Mechanism of Charge Transfer in the Transition Metal Ion Doped TiO₂ with Bicrystalline Framework of Anatase and Rutile: Photocatalytic and Photoelectrocatalytic Activity

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Abstract The high photocatalytic activity of the Mn²⁺ doped TiO₂ with bicrystalline framework of anatase and rutile is probed for the degradation of benzene under solar light with/without applied bias. The enhanced activity is attributed to the transfer of electrons from the rutile to electron trapping/lattice trapping sites of anatase and also to the impurity level created by the dopant which favours effective charge separation. The shallow detrapping nature of Mn²⁺ dopant additionally contributes to the overall enhancement in the photocatalytic activity especially in the presence of applied electric field.

Keywords Manganese doped TiO₂ \cdot Bicrystalline framework \cdot Synergistic effect \cdot Photoelectrocatalysis

1 Introduction

TiO₂ was doped with Mn²⁺ ion (Mn²⁺–TiO₂) in order to investigate its influence on the phase transition and its photocatalytic activity was probed for the degradation of benzene with/without bias under solar light. Anatase TiO₂ was prepared by sol–gel technique [1]. Manganese oxalate [MnC₂O₄] was used as the source for Mn²⁺ ion. Calculated amount of anatase TiO₂ along with metal ion salt solution was added in order to get dopant concentration in the range of 0.02, 0.06 and 0.1% and labelled as T2, T3 and T4 respectively while the undoped TiO₂ is labelled as T1. The samples were calcined at 550°C for 4.5 h and were characterized by powder X-ray diffraction (PXRD), BET surface area measurements, UV-absorption and diffuse reflectance spectroscopy (DRS). The details of the analytical techniques used for the characterization and design of the photoreactor can be found elsewhere [2–4]. Photoelectrocatalysis experiments are carried out with Princeton model 362 potentiostat. Both working and counter electrodes are platinum with a saturated calomel electrode (SCE) as a reference electrode. The experiments were carried out at various applied potentials +0.02, +0.05, +0.1 and +0.20 V. Experiments using solar light (natural sun light) were carried out between 11 am to 2 pm during the summer season in Bangalore, INDIA. At this interval the fluctuation in solar intensity was minimal. The latitudes and longitudes are 12.58 N and 77.38 E, respectively. The average intensity of the sunlight is found to be around 1200 Wm⁻². The intensity of solar light was concentrated using a convex lens and the reaction mixture was exposed to this concentrated solar light. UV light source of 125 W capacity with a photon flux of 7.75 mW/cm² whose wavelength emission is in the range of 350–400 nm is used for comparative study. The reaction was stirred continuously over the entire time span of the experiment. At desired time intervals the samples were collected and centrifuged to separate the photocatalyst and were subjected to UV-Visible spectroscopic analysis using Shimadzu UV-1700 pharospec UV-visible spectrophotometer. To compare the photo catalytic activity of the above mentioned catalysts, the experiments were simultaneously conducted to avoid the error arising due to fluctuations in solar intensity. The photocatalytic efficiency was compared with commercially available Degussa P-25 TiO₂ (P25).