PHOTOCATALYSTS FOR WATER POLLUTION PREVENTION

Albin Pintar

Department of Inorganic Chemistry and Technology, National Institute of Chemistry, Hajdrihova 19, SI-1001 Ljubljana, Slovenia

Plasmonic metals (Au, Ag) have an 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). SPR helps in generating electrons and holes. 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, known as the hot electron injection process [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 [3]. The plasmonic metals not only improve the photo-absorption via SPR, but also provide a Schottky barrier (SB) at the interface between the metal and the semiconductor. This SB can induce excellent charge separation in such nanostructures. The Schottky barrier height (SBH) has been suggested to be an important parameter influencing the efficiency of the plasmon induced electron injection at the metal/semiconductor interfaces [4].

We fabricated novel multi-segmented Au/TiO_2 NRAs as a representative example for investigating the harvesting of visible light, determination of the SB, and enhancement in photoelectron generation (Fig. 1). 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 favourable because the work function of amorphous TiO_2 is lower due to the large number of oxygen vacancies.

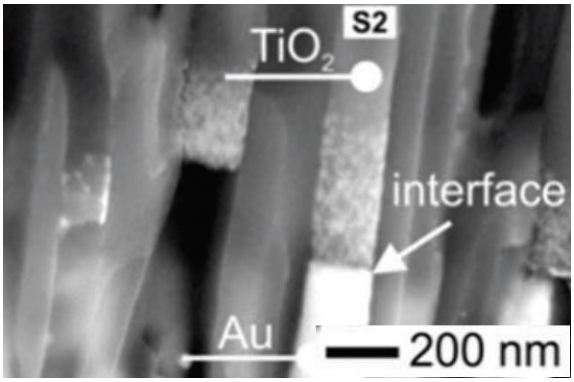

Fig. 1. SEM image of the multi-segmented Au/TiO_2 NRAs embedded inside the AAO membrane.

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 (Fig. 2). 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 [5]. Finally, PEC measurements (Fig. 3) showed that 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 multi-segmented Au/TiO_2 NRAs.

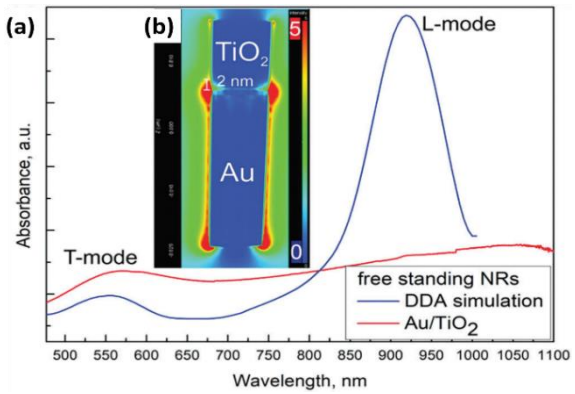

Fig. 2. (a) Comparison between UV-Vis DR spectra of Au/TiO_2 and DDA simulation on Au NR. (b) Enhancement in electric field intensity for a multi-segmented Au/TiO_2 NR.

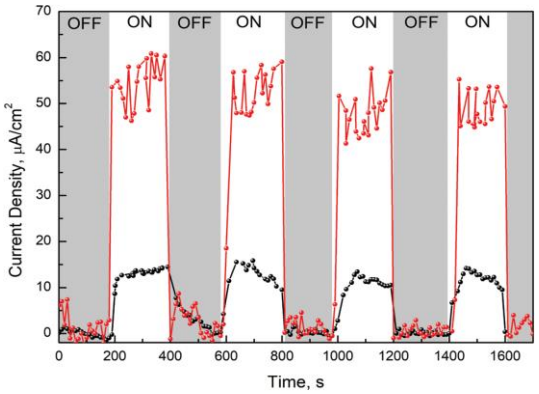

Fig. 3. Photoinduced current measurements on pure TiO_2 NRAs (black line) and multi-segmented Au/TiO_2 NRAs (red line) with and without light excitations.

The same phenomena were recently demonstrated to occur as well in the presence of Au/TiO_2 nanorod particles [6,7]. By systematically synthesize Au/TiO_2 nanorods with different Au loadings, where the morphological, structural and surface properties of TiO_2 support were kept constant, it was confirmed that the rate of a photocatalytic reaction is directly influenced by the height of Schottky barrier. It was proved that the SB height decreases and the extent of SPR effect increases with increasing the diameter/amount of Au ensembles on the catalyst surface, and that both properties are essential to obtain high visible-light triggered catalytic activity of Au/TiO_2 catalysts.

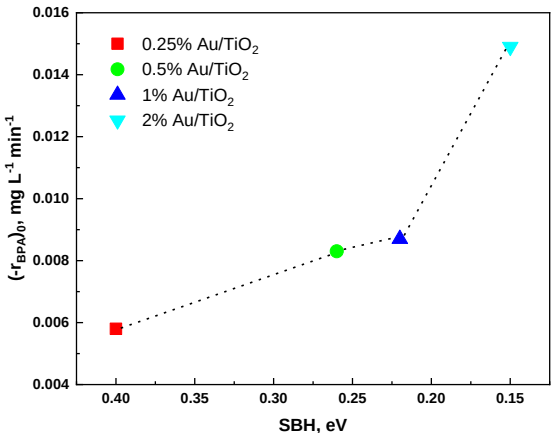

Fig. 4. Initial disappearance rate of water-dissolved bisphenol A (BPA) as a function of SBH obtained during the visible-light triggered photocatalytic degradation conducted in the presence of Au/TiO_2 solids. Operating conditions: V=250 ml, c_0=10.0 mg/l, T=25°C, $c_{cat.}$=125 mg/l.

Acknowledgements - The financial support from the Slovenian Research Agency (research core funding No. P2-0150) is acknowledged.

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] W. Hou, S.B. Cronin, Adv. Funct. Mater. 23 (2013) 1612.
[4] M.R. Khan, T.W. Chuan, A. Yousuf, M.N.K. Chowdhury, C.K. Cheng, Catal. Sci. Technol. 5 (2015) 2522.
[5] M.S. Arshad, Š. Trafela, K. Žužek Rožman, J. Kovač, P. Djinović, A. Pintar, J. Mater. Chem. C 5 (2017) 10509.
[6] G. Žerjav, J. Zavašnik, J. Kovač, A. Pintar, Appl. Surf. Sci. 543 (2021) 148799.
[7] G. Žerjav, M. Roškarič, J. Zavašnik, J. Kovač, A. Pintar, Appl. Surf. Sci. 579 (2022) 152196.