

## Enhanced Efficiency of TaON and BiOI-based Solar Cells by Au Nanoparticles

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### Abstract

Au nanoparticles were prepared by a chemical reduction method and were deposited on TaON nanoparticle or BiOI microsphere to prepare the composites of Au/TaON or Au/BiOI, respectively. The composites of Au/TaON and Au/BiOI were analyzed by UV-visible spectroscopy, XRD, and EDX. The films of these nanocomposites were prepared by a squeeze method and were applied to solar cell where Pt film was used as counter electrode. A water based solution of  $Ce^{3+}/Ce^{4+}$  was used as an electrolyte. It was found that Au deposited TaON or BiOI film shows higher current ( $I$ )-voltage ( $V$ ) curve under UV-visible light irradiation.

*Keywords:* Au; TaON; BiOI; Composite; Solar cell.

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## 1. Introduction

Semiconductor photocatalysts offer a potential approach for the conversion of solar energy conversion. Among various metal oxide semiconductors  $TiO_2$  has been widely studied. But it shows photoactivity only under UV light which accounts for merely <5% of the solar photons, thereby hampering its wide usages. There are many other promising oxide and nonoxide semiconductors which shows photoactivity under visible light such as  $WO_3$ ,  $Fe_2O_3$ ,  $CdS$ ,  $Bi_2S_3$ ,  $In_2S_3$ ,  $Ta_3N_5$ , TaON etc [1, 2]. Among these catalysts, TaON, which has a bandgap of 2.5 eV (absorption edge at 500 nm), has conduction and valence band edges of ca. -0.3 and +2.2V versus NHE (pH = 0), respectively, sufficient for splitting water into  $H_2$  and  $O_2$  [3]. But merely TaON films show low photo to current conversion efficiency in solar cell.

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Recently a new class of bismuth oxyhalide photocatalysts have been reported and among them BiOI was found to show higher photocatalytic activity than  $\text{TiO}_2$  under visible light irradiation [4]. Zhao *et.al.* [5] prepared BiOI microsphere particles and showed application to solar cell for the first time [5]. However, the efficiency of the solar cell was low for practical application. For the enhancement of the activity, encapsulation or adoration of semiconductor photocatalysts with highly dispersed noble metal nanoparticles such as Ag, Au and Pt are of great interest, because the nanoscale noble metals are usually a classic high-performance heterogeneous catalyst [6, 7]. Especially, the nanoparticles of gold have been attracting more attention because it has many color varieties in the visible region based on plasmon resonance, which is due to the collective oscillations of the electrons at the surface of the nanoparticles. The resonance wavelength strongly depends on the size and shape of the nanoparticles, the interparticle distance, and the dielectric property of the surrounding medium. So far, enhanced photocatalytic activities of TaON and BiOI by Au nanoparticles have not been reported. Here we report the successful preparation of Au/TaON and Au/BiOI nanocomposites by a simple method and their applications in solar cells.

## 2. Experimental

TaON was received as a gift from the University of Tokyo [3] and BiOI nanoplate microspheres were prepared by a solvothermal method [8]. The colloidal Au nanoparticles were prepared by the citrate reduction [9] from chloroauric acid (Wako Pure Chemical Industries, Ltd., Japan). The Au nanoparticles were condensed by using a high speed centrifugation machine running at 15000 rpm for 20 min and mixed with 300 mg of TaON or BiOI followed by sonication for 5min. Finally, Au deposited TaON or BiOI was dried at 40 °C. Chitosan solution was prepared by mixing chitosan flakes (Wake, 98%) with water and gradually dropping HCl solution to the mixture to maintain the pH near 3. After removal of the undissolved part, the pH value of chitosan solution was adjusted to about 5.0 by using an aqueous NaOH solution. The final concentration of chitosan solution was estimated to be 0.5 wt%.

