Nanoarchitectonics of a Au nanoprism array on WO$_3$ film for synergistic optoelectronic response

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Abstract

A layered photoelectrode consisting of a conductive indium tin oxide substrate, a WO$_3$ nanocrystalline film and an array of Au nanoprisms was fabricated via a multistep process. Scanning electron microscopy and atomic force microscopy showed that the Au nanoprisms had a uniform size and shape and formed periodic hexagonal patterns on the WO$_3$ film. The optical absorption of the photoelectrode combined the intrinsic absorption of WO$_3$ and plasmonic absorption of Au. Using this photoelectrode, we investigated the effect of the Au nanoprism array on the optoelectronic conversion performance of the WO$_3$ film. Photoelectrochemical measurement indicated that the array substantially enhanced the photocurrent in the WO$_3$ film. Electrochemical impedance measurements revealed that the Schottky junctions formed between Au and WO$_3$ can facilitate the separation of photogenerated carriers as well as the interfacial carrier transfer. In this study, we demonstrate that covering a semiconductor with plasmonic noble metal nanoparticles can improve its optoelectronic conversion efficiency.

Keywords: Au nanoprism array, WO$_3$ film, optoelectronic conversion, localized surface plasmon resonance

1. Introduction

Global energy and environmental concerns urge the development of sustainable solar energy production. Optoelectronic conversion is one of the important properties of semiconductors and metals as it transforms the incident photon energy into electric (photoconductive and photovoltaic) or chemical (photocatalytic and photoelectrochemical) potential [1]. In photocatalytic applications, for example, the photoexcited electrons and holes of a semiconductor photocatalyst acquire a certain redox potential to catalyze water splitting or decomposition of organic molecules [2–8]. To realize efficient solar photocatalysis, besides suitable electrochemical potential, semiconductor photocatalysts need to possess strong visible-light ($\lambda > 400$ nm) absorption and high optoelectronic conversion efficiency. Only several semiconductors, such as WO$_3$ [9–11], BiVO$_4$ [12–14], TiO$_2$, N$_x$ [15], In$_x$Ni$_{1-x}$TaO [16], ZnO/GaN [17] and CdS [18], have been found to meet these demands. Among them, WO$_3$ is one of the most promising candidates owing to its easy fabrication, simple composition, nontoxicity, appropriate electronic band gap and high photoactivity. These properties result in a good performance of optoelectronic devices based on WO$_3$ [19–23].

In contrast to semiconductors, optical absorption of nanosized noble metals, such as Au and Ag, originates from the localized surface plasmon resonance (LSPR) caused by the coherent electron oscillations at the interface between
a metal and a dielectric [24, 25]. Accordingly, plasmonic noble metal nanoparticles can act as photosensitizers to enhance the optical absorption of metal–semiconductor composite systems [26–34]. Moreover, the junctions formed between the semiconductor and noble metal nanoparticles can facilitate the separation of photogenerated electrons and holes, thereby improving the efficiency of photocatalytic and photoelectrochemical reactions [35–37]. Tian and Tatsuma [31] studied the plasmon-related photoelectrochemical performance of Au nanoparticles embedded into TiO₂ films under visible light irradiation. They found that the electrons in Au nanoparticles were excited via the LSPR and transferred to TiO₂, and the compensating electrons from the electrolyte solution were transferred to the Au nanoparticles. This result suggests that the incorporation of plasmonic noble metal nanoparticles to semiconductors can improve the optoelectronic conversion efficiency. The performance of noble metal nanoparticles on semiconductor support is affected by many factors, such as the particle size, shape and dispersion. Recent studies suggest that the homogeneous size distribution, highly symmetric morphology and exposed facets may improve the optical performance of isolated noble metal nanoparticles [38–41]. They therefore indicate the importance of controlling the properties of noble metal nanoparticles. The ordered arrangement of noble metal nanoparticles may also improve their properties as well as simplify modeling.

In this article, we demonstrate a general template-assisted fabrication to deposit Au nanoprism arrays on WO₃ film. The Au nanoprism can have a uniform size and shape and arrange in a periodical hexagonal pattern. In comparison with the bare WO₃ film and the WO₃ film randomly covered with nonuniform Au nanoparticles, the WO₃ film with an ordered Au nanoprism array exhibited additional plasmonic absorption bands in the visible and infrared spectral regions. Photoelectrochemical measurements reveal that the addition of the Au nanoprism array can significantly enhance the photocurrent in the WO₃ film.

2. Experimental details

2.1. Photoelectrode fabrication

The WO₃ photoanode covered with a gold nanoprism array was prepared in four steps as illustrated in scheme 1.

