

## **Enhanced Photocatalytic Activity of Composite Semiconducting/Plasmonic Materials: Towards Withholding of Heavy Metal Ions from Aqueous Solutions**

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**Abstract:** TiO<sub>2</sub> is a well-known photocatalytic material. Its combination with plasmonic nanoparticles (NPs) has been demonstrated in the literature in various ways. A vast majority of the publications have focused on reactions involving photocatalytic decomposition of organic compounds and water splitting. However, there is little evidence on the efficiency of such composite materials in the intermediate photo-oxidation step required to achieve the removal of heavy metals during water purification (e.g. Mn). In the present study we investigate the enhanced photocatalytic activity of TiO<sub>2</sub> ( $E_g = 3.2$  eV) and TiO<sub>x</sub>N<sub>y</sub> (N content set to provide samples with  $E_g$  either 2.8 eV, or 2.4 eV) with optically active Ag and Au NPs towards oxidation of Mn aqueous species (10 mg/L). The photocatalytic templates were immersed on aqueous solutions of Mn(II) oxy-anions. For the illumination of the samples we used a simple white LED lamp. XPS has been used to identify the retention of the metal ions and their oxidation state during photocatalysis. We demonstrate that the performance of the photocatalysts is a strong function of the  $E_g$  of the semiconductor, the properties of the NPs and the structure of devices. Two different structures examined where the metallic NPs were either on the top or beneath of the TiO<sub>x</sub>N<sub>y</sub> layer; in both cases enhanced photocatalytic was observed compared to pure (no NPs) TiO<sub>x</sub>N<sub>y</sub> and TiO<sub>2</sub>. We show that by tailoring the  $E_g$  and the size of the NPs it is possible to maximize the photochemical activity of a semiconductor and create more efficient devices for heavy metal purification of water.