Deposition of TiO₂ and Au: TiO₂ film and their Photoelectrochemical Properties

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Abstract

Gold (Au) nanoparticles were prepared by the electrochemical deposition of aqueous solution of auric chloride (AuCl₄) on the titanium dioxide (TiO₂) film. Before and after the electrochemical deposition, the TiO₂ film was soaked into dye solution of Rose Bengal. It is found that the photoelectrochemical properties were enhanced after the incorporation of Au nanoparticles along the TiO₂ film. Generally, the "hot electrons" were the main feature behind such properties and the hot electrons were the results of the incorporation of Au nanoparticles on the TiO₂ film that triggered the exothermic chemical process. Here dye molecules acted as a light absorber, where they converted the incoming photons from the sun rays into electron-hole pairs. The electron-hole pairs within TiO₂ showed the localized surface plasmon resonance (LSPR). In this process, the collective oscillations of free electrons confined at the metal surface (conductive substrates) were induced when the incoming incident frequency matched with collective oscillations of these free electrons and transferred them to the conduction band of semiconductor. This caused the enhancement of power conversion, i.e., photovoltage and photocurrent.

1. Introduction:

TiO₂ modified with Au has been extensively used as a cleaner for harmful water pollutants[1] due to its unique photoelectrochemical properties[2] and photocatalytic activity.[3] It has already been proven that titanium-based nanocomposites have unique optical and electrical behaviors such as surface plasmon resonance (SPR), photoluminescence, non-linear optical properties and catalytic activities.[4–7] As gold (Au) reveals a unique catalytic nature and action when it is deposited as nanoparticles on different metal oxides.[8] From the last few years different kinds of synthesis methods have been developed for the deposition of Au nanoparticles e.g. Au catalysts were prepared by several methods, such as co-precipitation,[9] deposition-precipitation (DP),[10] chemical vapor deposition (CVD),[11] laser vaporization,[12] modified impregnation[13] and photo-deposition (PD).[14] As reported earlier, the localized plasmonic nanostructures were obtained after the deposition of Au nanoparticles having different thicknesses with different exciting wavelengths.[15] When an optical beam is incident on the metal nanoparticles, electrons within nanoparticles get excited and collectively move with respect to the positive charges. This polarization of metal nanoparticles produces electric field across the two-point charges. Now when the incident frequency matches the collective oscillation of excited electrons within the nanoparticles, a condition for localized surface plasmon resonance (LSPR) is created.[16-18] In a particular nanostructure, the electrons are confined and oscillate with the same frequency as the incident energy, where they have resonance producing highly intense localized electromagnetic energy. These excited plasmons decay non-radiatively, producing "hot" electrons. Recent research is focused on harnessing these 'hot' electrons to increase the efficiency of the device.[19-21] Recently Moskovits *et al*. explained the charge transfer mechanism, in which the LSPR decay produces electron-hole pairs in the gold and the resulting hot electrons are then directly injected into TiO₂ by quantum tunneling.[22] Xiong *et al*. used nanoplates to improve the quantum efficiency of flexible photovoltaics (PV) devices. These nanoplates in PV help to convert and directly harvest near-infrared (NIR) light into plasmonic hot electrons, which are then injected into silicon.

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However, silicon nanowire arrays have light trapping properties.[23] Brennan *et al*. demonstrated a significant increase in the photocurrent due to the generation and separation of plasmonically generated hot electrons at the Au/TiO$_2$ interface.[24]

In the present work, a simple electrodeposition technique is used to deposit uniform distribution of Au NPs on the TiO$_2$ photoanode. Relatively, electrodeposition technique is a simple and inexpensive synthesis method. Au NPs are reported as a light harvesting (LH) material used in dye sensitized solar cells (DSSCs) with TiO$_2$ photoanodes. In this process, the Schottky barrier was formed at the interface of TiO$_2$/Au nanocomposite, in which Au NPs improved the cell performance with the help of better charge separation process.

