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A simple method for the synthesis of anatase-rutile mixed phase TiO_2 using a convenient precursor and higher visible-light photocatalytic activity of Co–doped TiO_2

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ABSTRACT

This work reports a novel and simple method for the synthesis of mixed phase TiO_2 (Anatase 70% and Rutile 30%). Refluxing aqueous solution of potassium titanyl oxide oxalate lead to direct crystallization of titanium oxalate complex $[Ti_2O_3(H_2O)_2(C_2O_4).3H_2O]$ and this complex on calcination at 450 ℃ for one hour yielded TiO_2 powder. The powder samples were characterized by XRD, Raman spectroscopy, FESEM-EDX, TEM, XPS, FT-IR, UV–Visible spectroscopy and BET techniques. The XRD, TEM and Raman spectra of TiO_2 indicates the coexistence of anatase and rutile phases. The XRD result shows that the primary particle size of anatase crystals is 8.3 nm and that of rutile crystals is 35 nm. From the UV–Visible DRS spectrum, the bandgap of TiO_2 was found to be 3.0 eV. Co–doped TiO_2 (Co:Ti ratio 1:99) was prepared by adding cobalt nitrate to the precursor solution. On Co–ion doping, anatase:rutile composition was changed to 84:16. The visible light photocatalytic activity of Co–doped TiO_2 was found to be better than that of undoped and Degussa TiO_2 due to higher visible light absorption caused by Co^{2+} energy levels due lowered bandgap.

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1. Introduction

Nanoparticles exhibit unique physical, chemical, and biological properties relative to bulk materials due to their large surface area and quantum confinement effect. They have tremendous applications as basic building blocks in the field of nanotechnology for various practical applications. The nanomaterials and their complexes with organic ligands have been widely studied for the degradation of pollutants, catalysis, as antibacterial and antifungal agents, for the extraction of poisonous metal ions, in hydrogen storage etc [1-7]. Various techniques have been reported to prepare nanomaterials in different shapes like nanoflower, nanosquare, nanohexagon, nanowires have been reported by many groups [8-10].

In recent years, TiO_2 has been explored for diverse applications such as pigments, sensors, photocatalysts, energy storage devices, solar cells etc [11-16]. It is a promising semiconductor material due to its commercial availability, chemical and thermal stability, low cost, non toxicity, and ease of handling [17,18]. TiO_2 belongs to n-type semiconductor. Titania can exist in three crystalline phases, *viz* anatase, rutile and brookite and these phases are having bandgap energy of 3.2 eV (380 nm), 3.0 eV (415 nm) and 3.6 eV (344 nm) respectively [19]. Controlled crystallisation of TiO_2 from solutions is a prerequisite for preparing high quality TiO_2 nanopowder [20]. Rutile phase is difficult to obtain at low temperature and it is usually prepared by calcinations of anatase at higher temperature [21,22]. The high temperature leads to agglomeration and larger particle size [23,24]. Rutile has also higher chemical stability and higher refractive index compared to anatase [25,26]. Zhang and Banfield demonstrated that the rutile is more stable than anatase but the stability reverses when the particle size is less than 14 nm [27]. There are several methods for the preparation of TiO_2. Most of the traditional methods involved corrosive precursors or complicated and expensive equipments. The reflux method is comparatively easy and has potential to fabricate TiO_2 with controlled morphology. It needs simple equipment, environmentally friendly process conditions. This method avoids the use of volatile precursors and release of harmful organic compounds. Commonly used precursors are titanium alkoxides or titanium chloride. But

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