For the preparation of the BiOI electrodes, BiOI nanoplate microspheres were dispersed in chitosan solution to form a 10 mg/mL solution and ultrasonicated for 5 min, and 0.3 mL of the colloidal solution was dropped on the pretreated ITO surface and allowed to dry at 50°C for 24 h. Both films of Au/TaON and Au/BiOI were used as a working electrode and Pt-based films were used as a counter electrode. The two electrodes were sandwiched and a mixture of  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (0.1M, wako, 99%) and  $\text{Ce}(\text{NO}_3)_4$  (0.05M, Sigma-aldrich, 99%) in a water based solution (35% ethanol and 65% water) was used as an electrolyte that was filled into a space between the two electrodes. All films were prepared on indium-tin-oxide (ITO, Aldrich) coated glasses which have a resistance of 8-12 ohms.

The UV-visible diffuse reflectance spectra of the photocatalysts were recorded using a UV-visible spectrophotometer (Shimadzu Corporation, MPS-2000) and  $\text{BaSO}_4$  as a reflectance standard. The size and surface condition of the submicrospheres were analyzed by a field-emission scanning electron microscope (FE-SEM, Hitachi, S-4100H) and a transmission electron micrograph (JEOL, JEM-3010 VII, operating at 300 kV). Crystal

structure identification was made by X-ray diffraction (XRD) using a PANalytical Advance X-ray diffractometer with  $\text{CuK}\alpha$  radiation. The XPS patterns were recorded on an X-ray photoelectron spectrometer (Shimadzu, ESCA-1000) using  $\text{MgK}\alpha$  X-ray as the excitation source and  $\text{C1s}$  (284.6 eV) as the reference line. The quantitative chemical composition of the Au/TaON and Au/BiOI composite nanocluster surface was also measured using an energy dispersive X-ray spectrometer (EDX, Philips, XL 30CP) attached to the cold field SEM. A xenon lamp (Inotex 300-W LX-300F) with an IR cut-off filter was used as a light source (power 1 sun). For the measurement of the performance of solar cell, an  $I$ - $V$  meter (Keithly 2400) was used. The  $I$ - $V$  meter was connected to a computer with a Peccell  $I$ - $V$  curve analyzer (PECK2400-N).

### 3. Results and Discussion

Fig. 1(a) shows the TEM images of Au nanoparticles prepared by the citrate reduction method. It is seen that most of the particles have spherical shape. The average diameters of the gold nanoparticles were about 20 nm.

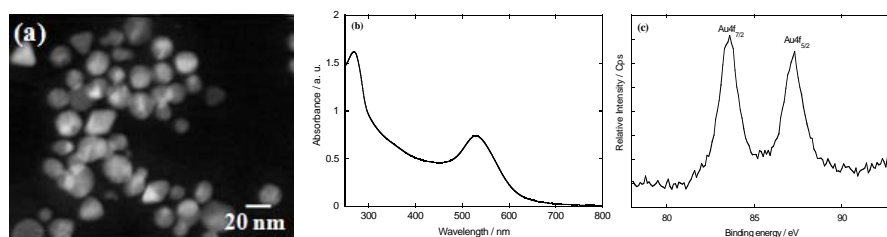


Fig. 1. (a) TEM image, (b) UV-visible reflection spectrum, and (c) XPS spectrum of Au nanoparticles.

The UV-visible spectrum of the prepared gold nanoparticles show a strong absorption peak at 530 nm for spherical gold nanoparticles (Fig. 1b). The X-ray photoelectron spectroscopy (XPS) was used to study for the surface composition and electronic states of the gold nanoparticles. Fig. 1c shows the typical gold XPS spectrum of 4f orbital in the as-deposited film. The spectrum shows the peaks at binding energies of  $\text{Au}4f_{7/2}$  at 83.8 and  $\text{Au}4f_{5/2}$  at 87.45 eV corresponding to the standard gold [9] the former of which is also found to be significantly different from  $\text{Au}^+ 4f_{7/2}$  (84.6 eV) and  $\text{Au}^{3+} 4f_{7/2}$  (87.0 eV) but similar to  $\text{Au}^0 4f_{7/2}$  (84.0 eV). The XPS results suggest that the Au species are present in the metallic state and their surfaces have no charge.