2. Experimental
2.1. Synthesis
Electrodeposition of Au NPs was carried out by immersing films in an aqueous electrolyte prepared from 1 mM HAuCl$_4$.H$_2$O at room temperature. TiO$_2$ photoanode was made as mentioned by Gomez *et al*.[25] The TiO$_2$ films were soaked in the aqueous rose Bengal dye before Au deposition for 2 hrs. After soaking, the films were removed from dye and dried in air. On one of these films，the Au NPs were deposited. The dye got detached from the film immediately after dipping it in the auric chloride solution. The electrodeposition was performed with a two-electrode system. TiO$_2$ photoelectrode was used as the working electrode and graphite rod as a counter electrode. The electrodeposition was carried out at 1 V at room temperature for a deposition time of 1 min. The gold deposited TiO$_2$ film was dried in air and again soaked in the aqueous rose Bengal dye for one and half hour. Thus, the two samples were prepared namely Sample-A without Au NPs and Sample-B with the Au NPs.

2.2 Characterization
The optical absorption of Au NPs was characterized using UV-VIS spectrophotometry (Jasco V-650) in the range of 200-800 nm. The X-ray diffraction (XRD) patterns were recorded by using an X-ray diffraction analyzer (XRD, Rigaku D/max-2400, Cu-K$_\alpha$= 0.154 nm). The particle size and morphology of deposited Au NPs were performed using transmission electron microscopy (TEM). The films with and without Au NPs were used as photoanodes to fabricate the DSSC with graphite coated transparent conducting oxide (here FTO over glass) as the counter electrode. The iodide electrolyte was purchased from Dyesol. The current and voltage of the fabricated device were obtained by Oriel sol 2A (Newport Corporation)-LED lamp at 1000W/m^2.

3. Results and discussion
In order to study the crystal structure and crystalline quality of the samples, the XRD measurements were performed. The recorded XRD patterns of the samples with and without Au NPs are given in Fig. 1. The XRD patterns confirm the crystalline nature of the samples. The observed wider full width at half maxima (FWHM) of sample-B (with Au) as compared to the sample-A indicates the increased crystallite size with the incorporation of the Au NPs. The broad diffraction peak at 25.3^0 confirms the anatase phase of TiO$_2$.[26] As compared to anatase phase, the peak positions are slightly shifted with the incorporation of the Au NPs and the intensities of diffraction planes became stronger. This shift may be due to the strain produced in the titania lattice as the ionic radius of gold (Au^{3+}= 0.99A^o) is slightly larger than that of titania (Ti^{4+} =0.68A^o). The high intensity diffraction peak at 37.8^0 confirms the presence of Au NPs.[8] The average crystallite size of the Au NPs was calculated using Debye-Sherrer formula and found to be around 37 nm for several TiO$_2$/Au samples.
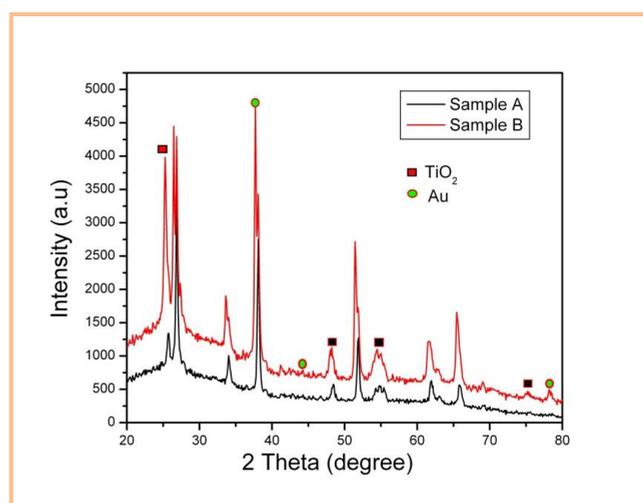

Fig. 1 XRD patterns of TiO$_2$ films without (A) and with (B) Au nanoparticles.

The TEM micrographs shown in Fig. 2(a-c) confirm the formation of Au NP deposited on the surface of TiO$_2$ film. The TEM images show that the deposited Au NPs are irregular spherical shape having an average particle size between 15 to 30 ± 5 nm. The selected area electron diffraction (SAED) pattern represents a ring diffraction pattern, which confirms the deposited Au NPs to be polycrystalline in nature as shown in Fig. 2(d).

