Here we report the fabrication of TiO₂ nanorod by using glancing angle deposition and confirm for the first time the novel way to induce the visible response of TiO₂ in photoelectrochemical water splitting, that is achieved by the utilizing of optical near-field (ONF) generated on nanorod structures. The ONF allows the so-called phonon-assisted excitation process, which excites TiO₂ with sub-bandgap photons via phonon energy, and hence induce the visible response. This study suggest that this kind of nanostructured photocatalyst is promising material for hydrogen production in fuel cell application. Moreover, we believe that the present approach can be applied not only to photocatalyst but also other solar-harvesting materials.

KEYWORDS: visible-response photocatalysts, optical near-field, photoelectrochemical water splitting, nanostructures fabrication, micro fuel cell

INTRODUCTION

The micro chemical system on chip with reported high efficiencies of mixing, reaction and separation has rapidly progressed. Recently, we have targeted to extended nano-scale (10⁻¹–10³ nm) to explore a new science in the space that bridges the gap between single molecule and condensed phase. We have previously clarified novel specific properties of liquid confined in extended-nano spaces such as enhanced proton exchange rate, increased viscosity, decreased dielectric constant, etc [1]. Taking these advantages, we are working on the development of a novel photo fuel cell device in which the fuel generation from photoelectrochemical water splitting cell using photocatalysts and fuel cell integrated onto one single microchip. However, the efficiency of reported photocatalysts still remains a big limitation due to the lack of response in visible region. There have been significant efforts to improve the visible response of TiO₂ based photocatalyst to date by chemically manipulating its bandgap, yet the doping of foreign elements forms recombination centers for photogenerated holes and electrons that conversely reduce the photocatalytic performance.

Recently, it has been reported by Ohtsu et al. that the optical near-field (ONF) generated at nanomeric surface of material allows the transition of electric dipole forbidden states that makes it behave like an apparent higher energy photon. This novel property has been confirmed to excite carriers with sub-bandgap photons in many materials[2-3]. This effect inspired us a way to induce the visible response of photocatalysts TiO₂ by using the ONF generated at the original surface roughness of material that has been confirmed previously[4]. Our method does not change the chemical structure of material, thus unlike conventional chemical approaches, it is expected to have few drawbacks on the overall photocatalytic performance of TiO₂. The fabrication of nanostructured TiO₂ is indispensable for the generation of ONF, however there are few methods that can well-control the size and nanostructures of the film reported so far. The objective of this study is to realize the visible response photocatalytic reaction by utilizing the ONF generated at nanorod TiO₂.
CONCEPT

Fig. 1(a) shows the concept of micro/nano photo fuel cell which can be considered as a self-charging and clean power device and no outside supply of fuel is needed. The specific properties of gas/liquid separation in micro/nanofluidics is expected to improve the fuel generation and storage. The enhancement of proton conductivity in nanochannels suggested us the usage of nanochannel-array as a novel class of proton exchange membrane. The principle of the excitation of TiO$_2$ with visible light using ONF is shown in Fig. 1(b). Under the irradiation of propagating visible light, ONF is generated at the nanostructured surface. The ONF can excite the coherent phonons in the nanostructures, together with the ONF, these excited coherent phonons form a coupled state which is called virtual exciton-phonon-polariton. This coupled state contributes to the phonon-assisted process, in which an electron is excited from the valence band of a semiconductor to the conduction band via energy of phonon.

EXPERIMENTAL

Since the nanostructures, especially the protrusion structures play a significant factor in the generation of ONF, we proposed that the 1D nanorod should be favorable structures. We introduce the Glancing Angle Deposition (GLAD) for the fabrication of TiO$_2$ nanorod. This method provides a simple way to develop well-aligned nanorod structure and controllable size and shape of rods by changing deposition parameters[5]. GLAD is a physical vapor deposition process in which the target flux is incident onto a substrate at an angle greater than $70^\circ$ with respect to substrate normal and the substrate is kept rotating at certain condition (Fig. 2(a)). The photocatalytic performance of TiO$_2$ photo anode was evaluated by photoelectrochemical (PEC) measurement with a 3-electrode cell setup in 0.5M NaClO$_4$ electrolyte and 0.5V (vs. Ag/AgCl) applied bias (Fig. 2(b)).

