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Investigation of Localized SPR and Grating-coupled SPR Enhanced Photocurrent of TiO_2 Films

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Abstract

We report the improvement of photocurrent activities of water splitting reaction catalyzed by AuNPs-TiO_2. The photocurrent of TiO_2 is enhanced by both localized surface plasmon resonance (LSPR) of gold nanoparticles and grating-coupled propagating surface plasmon GC-SPR of gold film. The AuNPs-TiO_2 nanocomposite are prepared by a simple wet chemical approach using TiO_2 (P25), $NaBH_4$ and $HAuCl_4$ as a supporting metal oxide, reducing agent and precursor of gold, respectively. The amount of loading gold is varied from 0.1% to 8% Au/TiO_2. TEM images suggest that the spherical shape gold nanoparticles can be directly deposited on the surface of TiO_2. The size of gold nanoparticles is approximately 3 – 5 nm. Photocurrent activities of AuNPs-TiO_2 nanocomposites are studied.

1. Introduction

Nowadays, the rapid development of economic systems causes the increase of global energy consumption. Environmental pollutions increase due to the releasing of by-products from the fossil fuel-electricity conversion process. Moreover, from the calculation, the expected times of depletion of the fossil fuel are 107, 37 and 35 years for coal, gas and oil, respectively [1]. Therefore, alternative energy sources, such as solar energy, become on demanding. Photocatalysts have been used to harvest the solar energy. TiO_2, one of those photocatalysts, is useful because it delivers the good chemical stability and low cost. However, only ~4% of solar photon can drive this photocatalyst because the TiO_2 itself can absorb photon which is in the UV region of the sunlight [2]. Therefore, the improvement of the photocatalytic activities of TiO_2 in the visible region have been attached defiance. It is known that localized surface plasmon resonance (LSPR) of gold nanoparticles, induced by visible light, can promote the formation of electron-hole pair in the near-surface region of the TiO_2 [3].

In this work, we study the photocurrent properties of AuNPs-TiO_2 nanocomposites. The improvement of the photocurrent could be assigned to the effect of the LSPR of gold nanoparticles. Furthermore, we investigate the improvement of the photocurrent of TiO_2 enhanced by the combination between LSPR of gold nanoparticles and the grating-coupled propagating SPR (GC-SPR) of gold grating film.

2. Experiments

Fabrication of AuNPs-TiO_2 nanocomposites

In general, for the preparation of 4% Au/TiO_2, TiO_2 (0.05 g) was dispersed in deionized water under vigorous stirring for 10 minutes. The pH of the suspension was adjusted to pH 1 using 0.1 M HCl. The suspension was left in ultrasonic bath for 1 hour. $HAuCl_4$ (0.5 mL, 50.8 mM) was added into the suspension under vigorous stirring. A solution of $NaBH_4$ (0.4M) was added into the suspension until the color of the suspension changed to purple. The suspension of AuNPs-TiO_2 nanocomposites was aged overnight and pre-concentrated to 250 mM using centrifugation.

Fabrication of AuNPs-TiO_2 nanocomposites on ITO glass substrate.

The suspension of AuNPs-TiO_2 nanocomposites (5 mL, 250.4 mM), polyvinyl alcohol PVA (4.3 mL, 3.75% w/v), DI-water (0.7 mL) and methanol (10 mL) were mixed together. The mixture was spin-coated on indium-doped tin oxide (ITO) glass substrate. The film was dried at ambient condition and calcined at 400 °C for 2 hours.

Fabrication of AuNPs-TiO_2 nanocomposites on gold grating substrate

The BD-Rs were cut into small rectangles with the dimension of 2.5 x 4.0 cm and submerged into conc. HNO3 to remove a dye layer on the BD-Rs. After dye removing, the BD-Rs were consecutively cleaned with liquid detergent, tap-water and twice in deionized water in ultrasonic bath, 15 minutes for each step, and dried by blowing with N_2. The cleaned BD-Rs were coated with 150 nm gold film through thermal evaporation. The gold gratings were coated with the AuNPs-TiO_2 nanocomposite dispersed in 50% methanol via spin-coating method. The photocatalyst electrodes were annealed at 90 °C for 30 minutes.