The UV-absorption spectra of the TiO$_2$ films without and with Au NPs are shown in Fig. 3. It is found that there is an increase in the optical absorption of the photoelectrode in the visible region due to the presence of the Au NPs as compared to the TiO$_2$ film without the Au NPs. The enhanced absorption peak at 561 nm in the visible region is due to the localized surface plasmon resonance (LSPR) of Au NPs and confirms the presence of Au NPs on the surface of TiO$_2$ film. The LSPR wavelength of Au NPs mainly depends on the size, shape and the surrounding environment.[27] It may be noted that the absorption of dye increases due to the incorporation of Au NPs. Similar broadening of the resonance bands of noble metals has been reported earlier.[28-30] The photocurrent density- voltage characteristics (I-V curves) with and without Au NPs are

shown in Fig. 4(a). The Au NPs incorporated DSSC showed a significant increase in the photocurrent density from 6.33 to 8.3 µA/cm², the open circuit voltage (V_{oc}) was increased from 0.17 to 0.23 V. The improved cell performance can be mainly due to two factors: the existence of the Schottky barrier at the TiO_2/Au interface and increased optical absorption of the nanocomposite photoelectrode.[31,32] The formation of the Schottky barrier in the TiO_2/Au nanocomposite photoelectrode and the possible electron transfer path in the TiO_2/Au DSSC are schematically shown in Fig. 4(b).
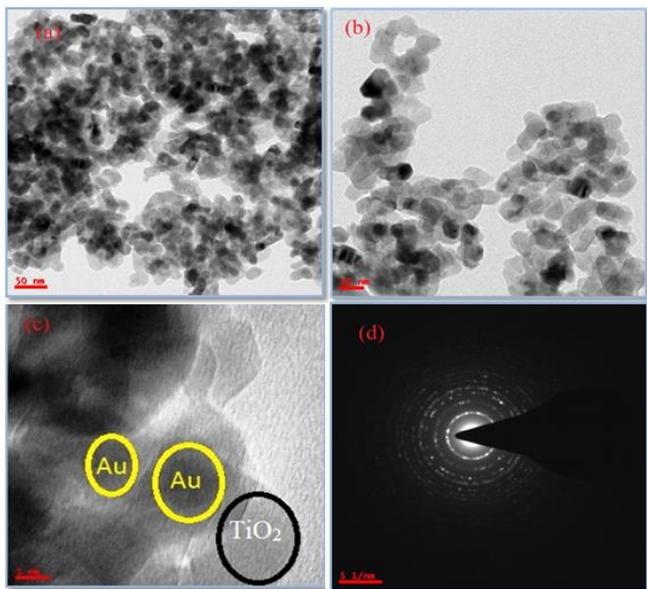

Fig. 2 (a-c) Low and high magnification TEM micrographs of TiO_2 films with Au NPs, and (d) corresponding selected area electron diffraction (SAED) patterns.

Upon light absorption, the excited electrons from the dye are injected into the Au NPs deposited on the surface of TiO_2 photoelectrode, resulting in an accumulation of electrons in the Au NPs. As a result, the Fermi energy of the Au NPs ($E_{f,Au}$) is shifted higher and thus the transfer of electrons from the Au NPs to the conduction band of TiO_2 occurs to establish a charge equilibrium in the system.[33] Additionally, some of the electrons from the dye molecules can also be directly injected into the conduction band of TiO_2, since the surface of the TiO_2 photoelectrode is not completely covered by the Au NPs. Due to the Schottky barrier present at the TiO_2/Au interface, the electrons reaching the conduction band of TiO_2 cannot reverse their path towards the oxidized dye molecules or the redox electrolyte, whose energy levels are lower than the conduction band of TiO_2.[30]
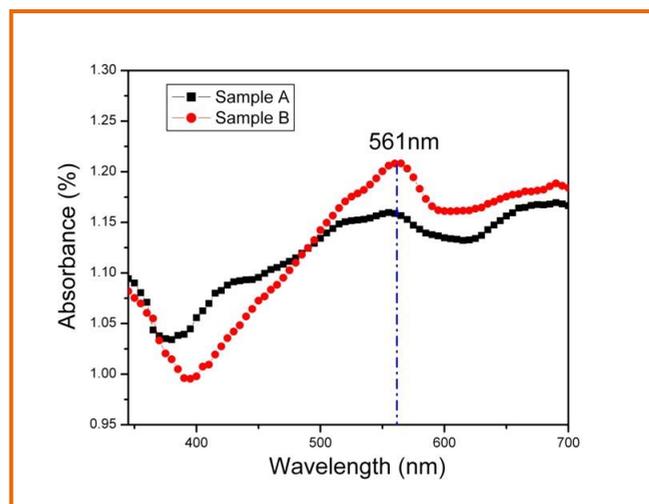