2.1.1 WO₃ film on indium tin oxide substrate. WO₃ films were electrochemically deposited [42] on an indium tin oxide (ITO) substrate (sheet resistance 10 Ω cm⁻², Furuuchi Chemical Corp., Japan). The precursor electrolyte consisted of 0.45 mL of H₂O₂ (30%), 0.83 mL of HClO₄ (60%) and 50 mL of an aqueous solution of Na₂WO₄ (25 mM). The film deposition was carried out in an electrochemical station (ALS/CH model 650 A, Japan) in a three-electrode mode: the ITO substrate acted as the working electrode (cathode), a piece of Pt sheet as the counter—electrode (anode) and a Ag/AgCl electrode as the reference electrode. In the reference Ag/AgCl electrode, saturated (4 M at 20 °C) KCl was used as electrolyte. A bias voltage of −0.2 V versus Ag/AgCl was applied to the ITO substrate for 1200 s and then lowered to −0.05 V for 600 s. The prepared WO₃ film was annealed at 500 °C for 3 h.

2.1.2 Single-layer template of 2D polystyrene sphere array on WO₃ film. Monodispersed polystyrene (PS, 10 wt% in an aqueous suspension) spheres with a diameter of 670 nm were purchased from Duke Scientific Company (USA). An aqueous colloid was prepared, which contained 2 wt% PS spheres and 1.5 × 10⁻³ wt% polyvinylpyrrolidone (Mw = 55 000; Aldrich, USA). Polyvinylpyrrolidone was added to assist the assembly of the PS spheres into a close-packed array [43]. A single-layer template of two-dimensional PS sphere array was fabricated on the WO₃ film using the capillary-force-induced convective self-assembly method in a wedged-shaped cell [44]. As shown in figure 2(a), the cell consisted of a glass slide (top) and the as-prepared WO₃ film (bottom) inclined at an angle of 2°. After a small volume (approximately 40 µl) of PS sphere colloid was introduced into the cell, it was placed in a thermostated container and kept at 27 °C for 12 h. This allowed the capillary force induced by water evaporation to self-assemble PS spheres into a 2D array on the WO₃ film. Two conditions were essential for the formation of a 2D array of PS spheres: the electrochemically deposited WO₃ film provided a large and flat surface, and the PS spheres were selected to have a highly homogeneous size of 670 ± 10 nm.

2.1.3 Hexagonal array of Au nanoprisms on WO₃ film. The single-layer template consisting of a 2D array of PS spheres was used as a mask, through which gold was thermally evaporated on the WO₃ film in a vacuum of 6 × 10⁻⁷ Torr.
After evaporation, the PS template was peeled off using an adhesive tape.

2.1.4 Deposition of irregular Au nanoparticles on WO₃ film.
Irregular Au nanoparticles were deposited on the WO₃ film by a photocatalytic reduction method. The WO₃ film was soaked in 5 mM aqueous HAuClO₄ solution for about 30 min while being illuminated with UV-visible light from a 500 W Xe lamp (Optical ModuleX; Ushio Inc., Japan). This process reduced the adsorbed Au³⁺ to Au.

2.2. Characterization

The prepared samples were characterized by x-ray diffraction (XRD, Cu Kα radiation, JEOL JDX-3500, Japan), diffuse reflectance spectroscopy (V-570, JASCO Corp., Japan), field-emission scanning electron microscopy (SEM, JSM-6701F, JEOL, Japan), energy-dispersive spectrometry (EDS, JED-2300 Energy Dispersive X-ray Analyzer, JEOL, Japan) and atomic force microscopy (AFM, SPM-9600, Shimadzu Corp., Japan). AFM images were recorded in the tapping mode using a silicon tip.

2.3. Photoelectrochemical measurement

A photoelectrochemical cell \{WO₃ : Au|Na₂SO₄|Pt(Hg/Hg₂Cl₂)\} was assembled where the WO₃ film served as anode, aqueous Na₂SO₄ (0.1 M) solution as electrolyte, a Pt electrode as cathode and a saturated calomel electrode (Hg/Hg₂Cl₂, SCE) as the reference electrode. In the reference Hg/Hg₂Cl₂ electrode, saturated (4 M at 20 °C) KCl was used as electrolyte. A 500 W Xe lamp (Optical ModuleX; Ushio Inc., Japan) was employed as the light source. It was filtered with long-pass filters (e.g. L42 and L52: Hoya Corp., Japan) to provide visible-light irradiation of the WO₃ photoelectrode. In photocurrent measurements, the voltage was ramped at a rate of 0.01 V s⁻¹, and the light intensity was modulated at regular intervals. In the electrochemical impedance spectroscopy (EIS) measurements, the frequency was scanned from 10⁵ to 10⁻¹ Hz at an applied bias voltage of 0.1 V versus Hg/Hg₂Cl₂ under visible-light irradiation (λ > 420 nm, L42 cut-off filter). The incident photon-to-electron conversion efficiency (IPCE) was calculated as

