

Plasmonic nanoparticles/reduced graphene oxide sensitized hierarchical TiO₂ nanorods for solar water splitting



Hsin-Chia Ho¹, Kai Chen^{2,3}, Tadaaki Nagao^{3,4,5}, Chun-Hway Hsueh¹

¹Department of Materials Science and Engineering, National Taiwan University

²Institute of Photonics Technology, Jinan University

³International Center for Materials Nanoarchitectonics, National Institute for Materials Science (NIMS)

⁴CREST, Japan Science and Technology Agency

⁵Department of Condensed Matter Physics, Graduate School of Science, Hokkaido University

E-mail: d03527002@ntu.edu.tw

1. Introduction

Metallic nanoparticles exhibiting distinctive localized surface plasmon resonance (LSPR) have been widely employed for photoelectrochemical (PEC) water splitting, due to their remarkable optical scattering as well as near-field nanofocusing of light, which efficiently enhance the photoactivity of semiconductors [1]. On the other hand, reduced graphene oxide (rGO) with large surface area and excellent electrical conductivity has also attracted much attention in the field of photocatalyst [2].

In this study, Au triangular nanoprisms (TNPs) and rGO sheets were deposited on the surface of hierarchical TiO₂ branched nanorod (b-NR) arrays, which were grown by hydrothermal methods. The photoactivity enhancement was evaluated using three-electrode system illuminated with simulated solar light. The effects of Au TNPs and rGO on the photoresponse of TiO₂ b-NRs were examined by incident photon-to-electron conversion efficiency (IPCE) measurements. In addition, the charge transport resistance between the photoanode and electrolyte was studied via electrochemical impedance spectroscopy (EIS).

2. Results and discussion

The SEM image of the heterostructure Au TNPs@rGO@TiO₂ b-NRs is shown in Figure 1(a). rGO sheets were uniformly distributed on the surface of TiO₂ b-NRs, and some of them could intercalate into the spaces between TiO₂ b-NRs and bridge the nanorods together. The distinct connections implied that the charge carriers generated from TiO₂ could be transported more easily through highly conductive rGO sheets than pristine TiO₂. Au TNPs with the average size of 40 nm were strongly anchored on the surface of TiO₂ b-NRs and rGO sheets via molecular linker and organic functional groups, respectively. Upon illumination with simulated solar light (AM 1.5G, 100 mW/cm²), TiO₂ b-NRs exhibited higher photocurrent density than that of TiO₂ NRs, which is attributed to the larger surface areas of the former (see Figure 1(b)). After incorporation of rGO sheets, the photocurrent was further enhanced due to the high charge carriers' transportation efficiency of graphene.

Au TNPs@rGO@TiO₂ b-NRs exhibited the highest photocurrent which is attributed to the synergistic effect of LSPR from Au TNPs and highly conductive rGO sheets. IPCE measurements (Figure 1(c)) indicated that the absorption edge of TiO₂ b-NRs could be extended to ~600 nm in the presence of rGO sheets. In addition, the photoresponse of Au TNPs@rGO@TiO₂ b-NRs matched well with the extinction spectrum of Au TNPs solution, and the photoactivity of TiO₂ could be effectively extended to the entire visible region.

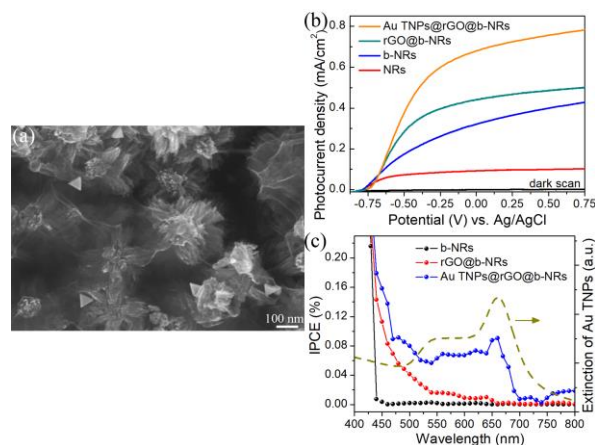


Figure 1. (a) SEM image of Au TNPs@rGO@TiO₂ b-NRs. (b) Linear sweep voltammetry response of four different samples. (c) IPCE of TiO₂ b-NRs, rGO@TiO₂ b-NRs, and Au TNPs@rGO@TiO₂ b-NRs.

3. Conclusion

Au TNPs@rGO@TiO₂ b-NRs was found to exhibit the highest photoactivity. The synergistic effect of LSPR from Au TNPs and excellent conductivity of rGO sheets contributes to the pronounced PEC performance.

Acknowledgements

The work was supported by the Ministry of Science and Technology, Taiwan under Contract no. MOST 105-2923-E-002-015-MY2, JSPS Kakenhi project and JST CREST. The experiments were partly performed in the MANA Foundry, National Institute for Materials Science, Japan and are gratefully acknowledged.

References

- [1] Linic, S., *et al.*, Nat. Mater., **10** (2011) 911.
- [2] Zhang, N., *et al.*, Chem. Rev., **115** (2015) 10307-10377.