

Physico-chemical nanomaterials science

Doping of nano-sized tin oxide and hydroxide and their physico-chemical properties

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Tin dioxide SnO₂ is a wide band gap n-type semiconductor which receives major attention in the fields of solar cells, gas sensors, lithium-ion batteries. However, the broad band gap and slight absorption of radiation with wavelength >400 nm prevent its photocatalytic activity under visible light. Introduction of "extrinsic" defects into oxides structure i.e their doping with metal or non-metal is one of the ways to improve the photocatalytic properties in processes of pollutants degradation. This approach is unexplored for tin oxide.

We doped low-dispersed powder SnO₂ and high-dispersed gel SnO(OH)₂ using ultrasound and next thermal treatments (UST and TT). Metals with a valence of I-VI were used as dopants. The sono-doping of powder results in some disordering of crystal structure but dispersity (specific surface area S) does not change. At the same time, the doped SnO(OH)₂ gels are X-ray amorphous but S value reduces and pore size slightly increases. The dopant moieties are embedded into porous structure of gel. In both cases, XRD does not detect the separate phase of metal-oxide species. The absorption edge λ for initial SnO₂ and SnO(OH)₂ is 323 and 304 nm which corresponds to band gap $E_g = 3.83$ and 4.08 eV, respectively. Alone UST without dopants has no effect on this characteristic. Conversely, sonochemical doping causes bathochromic shift of absorption edge and corresponding band gap narrowing. Thus, $\Delta\lambda$ value achieves 100 nm and E_g decreases to 3.05 eV for high-dispersed SnO(OH)₂ doped with Ag. On the other hand, absorption of visible light is increased 2-3 times compared with un-doped samples. This is due to the fact that the introduction of doping elements leads to the creation of new energy levels in the band gap.

As a result, doped samples are increasing their photocatalytic activity under visible irradiation in many times. Especially, it concerns the samples based on gel possessing higher specific surface area (particle size of 5-10 nm) and OH-groups content. For example, the rate constant of safranin T degradation K_d increases on the order and for rhodamine B - nearly 200 times for samples, doped with Ag, compared with un-doped sample. The K_d values achieves 10^{-2} - 10^{-3} s⁻¹. The degree of dyes mineralization is equalled 65-80%. It should be noted that the mechanism of dyes decomposition is also changed, as a result of doping.