RESULTS AND DISCUSSION

(1) The fabrication and size control of TiO$_2$ nanorod

The scanning electron microscopy, top view and cross sectional images of nanorod films shown in the Fig. 3 reveal the formation of vertical and isolated nanorods. The deposition onto a flat ITO (Indium Tin Oxide) coated glass substrate leads to the growth of nanorod less than 100nm in diameter, meanwhile, the using of pyramid-like nano-patterns on the FTO (F: doped Tin Oxide) substrate which serves as nucleation sites for the incoming target flux allows the growth of rods larger than 100nm. The as-deposited films were post-annealed under oxygen flow at 550°C to convert films into anatase phase. For the reference purpose, we fabricated the flat film made of Degussa P-25 TiO$_2$ nanoparticles by spin-coating.

(2) The visible response photocatalytic performance of TiO$_2$ film

The power dependence of photocurrent in Fig. 4 (a), (b) shows the photocatalytic performance of fabricated films under UV (365nm) and visible (488nm) irradiation, respectively. Under UV irradiation, the nanorod TiO$_2$ films perform response currents comparative to that of the reference P-25 film; while under visible (488nm) irradiation, more than 2 orders of magnitude enhancement of photocurrents in 150nm nanorod sample has been observed. The introduction of nanorod structures has led to the large enhancement only in the visible region that excludes the possibility of photocurrent derived from enhanced specific surface area and improved charge separation and transport properties. The linear dependence in a wide range of light power density($10^{-5}$-$10^{8}$ mWcm$^{-2}$) the excitation of TiO$_2$ by multi-photon non-linear absorption. It is also worthy to note that, even under visible irradiation the photocurrent has been acquired in the range of $10^{-5}$A, that eliminates the factors of thermal effect or background noise during the measurement.

(3) Verification of the ONF-induced excitation of TiO$_2$ by visible light
There are limited investigations in which the oxygen vacancy states, or the midgap states can contribute to the visible response of doped TiO$_2$ material. Therefore, it is indispensable to exclude the possibility of visible response enhancement by oxygen vacancies in our samples prepared by GLAD method. In general, the photoluminescence (PL) spectroscopy study could give us the information about surface state, such as defect state and oxygen vacancy of semiconductor. Nevertheless, little is known about the PL properties of TiO$_2$ at room temperature, for TiO$_2$ is an indirect semiconductor. To investigate the oxygen vacancy by PL spectroscopy, we conducted the measurement at low temperature (12K) with the excitation at 325nm. The fitted spectra in the Fig. 5 showed the same tendency in PL characteristic of nanorod and P-25 film samples. The peaks around 500nm and 550nm can be ascribed to the oxygen vacancies on the surface and intrinsic defects in the bulk, respectively. This result demonstrates that there is no significant difference in peak intensity of the PL spectra, or no relevant relations between oxygen vacancies concentration and the visible photo-response currents observed in PEC measurement. It can be concluded that the enhancement of visible response in nanorod samples does not relate to the oxygen vacancy.

CONCLUSION AND PERSPECTIVE

Our result confirmed for the first time a novel physical approach to excite TiO$_2$ with visible light by utilizing the ONF generated at nanorod structure. This study opens a new perspective for the development of visible-light driven nanostructure photocatalysts. We also have a plan to utilize the ONF effect during the fabrication process so that the nanostructure of the film could be formed in a self-organized manner and the obtained structures should lead to a significant ONF-induced visible response photocatalytic performance. In the next step, we will apply this method into the development of water splitting system in a microchip.

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Figure 4. Photoelectrochemical performance of (a) UV 365nm (b) 488nm irradiation

Figure 5. PL spectra at 12K of fabricated films