

Nanocomposites and nanomaterials

Nitrogen and metal ion co-doped titania photocatalysts films synthesized by sol-gel and pulsed laser deposition methods: similarities and differences

**O. Linnik¹, N. Chorna¹, N. Smirnova¹, N. Stefan², C. Ristoscu²,
G. Popescu-Pelin², I.N. Mihailescu²**

¹ *Chuiiko Institute of Surface Chemistry, National Academy of Science of Ukraine, 17 General Naumov str., Kyiv, 03164, Ukraine.
E-mail:okslinnik@yahoo.co.uk*

² *National Institute for Lasers, Plasma and Radiation Physics, 409 Atomistilor street, Magurele, PO Box MG-36, RO-77125, Ilfov, Romania.*

The relationships between photocatalytic activity and composition, optical, structural as well as surface properties of nitrogen/metal ion co-doped titania films synthesized by sol-gel (SG) and pulsed laser deposition (PLD) methods are examined. The metal ions, such as Zr^{4+} , Fe^{3+} or Zn^{2+} , were used for titania films co-doping in both methods, while urea and the mixture of $N_2:CH_4 = 5:1$ were the non-metal source in SG and PLD, respectively. All films were thermally treated at 450 °C.

The PLD films exhibited a continuous absorbance in the visible part of the spectrum. The sol-gel films also absorbed considerably the visible light with a maximum ranging from 400 to 450 nm. The band gap energy values of nanocomposites were found to be lower or equal to N/TiO₂ one.

As shown by XRD and Raman measurements, crystalline anatase phase was obtained in case of SG films. Contrary, the PLD composites contain a mixture of anatase and rutile or rutile only. The elemental ratio M:Ti:O was inferred by EDS analysis. The content of oxygen atoms, lower than stoichiometric one, was explained by the nitrogen incorporation into the metal oxide lattice.

Incorporation of substitutional and/or interstitial nitrogen in titania lattice was detected by XPS for both techniques. However, their ratio depended on the conditions and method of synthesis as well as metal ions nature. An effective substitutional nitrogen incorporation was noted for PLD composites obtained in low-pressure gas atmosphere. The mechanism of PLD doping and the role of methane in the efficiency of nitrogen incorporation were proposed.

It is concluded that metal ions co-doping facilitated the nitrogen incorporation into titania, leading to the increase of semiconductive films photocatalytic activity. Based on the experimental results, the possible mechanisms of primary photocatalytic processes are proposed.