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TiO2-Acetylacetone charge-transfer complex: an efficient photocatalyst for NOx and aqueous pollutants abatement under reduced power visible-light

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TiO2-Acetylacetone charge-transfer complex: an efficient photocatalyst for NOx and aqueous pollutants abatement under reduced power visible-light Lucas A. Almeida, Anja Dosen, Juliana Viol and Bojan A. Marinkovic Department of Chemical and Materials Engineering, Pontifical Catholic University of Rio de Janeiro (PUC-Rio), Rio de Janeiro 22453-900, Brazil; lucasalmeida@aluno.puc-rio.br; adosen@puc-rio.br;juliana-viol@puc-rio.br; bojan@puc-rio.br TiO2-based nanomaterials have been widely studied for photocatalytic applications. The formation of charge-transfer complexes (CTCs), between bidentate organic ligands, such as acetylacetone (ACAC), and nanocrystalline TiO2, promotes visible light absorption and constitutes a promising alternative for air purification and aqueous depollution under reduced visible light power. However, several fundamental issues of this alternative, such as the photocatalytic efficiency, the TiO2-ACAC interactions, and the role of reactive oxidizing species (ROS) of these CTCs, are not fully understood. In this study, several characterization techniques were applied to evaluate the effect of the acetylacetone content on TiO2-ACAC CTCs. The TiO2-ACAC, synthesized by the sol-gel route and calcined between 300 and 400 °C, were submitted to photocatalytic tests to evaluate the abatement of NOx gas and aqueous pollutants (such as chlorophenol and tetracycline) using 24 W and 26 W visible residential lamps, respectively. Furthermore, the ROS scavengers, such as isopropanol and benzoquinone, were used for studying the photocatalytic role of •OH and •O2? radicals. Thermogravimetry analysis coupled with a mass spectrometer together with Infrared Spectroscopy analysis revealed the presence of strong TiO2-ACAC bonds up to 400 °C. TiO2-ACAC xerogel calcined at 300 °C (TiO2-A300) absorbed over the entire visible spectrum and showed the ligand-to-metal charge transfer mechanism (LMCT). TiO2-A300 photodegraded ~100% of NOx, until 1 h, 68.6% of tetracycline, and 31.3% of chlorophenol after 6 h. The •O2? radicals are predominantly responsible for the high efficiency of TiO2-ACAC CTC under reduced visible light. However, the •OH radicals are not efficiently generated in the CTC. Therefore, TiO2-ACAC CTC is able to efficiently degrade both NOx gas and aqueous pollutants. Furthermore, the use of other bidentate ligands in TiO2 sol-gel synthesis can further enhance the photocatalytic activity of TiO2-based nanomaterials.