Fig. 3 Absorption spectra of TiO_2 films without(A) and with (B) Au nanoparticles.
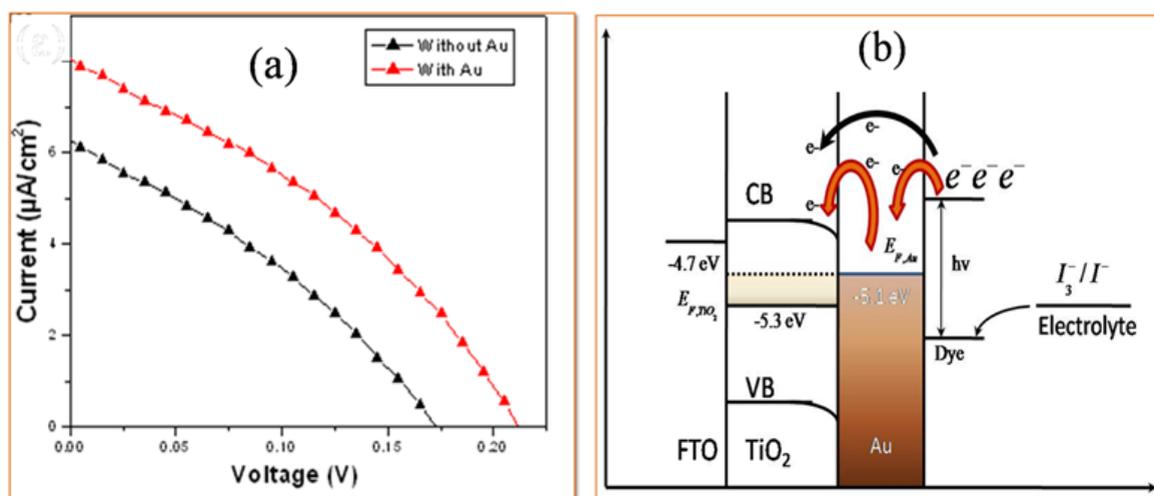

Fig. 4 (a) Current density versus voltage characteristics of the fabricated DSSC without (A) and with (B) Au NPs; and (b) energy band diagram showing the Schottky barrier formed at the TiO_2/Au interface (inspired from [31]). The arrow mark in Au represents the position of the Fermi level of gold after electron injection from RB dye.

Table 1 shows the performance of DSSC with and without incorporation of Au NPs. It is observed that the enhancement in the overall power conversion efficiency (PCE, η) with Au NPs is of 20% as compared to DSSC without Au NPs. Such an improvement in the cell performance is mainly due to the higher visible light optical absorption of the Au NPs through the increased dye absorption.

Table 1. The performance of DSSC with and without Au NPs. The area of the cell considered is 0.25 cm^2.

Sample	V_{oc} (V)	J_{sc} (μA/cm^2)	FF (%)	η (%)
Without Au NPs	0.17	6.3	31.67	0.002
With Au NPs	0.23	8.3	34.35	0.003

4. Conclusions

We have studied the role of 'hot electrons' generated through the surface plasmon decay on the efficiency of the device by incorporating the Au NPs on the surface of TiO$_2$ photoanode. TEM confirmed the presence of Au NPs on the TiO$_2$ surface. As the Schottky barrier was formed at the TiO$_2$/Au nanocomposite interface, the optical absorption of the dye molecule was increased and hence there was an increase in the device parameters. The device can be more efficient if we improve the chances of dye absorption process, which will inject more electrons into the Au NPs deposited on the surface of TiO$_2$ photoanode.

Supporting information

Not applicable.

Conflict of interest

There are no conflicts to declare.

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