Activities of various TiO₂ nanostructures in photocatalytic decomposition of methylene blue and toluene were determined in order to shed light on the relationship between structures and photocatalytic activity. Commercially available P-25 samples were used in the present work. In addition, TiO₂ nanostructures were synthesized using atomic layer deposition (ALD). We show that change in the surface structure of TiO₂ upon various surface treatments results in variation in photocatalytic activity. In particular, increase in the number of OH groups on the surface leads to the enhancement in photocatalytic activity. Surface OH groups increases adsorption reactivity of organic reactants, thereby increasing activity in photocatalytic decomposition of methylene blue and toluene.