Plasmonic phenomena and photoelectron generation in Au/TiO_2 nanorod arrays for visible light harvesting

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Plasmonic metals have extremely large absorption/scattering cross-sections in the visible range and the ability to strongly focus light close to their surface. Therefore, they can offer new opportunities to overcome the limited efficiency of TiO_2 for utilizing it in various solar conversion devices such as photocatalysts and photovoltaic cells [1]. The underlying physical phenomenon for improved visible light interaction is based on surface plasmon resonance (SPR). It has been widely recognized that the hot electrons originate from the decay of the SPR and can be injected into the conduction band of TiO_2 [2]. Thus, combining the plasmonic metals with TiO_2 can enhance the light interaction of TiO_2 through scattering, absorption, sensitization and hot electron injection. The plasmonic metals not only improve the photoabsorption via SPR, but also provide a Schottky barrier (SB) at the interface between the metal and the semiconductor that induces excellent charge separation in such nanostructures.

We have fabricated novel multisegmented Au/TiO_2 NRAs as a representative example for investigating the harvesting of visible light, determination of the SB, and enhancement in photoelectron generation. The TiO_2 and Au/TiO_2 NRAs were fabricated by means of the template-assisted electrodeposition technique into AAO membranes. The XRD patterns of TiO_2 and Au/TiO_2 NRAs confirm that TiO_2 is present in an amorphous form. This is favorable because the work function of amorphous TiO_2 is lower than that of crystalline TiO_2 due to the large number of oxygen vacancies. UV-Vis DR spectra for the free standing NRAs show, for pristine TiO_2, strong absorption in the UV-range, and for Au/TiO_2 sample a stronger absorption in the whole visible region. In Au/TiO_2 NRAs the broad peak at around 550 nm is associated with the transverse mode (T-mode) and another hump extends to the near IR region, which can be attributed to the longitudinal mode (L-mode) of Au NRAs. This indicates that the Au/TiO_2 NRAs exhibit plasmonic behaviour under visible light irradiation. The T-mode perfectly matches with the discrete dipole approximation (DDA) simulation data. However, the strong peak for the L-mode is less expressed. The latter is significantly affected by a change in Au segment lengths, presence of TiO_2 segments and the arrangement of Au NRAs, which can result in broadening and intensity loss of the L-mode. The plasmonic resonance energy transfer (PRET) enhancement is dominant at the extremities of the Au segment, which penetrates into the TiO_2 segment for about 2 nm and creates a pathway for hot electron injection. XPS analysis shows that Au in the Au/TiO_2 NRAs is negatively charged due to the electron transfer from oxygen vacancies in TiO_2 to achieve Fermi level equilibrium. This is due to the formation of the SB at the interface between Au and TiO_2. The VBM of Au/TiO_2 shifts towards a lower binding energy by 0.23 eV compared to pristine TiO_2 NRAs [3]. Finally, we conducted PEC measurements in a three-electrode cell arrangement on pristine TiO_2 and multisegmented Au/TiO_2 NRAs. The photocurrent density of Au/TiO_2 NRAs is 4 times larger than that of the pristine TiO_2, which is associated with the plasmon-sensitized process via hot electron injection and PRET enhancement from Au to TiO_2 segments. Obviously, the synergistic effect of the local PRET enhancement and the hot electron injection significantly increases the electron/hole pair generation in multisegmented Au/TiO_2 NRAs.

References

[1] Z. Xuming, C. Yu Lim, L. Ru-Shi, T. Din Ping, Rep. Prog. Phys. 76 (2013) 046401; [2] X.-C. Ma, Y. Dai, L. Yu, B.-B. Huang, Light: Sci. Appl. 5 (2016) 16017; [3] M.S. Arshad, Š. Trafela, K. Žužek Rožman, J. Kovač, P. Djinović, A. Pintar, J. Mater. Chem. C 5 (2017) 10509.