3. Results and discussion

After the doping process, the color of the dispersed nanocomposites gradually changed from milky white to dark purple while that of the amount of AuNPs was increased from 0 to 8%. In addition, TiO_2 (P25) has absorption band in UV region. The color change could be originated by the presence of gold nanoparticles on the surface of TiO_2. UV-visible absorption measurement was used to investigate the optical properties of the AuNPs-TiO_2 nanocomposites. As shown in Fig 1A, the results revealed the increase of absorption in visible region. As Au/TiO_2 increased from 0 – 8%, the absorption intensities at ~575 nm corresponded to the center of LSPR of AuNPs increased. The band broadening of the SPR absorption peaks was observed and implied to the diversity of the shape and size of the plasmonic nanoparticles. As shown in Fig 1B and 1C, TEM image revealed the present of spherical gold nanoparticles on the surface of TiO_2 after doping process. The size of gold nanoparticles was approximately 3–5 nm. Since the LSPR of gold nanoparticles facilitates the optical activities of TiO_2 in visible region, the photocatalytic activities of TiO_2 in particular photoinduced water splitting reaction are expected to be improved upon white light irradiation.

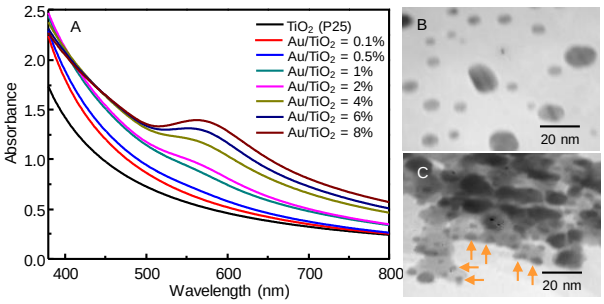

Figure 1 (A) UV-Vis absorption spectra of AuNPs-TiO_2 nanocomposites with various amount of gold loading content. TEM images of AuNPs-TiO_2 nanocomposites with difference gold loading content: (B) 0%, and (C) 0.5% Au/TiO_2. The scale bars indicate 20 nm. The arrows in (C) indicate gold nanoparticles.

The photocatalytic activities of the AuNPs-TiO_2 nanocomposites directly depend on the photo-induced electron-hole pair generation ability of those nanocomposites. In UV region, TiO_2 handles the production of those charge carriers species via absorption of high-energy photons providing the electron in the conduction band and the hold in the valence band of the semiconductor. The LSPR of plasmonic nanoparticles induced by visible light establishes the localized electric field near the surfaces of AuNPs which facilitates the generation of electron-hole pairs of the adjacent semiconductor. Fig 2A shows the photocurrent of the nanocomposite under UV illumination. The obtained photocurrent from 0, 0.1, and 0.5% of Au/TiO_2 were 0.29, 0.50, and 0.34 µA, respectively. The photocurrents lower than 0.29 µA were observed with the further increase of gold content in the nanocomposites more than 0.5% of Au/TiO_2. Fig 2B shows the photocurrent of the nanocomposite upon polychromatic visible illumination. The archived photocurrents were raised as the gold content in the nanocomposites increased and showed the maximum photocurrent of 1.45 µA at 2% of Au/TiO_2

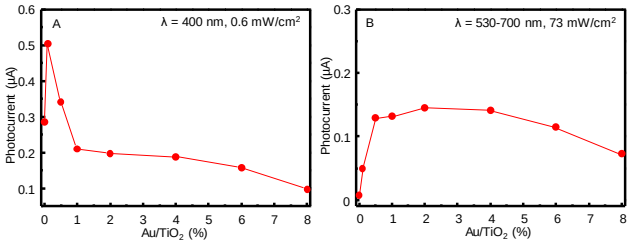

Figure 2 The short-circuit photocurrent of AuNPs-TiO_2 nanocomposite with various loading amount of gold nanoparticles irradiated under illumination with the wavelength at (A) 400 nm and (B) 530-700 nm.

4. Conclusion

The current investigation revealed the improvement of photocurrent properties of AuNPs-TiO_2 nanocomposites compared to the original TiO_2 under visible illumination. The enhancement of the photocurrent could be attributed to the effect of LSPR of gold nanoparticles. The further investigation, including the effect of the grating couple SPR of gold film, will be presented in detail. The AuNPs-decorated TiO_2 nanocomposites can be applied as a potential material for photocatalyst and dye-sensitized solar cell applications.

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