Fig. 2(a, b) shows the representative scanning electron microscopy (SEM) images of BiOI and TaON films. The particle sizes of TaON ranges from 200 nm to 300 nm. The as-prepared BiOI sample consists of spherical particles with size of 2–5  $\mu\text{m}$ . The higher magnification SEM image (data not shown) revealed that the BiOI spherical particles are composed of nanoplates of about several nanometers in thickness. The nanoplates were aligned radially and tightly to further form hierarchical microspheres.

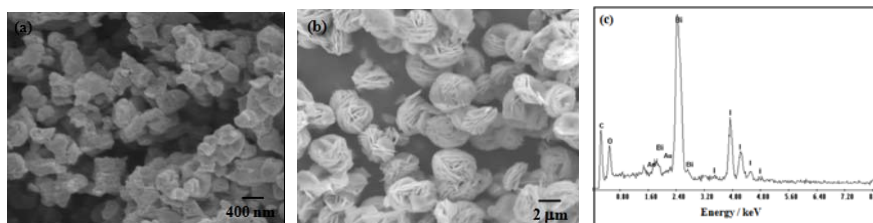


Fig. 2. (a) FE-SEM images of TaON nanoparticles, (b) BiOI nanoplate microspheres, and (c) EDX spectrum of Au/BiOI composites.

The EDX analysis was employed to obtain the quantitative information on the amount and the distribution of Au and TaON or BiOI species in the sample. Fig. 2c shows the EDX spectrum of Au/BiOI composite showing the presence of Bi, O, I, Au and the carbon peak appears from the carbon tape used for sampling. Similarly EDX analysis was performed for Au/TaON composite and it showed the presence of Ta, O, N and Au only (data not shown). It was found that the amounts of Au in BiOI or TaON are 1.9 and 1.7 wt%, respectively.

The UV visible reflection spectra of various composites are shown in Fig. 3 (a). It is seen that TaON and BiOI have adsorption edges at 500 and 650 nm, respectively. Au deposited TaON shows two peaks at 500 and 530 nm. The peak appeared at 530 nm is due to the light absorption by Au nanoparticles. However, in case of Au/BiOI nanocomposite the absorption peak of Au is overlaid by that of BiOI.

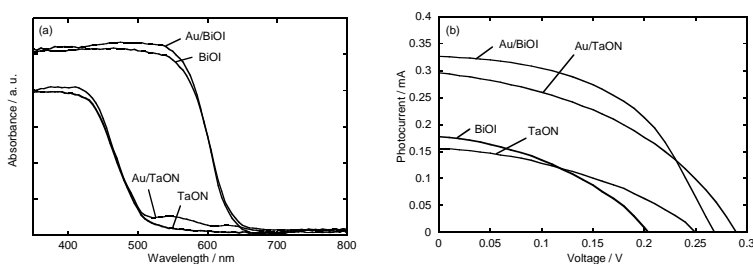


Fig. 3. (a) UV-visible reflection spectra of TaON, BiON, Au/TaON, and Au/BiOI, (b) and I-V curve analysis of TaON, BiOI, Au/TaON, and Au/BiOI based solar cells.

The characteristics of I-V curves of TaON, BiOI, Au/TaON, and Au/BiOI -film solar cells are shown in Fig. 3b. It is seen that the open circuit voltage is higher for the TaON-based solar cell but the closed circuit current is higher in case of the BiOI-film solar cell. These differences arise from the different band positions, light absorption ability of the semiconductor materials [10]. Also, it was found that the solar cells composed of Au/TaON or Au/BiOI films had higher photon to current conversion efficiency. In case of TaON the

absorption edge is shifted to the longer wavelength due to the presence of Au nanoparticle as seen from UV visible spectra. But the absorption wavelength of Au nanoparticle is overlaid by the absorption edge of BiOI. It can be concluded that in both cases Au nanoparticles absorb light and transfer electron to the semiconductor material which helps to enhance the efficiency of the solar cells.

#### 4. Conclusion

The performance of TaON and BiOI based solar can be enhanced by Au nanoparticles. However, the amount of Au nanoparticles could not be controlled by the present method and the amount of Au nanoparticles was too low. It is expected that if the amount of deposited Au nanoparticles deposited on TaON or BiOI could be increased, the performance of the solar cell will also be increased. Further research is underway in our laboratory.

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