TiO_2-based nanocomposites with metallic nanostructures on nanobranched substrate for photocatalytic water splitting

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1. Introduction

Plasmon-induced photocatalyst has found its application in the clean and renewable energy issue due to its combination of the large absorption and resonance in the visible region for plasmonic nanostructures with the ability of producing the electron-hole pairs in the ultraviolet range for semiconductors (e.g., TiO_2). The Schottky barrier at the interface between metals and semiconductors could assist in separating electrons and holes, and increase the photocatalytic efficiency because the Fermi levels of plasmonic metals are lower than semiconductors. Several mechanisms have been proposed for different systems, including plasmonic heating, plasmonic-excited charge transfer, resonant energy transfer, and plasmonic-enhanced scattering, but none could perfectly explain all the phenomena to date [1]. In this study, Au and Ag nanotriangles synthesized by reduction of metal precursor were deposited on the surface of nanobranched TiO_2 arrays, which were prepared by hydrothermal methods. The photoactivity enhancement was evaluated using three-electrode system illuminated with the solar simulator. Finite-difference time-domain (FDTD) method was performed to investigate the electric field enhancement at the interface between Au (or Ag) nanoparticles and TiO_2 arrays upon illumination.

2. Results and discussion

Based on the photosynthesis method, silver nanotriangles could be obtained from small nanospheres under illumination of incident light with wavelength of 589 nm. After irradiation, nanotriangles with edge length of about 130 nm coexisted with small amount of truncated and irregular nanoparticles, as shown in Figure 1(a). On the other hand, gold nanotriangles with edge length of about 40 nm were synthesized using a rapid seedless process (Figure 1(b)). Plasmonic nanotriangles were thereafter deposited on the surface of hydrothermal synthesized nanobranched TiO_2 arrays using bridging polymeric monolayer, mercaptopropionic acid with attachments of the carboxylic acid group to TiO_2 and the thiol group to surfaces of silver and gold.

Photoactivity behaviors of bare nanobranched TiO_2, silver- and gold-decorated nanobranched TiO_2 electrode conducted by three-electrode system with Ag/AgCl as the reference electrode and Pt wire as the counter electrode were shown in Figure 1(c). Upon illumination with simulated solar light (AM 1.5G, 100 mW/cm^2), three photoelectrodes exhibited significant photoresponse, with the photocurrent densities of Au-TiO_2 > Ag-TiO_2 > bare TiO_2. It was speculated that gold nanotriangles with the smaller size and sharper apex induced stronger electric field enhancements upon resonance excitation compared to the larger silver nanotriangles and consequently contributed to the higher photoactivity by hot electron transfer from plasmonic metal to semiconductor.

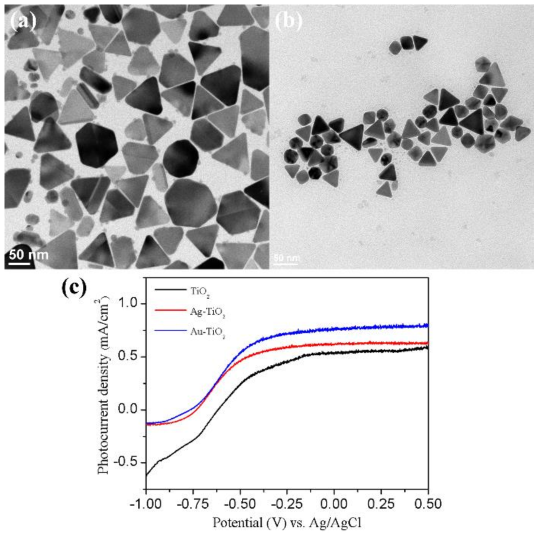

Figure 1. TEM images of (a) Ag nanotriangles and (b) Au nanotriangles. The scale bar is 50 nm. (c) Linear sweep voltammagrams of bare TiO_2, Ag- and Au-decorated TiO_2 photoelectrode upon illumination of simulated solar light.

3. Conclusion

Photoactivity behaviors with silver and gold nanotriangles chemically deposited on the surface of nanobranched TiO_2 electrode were found to be better than the bare TiO_2. Plasmonic resonant characteristic of subwavelength metal nanoparticles was believed to enhance the photocatalytic efficiency of photocatalyst through hot electron transfer.

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References

[1] Zhang, X., *et al.*, Rep. Prog. Phys., **76** (2013) 046401.