## Influence of platinum loading on the height of the Schottky barrier in TiO<sub>2</sub>-based photothermal catalysts

## Gregor Žerjav, Albin Pintar

Department of Inorganic Chemistry and Technology, National Institute of Chemistry, Hajdrihova 19, Ljubljana, Slovenia) gregor.zerjav@ki.si

Titanium dioxide (TiO<sub>2</sub>) is a well-established semiconductor material that offers significant potential for photocatalytic applications due to its stability, low cost and environmental compatibility. However, due to its large bandgap (~3.2 eV), its photoactivity is mainly limited to the ultraviolet region of the spectrum, which significantly limits its efficiency in visible light, which accounts for the majority of solar radiation. A promising strategy to overcome this limitation is the incorporation of plasmonic noble metals such as platinum (Pt), which can enhance the absorption of visible light through localised surface plasmon resonance (LSPR). Under light irradiation at LSPR wavelengths, noble metal nanoparticles generate energetic "hot electrons" that can be injected into the conduction band of TiO<sub>2</sub>. The success of this charge transfer and thus the photocatalytic efficiency is strongly influenced by the Schottky barrier height (SBH) at the metal–semiconductor interface. [1-5]

In this study, we investigate the influence of different Pt loadings (0.5–2 wt%) on the structural, optical, electronic and catalytic properties of TiO<sub>2</sub>+Pt materials synthesised by wet impregnation. A comprehensive physicochemical characterisation was performed using techniques such as X-ray photoelectron spectroscopy (XPS), scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS), transmission electron microscopy (TEM), X-ray diffraction (XRD), nitrogen physisorption and UV-Vis diffuse reflectance spectroscopy (UV-Vis-DR). XPS analysis provided precise measurements of SBH, which decreased with increasing Pt content (from 0.42 eV at 0.5 wt% Pt to 0.16 eV at 2 wt% Pt). SEM-EDS confirmed the homogeneity of Pt dispersion and agreement with nominal loadings, while XRD and TEM indicated that the crystallinity and morphology of the TiO<sub>2</sub> support were preserved. Nitrogen physisorption data showed stable surfaces and pore structures for all samples. UV-Vis-DR spectra showed an increased absorption of visible light due to the LSPR effect of Pt.

Catalytic tests (Figure 1) showed that bare  $TiO_2$  was inactive for NO<sub>2</sub> reduction below 100 °C, while  $TiO_2+Pt$  catalysts enabled photothermal NO<sub>2</sub> reduction at 30 °C due to the Pt-LSPR effect. However, with increasing SBH, the photothermal activity decreased as the "hot electrons" needed more time to overcome the higher SB. This delay led to an accumulation of "hot electrons" at the Pt-TiO<sub>2</sub> interface, increasing the recombination with the holes generated by Pt and reducing the transfer of the "hot electrons" to the TiO<sub>2</sub> support.

Our results emphasise the crucial role of the Schottky barrier in the development of efficient plasmonic photocatalysts. The TiO<sub>2</sub>+Pt systems showed dual functionality as thermal and photothermal catalysts for NO<sub>2</sub> reduction, illustrating their adaptability in hybrid catalytic environments. These results contribute to the development of advanced light-driven catalytic systems for environmental remediation and beyond.

## References

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**Figure 1:** Temperature-dependent  $NO_2$  reduction profiles on pure TP and TP+Pt catalysts. The dashed curves and the yellow shaded area represent the  $NO_2$  reduction with visible light, while the solid curves and the red shaded area show the  $NO_2$  reduction as a function of temperature.