\[
IPCE = \frac{hcI}{\lambda P},
\]

where \(P\) and \(\lambda\) are the intensity (W cm⁻²) and wavelength (nm) of the incident monochromatic light, \(I\) is the photocurrent density (µA cm⁻²), \(h\) is Planck’s constant and \(c\) is the speed of light in vacuum. Monochromatic light was obtained by filtering the Xe lamp with a monochromator (M10; Jasco Corp., Japan).
3. Results and discussion

3.1. WO$_3$ film on indium ITO substrate

Figure 1(a) shows an SEM image of the WO$_3$ film deposited at a bias voltage of $-0.2$ to $-0.05$ V versus Ag/AgCl reference electrode. The WO$_3$ film is continuous and has a smooth surface. The high-resolution image of figure 1(b) reveals that the film is composed of nanocrystals with a uniform size of about 50 nm. The cross-sectional SEM image (figure 1(c)) shows that the WO$_3$ nanocrystals are compactly packed in a film that is of 300 nm thickness and is tightly attached to the ITO substrate. These SEM images reveal a high quality of the electrochemically deposited WO$_3$ film. Visually, the film was transparent and uniformly flat. The XRD pattern (figure 1(d)) of the WO$_3$ film annealed at 500$^\circ$C for 3 h revealed a well-crystallized, pure monoclinic phase (JCPDS No. 01–075-2072).

3.2. Polystyrene sphere array on WO$_3$

The SEM image of figure 2(b) shows that the PS spheres arranged into a close-packed hexagonal pattern on the WO$_3$ film. This pattern was covering most of the film, with occasional sphere vacancies inside a domain and line defects (misalignments) between two domains. Observation of the vacancies (figure 2(c)) confirmed the single-layer structure of the PS sphere array.

3.3. Au nanoprism array on WO$_3$

The Au nanoprisms showed a bright contrast in the SEM images (figure 3(a)); they were arranged in a hexagonal pattern, and their chemical composition was verified by EDS (figure 3(b)). The prisms were shaped as equilateral triangles with sharp tips as confirmed from the AFM images of figure 3(c). Their average height and side length were measured as about 90 and 170 nm, respectively, from the AFM image of figure 3(d). The diagonal period of the hexagonal nanoprism lattice was about 670 nm, which is equal to the diameter of the PS spheres.

3.4. Optical absorption

The effect of the Au nanoprism array on the optical properties of WO$_3$ film was studied by optical absorption spectroscopy. The nanoprism array increases the optical absorption of WO$_3$ in the range of 300–1000 nm (figure 4(a)), and the absorbance difference spectrum is shown by the red curve in figure 4(b) as ‘absorbance gain’. The increase in absorption between 400 and 500 nm was attributed to the multiple scattering of light by the Au nanoprisms [45, 46], which increases the effective optical path length.

To demonstrate the LSPR effect of Au nanoprisms, a reference spectrum was recorded from a hexagonal array of Au nanoprisms on glass and added as a blue dashed curve to figure 4(b). The spectrum consists of two bands: one...
Figure 4. (a) Optical absorption spectra of bare WO$_3$ film (black curve) and Au-nanoprism-coated WO$_3$ film (red curve). Their difference is shown by the red solid curve in (b). The blue dashed curve in (b) is the reference absorption spectrum of the Au nanoprisms array on glass.

centered at 550 nm was assigned to the in-plane quadrupole resonance and the other at 800 nm to the in-plane dipolar resonance of the Au nanoprism [47, 48]. As a macroscopic manifestation of this LSPR effect, the sample showed a brilliant green reflection under white light illumination (inset in figure 4(b)). Similar plasmon resonances are observed for the Au nanoprism on WO$_3$; they are slightly redshifted owing to the high refractive index of WO$_3$ ($n_{WO_3} = 2.5$) [49]. The LSPR in Au nanoprism expanded the optical absorption of WO$_3$ from visible to infrared spectral range.

3.5. Optoelectronic conversion

A photoelectrochemical (PEC) cell [ITO/WO$_3$ : Au|Na$_2$SO$_4$|Pt(Hg/Hg$_2$Cl$_2$)] was set up to test the optoelectronic conversion performance of the WO$_3$ films. Figure 5(a) shows the current–voltage ($I$–$V$) characteristics of the cell under chopped illumination ($\lambda > 400$ nm). The photocurrent produced by the WO$_3$-Au-nanoprisms is 2 times higher than that from the bare WO$_3$ film. This improvement in the optoelectronic conversion results from at least three advantageous functions.

