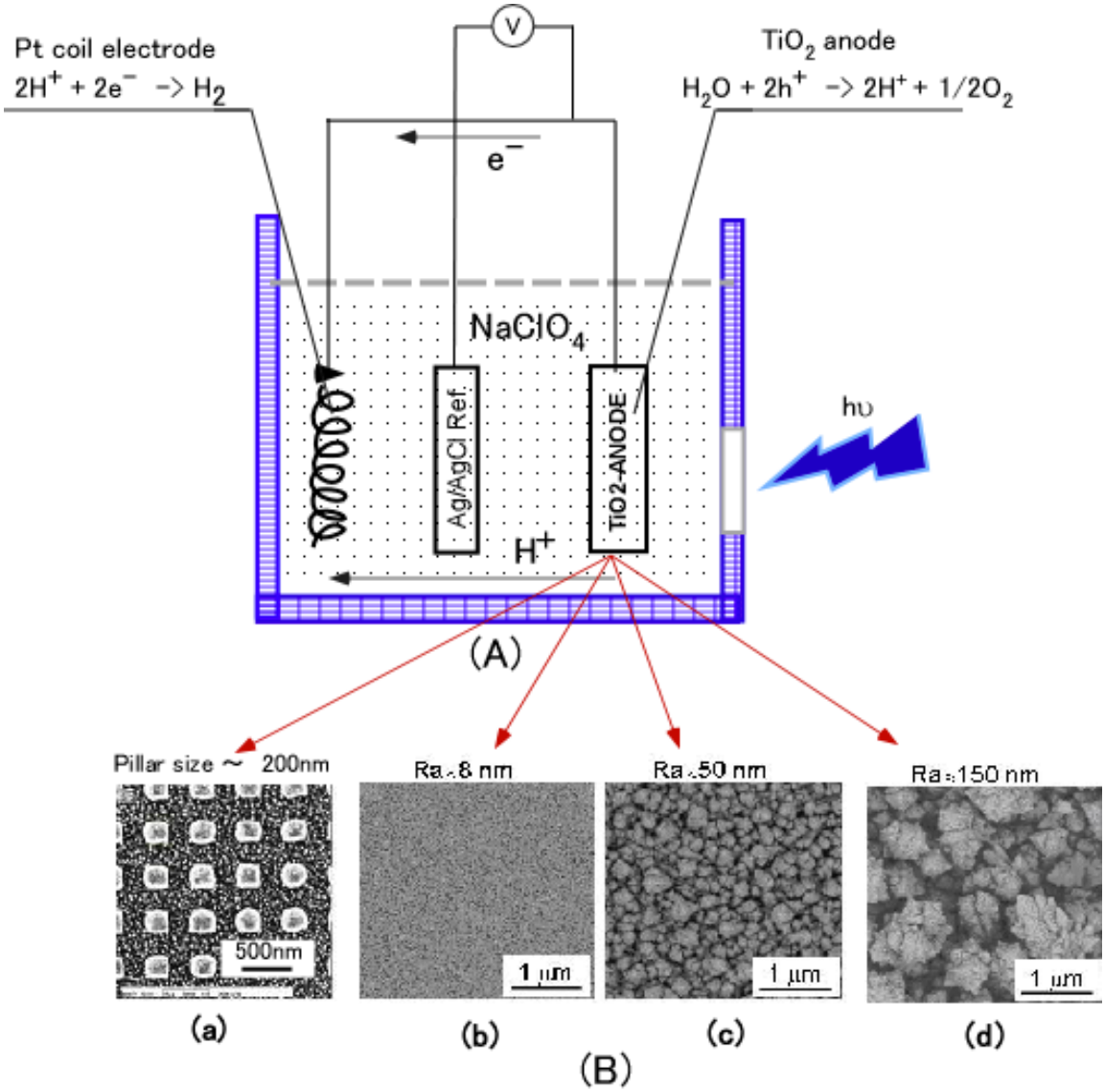

Fig. 2 (A) PEC cell set up (B) SEM images of (a) nano-pillar and thickness (b) 0.1 μm, (c) 0.5 μm, (d) 1.0 μm CVD samples respectively

RESULTS AND DISCUSSION

Fig. 2B shows the SEM images of nano-pillar samples and CVD samples. In case of CVD samples, the thicker film shows the larger grain size and protrusion structure that promise a better ONF effect.

