Visible Light Photocatalyst Based on Plasmon-enhanced Two-photon Absorption

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1. Introduction

The need for environmentally sustainable sources of energy has driven new momentum to the research for materials that may allow efficient solar water splitting. Titania is a well studied material for water splitting since the discovery by Honda and Fujishima [1] but its large bandgap limits its use for solar applications. In the past various approaches have been tried up to now to increase the photocatalytic activity of titania, but all present major disadvantages. As an idea, recently metallic nanoparticles came to be recognized as good candidate to improve the visible light activity of titania, due to their interesting chemical and optical properties. In this work, we focused on the latter to take advantage of the intense near-field light that is originated near metallic nanoparticles when their localized surface plasmon resonances (LSPRs) are excited by incident light. This intense near-field light is deemed to induce two-photon absorption (TPA) in the titania nanocrystals deposited on the top of the gold nanoparticles (AuNPs) provided that the LSPR of the array corresponds to twice the wavelength of the titania bandgap.

2. Experimental details

A suitable 2D-array of AuNPs, an array whose plasmonic peak maximum (λ_{LSPR}) corresponds to twice the value of the titania bandgap, was fabricated based on our hybrid method [2] (see Fig. 1a). Afterwards, TMOS is deposited on the 2D array to enable strong attachment of titania nanocrystals to the AuNPs 2D array thanks to covalent bond. A thin titania layer is then deposited on the TMOS-terminated-2D array via immersion in a titania solution. Finally the sample, annealed at low temperature (85 °C), can be used to perform photocatalytic reactions, such as Methylene Blue (MB) photodegradation. The highest photodegradation rate was achieved with visible light irradiation of the MB-coated layered device, as shown in Fig. 1b. The photocatalytic activity of the layered device under solar irradiation was also proven to be twice higher than titania reference sample. Then, the plasmonic origin of the photocatalytic activity was verified by action spectra and by light power dependency of photoreaction rate. A second power dependency of the photodegradation rate versus incident power confirmed the TPA origin of the visible light photocatalysis.

3. Conclusions

The layered device developed by a bottom-up approach in our laboratory has many advantages compared to conventional technologies up to date, that is to say it is cheap, can easily be scaled up and does not need clean room facilities nor high temperature annealing. The ability of this device to perform photocatalysis with visible light has been proven and its good performance was also verified under solar light irradiation and by comparing UV and visible light response. The mechanism responsible for the visible light activity was also clarified to be TPA, therefore opening the door for new interesting applications taking advantage of this effect.



Fig. 1: a) scheme of the working principle of the TPA-induced photocatalyst. b) comparison of photocatalytic activity of device and reference samples under visible and UV irradiation.

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References

- [1] A. Fujishima; K. Honda, Nature. 238 (1972) 37–38.
- [2] K. Isozaki; et al., Appl.Phys.Lett. 97 (2010) 221101.