Firstly, the Au nanoprisms array enhanced the optical absorption of the WO$_3$ film. As discussed above, the nanoprisms acted as light scattering centers (light traps) that would provide more photons for exciting charge carriers in WO$_3$.

Secondly, the electrons excited via plasmon resonances in Au nanoprism can be injected into the conduction band of WO$_3$ and induce photocurrent. These resonances can be excited in a broad spectral range that widens the spectral response of the WO$_3$-Au-nanoprisms film compared with the bare WO$_3$ film. The $I$–$V$ measurement shown in figure 5(b) reveals no response to $\lambda > 500$ nm light in the bare WO$_3$ film because of its wide band gap of 2.6 eV (monoclinic phase) that corresponds to $\lambda = 475$ nm. In contrast, the photocurrent...
could be measured in the WO$_3$-Au-nanoprisms film under the same illumination.

The third function results from the Schottky junctions formed between Au nanoparticles and WO$_3$, which facilitates the separation of photogenerated carriers as well as the interfacial carrier transfer. The separation of photogenerated carriers was studied by EIS. Figure 5(c) shows the EIS response of the WO$_3$ films to the illumination with $\lambda > 400$ nm at a bias voltage of 0.1 V versus the SCE reference electrode. In the EIS spectra, the size of the arc radius on the EIS Nyquist plot correlates with the reaction rate at the surface of the photoanode [50, 51]. The arc radius for the WO$_3$-Au-nanoprisms film is smaller than that for the bare WO$_3$ film, indicating that the photogenerated electrons and holes were effectively separated and the interfacial carrier transfer was increased. In comparison with the bare WO$_3$ film, the impedance components of the WO$_3$-Au-nanoprisms film were reduced because of the more efficient electron drift mobility.

3.6. Comparison with irregular Au nanoparticles

To elucidate the effect of the periodicity of the Au nanoparticle array on the improvement of optoelectronic properties, we fabricated a photoelectrode in which a WO$_3$ film was randomly covered with Au nanoparticles of irregular shape and size (figure 6(a)). This sample was denoted as WO$_3$–Au and its incident photon-to-electron conversion efficiency (IPCE) was compared with that of the WO$_3$ photoelectrode containing the Au nanoprisms array (figure 6(b)). The SEM image of figure 6(a) shows that the Au nanoparticles have irregular shape and size (tens to hundreds of nanometers) and are randomly dispersed on the WO$_3$ film. Under illumination with monochromatic light ranging from 380 to 460 nm, the WO$_3$-Au-nanoprisms photoelectrode shows much higher IPCE than the WO$_3$–Au photoelectrode. This enhancement can be ascribed to the LSPR effect of the Au nanoprisms array, which provides more incident photons to the WO$_3$ layer via multiple scattering. The WO$_3$-Au-nanoprisms film shows a stronger optical absorption than the WO$_3$–Au film (figure 6(c)); in particular, the LSPR absorption band around 850 nm is present in the former but not in the latter sample. This difference can be explained by the strong dependence of the plasmon resonance wavelength on the size, shape and spacing between Au nanoparticles. In comparison with the irregular Au nanoparticles, the ordered array of Au nanoparticles with a uniform size and shape induced a much stronger LSPR effect.

4. Conclusions

A layered photoelectrode consisting of a nanocrystalline WO$_3$ film covered with an array of Au nanoparticles was fabricated via a multistep process, which included the electrochemical deposition of the WO$_3$ film on an ITO substrate, self-assembly of a single-layer array of PS spheres on the WO$_3$ film, and thermal deposition of Au on the WO$_3$ film using the PS array as a mask. The resulting Au nanoprisms had a uniform size and shape and formed a periodic hexagonal pattern on the WO$_3$ film. Compared with the bare WO$_3$ film and a WO$_3$ film randomly covered with irregular Au nanoparticles, the WO$_3$-Au-nanoprisms film had additional optical absorption bands in the visible to near-infrared spectral range. In this film, the intrinsic optical absorption was enhanced and the impedance components reduced due to the LSPR effect in the Au nanoprisms. Photoelectrochemical and EIS measurements revealed the formation of the Schottky junction between the
Au nanoprisms and WO₃ film, which may allow the transfer of the plasmon-induced electrons from Au nanoprisms to WO₃. These factors resulted in a higher optoelectronic conversion efficiency of WO₃ when covered with the Au nanoprism array. Our study presents a promising approach to develop visible-light-sensitive photoelectrodes utilizing the localized surface plasmon resonance.

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