The X-ray diffraction (XRD) spectra show that, TiO_2 thin film in nano-pillar sample was a mixed phases of rutile and anatase at the ratio 5:1, while the film deposited by CVD showed all anatase crystal phase.

For nano-pillar samples, under both UV and visible irradiation, there was no significant difference in photo-response current between nano-pillar fabricated and non-fabricated film. This result suggested that the nano-scale of nano-pillar was not sufficient to generate optical near-field and consequently not able to contribute the effect large enough to be observed in our measurement. However, we could not introduce the finer nanostructure by this top-down method. The visible response of both patterned and non-patterned samples can be attributed to the absorption of surface defects such as oxygen vacancies.

Fig. 3 shows the UV and 488nm photo response of CVD samples. Under UV irradiation, the TiO_2 films with the larger grains showed the larger photo currents due to the enhancement of specific surface area(Fig. 3A), while under visible irradiation, the more significant difference between samples with different surface roughness has been observed. For example, the 1μm-thick sample showed a double higher Incident-photon-to-current conversion efficiency (IPCE) under UV irradiation, while a 3 times higher IPCE under 488nm irradiation, compared with the 100nm-thick sample. This enhancement could be attributed to the optical near-field nonadiabatic multi-step excitation process.

The investigation to separate the photo response current derived from absorption of surface defect and optical near-field effect is undergoing. Besides, towards the improvement of optical near-field generation, the Glancing Angle Deposition (GLAD) sputtering method is being introduced to control the fine TiO_2 nanorod structure with optimized size, and the size dependence of the optical near-field effect is under investigation.

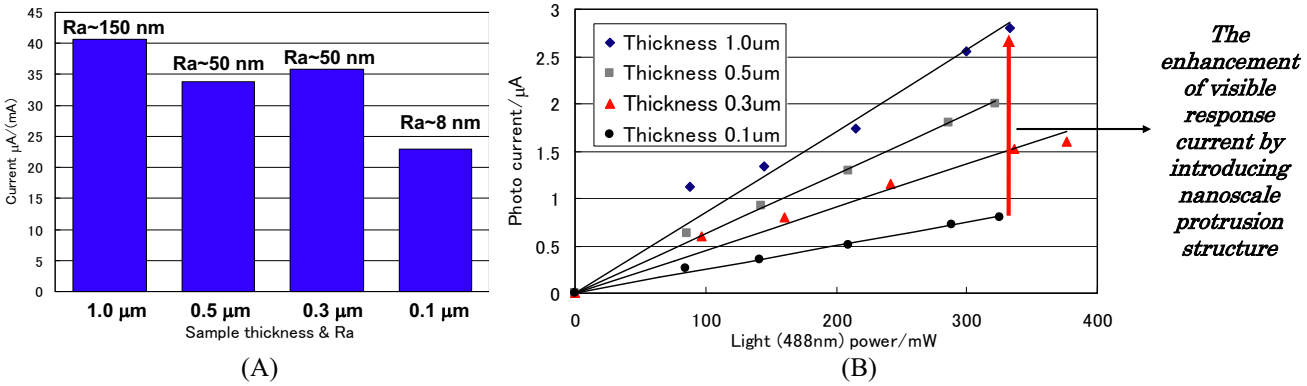

Fig. 3 Photo response current of CVD samples under(A) UV & (B) 488nm irradiation

CONCLUSION

We have prepared nanostructured TiO_2 thin film and investigated the phonon-assisted optical near-field excitation by PEC measurement. Our results confirmed the excitation of TiO_2 with sub-bandgap photon by using the novel non-adiabatic transtition property of optical near-field. The fine nanomeric surface structure of the materials was realized to be the most significant factor in this effect. This study suggested a novel approach to develop visible-light reponse photocatalytic materials using optical near-field by merely introducing nanoscale structure and morphology.

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