

## The Effect of Ionic Liquid Anion Type on the Properties of TiO<sub>2</sub> Particles

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**Abstract :** In recent years, photocatalytical processes have been intensively investigated for destruction of pollutants, hydrogen evolution, disinfection of water, air and surfaces, for the construction of self-cleaning materials (tiles, glass, fibres, etc.). Titanium dioxide (TiO<sub>2</sub>) is the most popular material used in heterogeneous photocatalysis due to its excellent properties, such as high stability, chemical inertness, non-toxicity and low cost. It is well known that morphology and microstructure of TiO<sub>2</sub> significantly influence the photocatalytic activity. This characteristics as well as other physical and structural properties of photocatalysts, i.e., specific surface area or density of crystalline defects, could be controlled by preparation route. In this regard, TiO<sub>2</sub> particles can be obtained by sol-gel, hydrothermal, sonochemical methods, chemical vapour deposition and alternatively, by ionothermal synthesis using ionic liquids (ILs). In the TiO<sub>2</sub> particles synthesis ILs may play a role of a solvent, soft template, reagent, agent promoting reduction of the precursor or particles stabilizer during synthesis of inorganic materials. In this work, the effect of the ILs anion type on morphology and photoactivity of TiO<sub>2</sub> is presented. The preparation of TiO<sub>2</sub> microparticles with spherical structure was successfully achieved by solvothermal method, using tetra-tert-butyl orthotitanate (TBOT) as the precursor. The reaction process was assisted by an ionic liquids 1-butyl-3-methylimidazolium bromide [BMIM][Br], 1-butyl-3-methylimidazolium tetrafluoroborate [BMIM][BF<sub>4</sub>] and 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF<sub>6</sub>]. Various molar ratios of all ILs to TBOT (IL:TBOT) were chosen. For comparison, reference TiO<sub>2</sub> was prepared using the same method without IL addition. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), Brenauer-Emmett-Teller surface area (BET), NCHS analysis, and FTIR spectroscopy were used to characterize the surface properties of the samples. The photocatalytic activity was investigated by means of phenol photodegradation in the aqueous phase as a model pollutant, as well as formation of hydroxyl radicals based on detection of fluorescent product of coumarine hydroxylation. The analysis results showed that the TiO<sub>2</sub> microspheres had spherical structure with the diameters ranging from 1 to 6 μm. The TEM micrographs gave a bright observation of the samples in which the particles were comprised of inter-aggregated crystals. It could be also observed that the IL-assisted TiO<sub>2</sub> microspheres are not hollow, which provides additional information about possible formation mechanism. Application of the ILs results in rise of the photocatalytic activity as well as BET surface area of TiO<sub>2</sub> as compared to pure TiO<sub>2</sub>. The results of the formation of 7-hydroxycoumarin indicated that the increased amount of ·OH produced at the surface of excited TiO<sub>2</sub> for samples TiO<sub>2</sub>\_ILs well correlated with more efficient degradation of phenol. NCHS analysis showed that ionic liquids remained on the TiO<sub>2</sub> surface confirming structure directing role of that compounds.

**Keywords :** heterogeneous photocatalysis, IL-assisted synthesis, ionic liquids, TiO<sub>2</sub>

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