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Structural and photocatalytic studies of hydrothermally synthesized Mn^{2+}–TiO_2 nanoparticles under UV and visible light irradiation

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Keywords: Mn^{2+}–TiO_2, synthesis, characterization

Abstract

Pure TiO_2 and Mn^{2+}–TiO_2 nanoparticles have been prepared by simple hydrothermal method with different Mn^{2+} concentrations. Obtained samples were analysed to determine it's structural, optical, morphological and compositional properties using x-ray diffraction, UV-DRS, Raman, photoluminescence, XPS, TEM and EDS analysis. The EDS micrograph confirms the existence of Mn^{2+} atoms in TiO_2 matrix with 0.86, 1.60 and 1.90 wt%. The crystallite size as well as band gap decreases with increase in Mn^{2+} concentration. The average particle size obtained from TEM was found 8–11 nm which is in good agreement with XRD results. Raman bands at 640, 518 and 398 cm^{-1} further confirmed pure phase anatase in all samples. XPS shows the proper substitutions of few sites of Ti^{4+} ions by Mn^{2+} ions in the TiO_2 host lattice. The intensity of PL spectra for Mn^{2+}–TiO_2 shows a gradual decrease in the peak intensity with increasing Mn^{2+} concentration in TiO_2, it implies lower electron-hole recombination rate as Mn^{2+} ions increases. The obtained samples were further studied for its photocatalytic activities using malachite green dye under UV light and visible light.

1. Introduction

Semiconductor photocatalysis (TiO_2) has been widely used in cleaning the living environment, because of its outstanding properties like high stability, low cost, abundant in resources and non-toxicity. TiO_2 has extensive applications such as photocatalysis, dye-synthesized photoanodes in new type solar cells, opacifiers in pigments, catalytic supports, self-cleaning materials, cosmetics, plasma coatings etc [1–3].

Among various photocatalysis, titania, particularly anatase TiO_2 has been extensively used in photocatalytic environmental applications. Especially, textile industries produce large amount of colour dye effluents which are toxic and non-biodegradable. The photocatalysed degradation of dye in solution is initiated by illuminating the TiO_2 photocatalyst with light of energy higher than its band gap, electron excite from valence band to conduction band leaving holes in valence band. These photo excited electrons and holes oxidizes or deoxidizes adsorbates on the surface of catalyst [4–6]. The hole (h^+_{VB}) with high oxidative potential permits the direct oxidation of the dye to reactive intermediates. Hydroxyl radical (•OH) is also responsible either for decomposition of water or it is formed by the reaction of the hole with (OH^-). •OH radical is an extremely strong, non-selective oxidant ($E_0 = +3.06$ V), which leads to the partial or complete mineralization of several organic chemicals [5] equations (1)–(4).

$$TiO_2 + h\upsilon \rightarrow TiO_2(e^-_{CB} + h^+_{VB}), \quad (1)$$

$$h^+_{VB} + \text{dye} \rightarrow \text{dye}^{\bullet +} \rightarrow \text{oxidation of the dye}, \quad (2)$$

$$h^+_{VB} + H_2O \rightarrow H^+ + \bullet OH, \quad (3)$$

$$\bullet OH + \text{dye} \rightarrow \text{degradation of the dye}. \quad (4)$$

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α-MoO_3-C composite as counter electrode for quantum dot sensitized solar cells

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ABSTRACT

Counter electrodes plays a vital role in electron transport in operation of QDSSCs. The lower charge transfer resistance at counter electrode - electrolyte interface fecilitates improvement in photoconversion efficiency. The present study describes a novel and facile Spray Pyrolysis method for fabrication of low cost α-MoO_3-Carbon composite (α-MoO_3–C) material which is used as counter electrode (CE) in QDSSCs. The QDSSC with TiO_2 photoanode sensitized by cadmium sulphide (CdS) QDs and polysulfide as electrolyte and α-MoO_3-C composite as counter electrode exhibited solar energy-to-electricity conversion efficiency of 1.29%, which is better than those of the cells that used platinum and Cu_2S as counter electrodes. QDSSCs with α-MoO_3-C composite used as counter electrode gives stable and reproducible performance. The improvement in efficiency with α-MoO_3-C composite Counter electrode was mainly driven by the improvement in photocurrent density and decrease in charge transfer resistance at counter electrode – electrolyte interface. Electrochemical impedence spectroscopy studies are carried out to understand electron transport in the device at various interfaces. α-MoO_3-C composite has shown more electrocatalytic response for the reduction of redox species of the polysulfide than platinum and Cu_2S.

1. Introduction

The quantum dot-sensitized solar cells (QDSSCs) are emerging third-generation photovoltaic technologies with efficiencies that have reached over 11% [1]. QDs as sensitizers have several merits including possibility of multiple exciton generation [2]. higher light extinction coefficient [3], larger intrinsic dipole moment that lead to rapid charge separation [4]. Also quantum confinement in these nanostructures allows for tunable optical properties across the solar spectrum [5]. In view of the above, number of parameters of QDSSC are responsibe for improvement in efficiency of QDSSC like photo anode structure, the type of QD sensitizers, counter electrode material and electrolyte composition. Among all the prominent materials for QD sensitizers, CdS is widely used due to their easy preparation. Counter electrode is also an important component in QDSSCs that affects the performance of cell. There are number of materials used as counter electrodes in QDSSC like noble metals i.e. Platinum [6,7], metal sulphides like CuS [8], CoS [9], PbS [10], Cu_2S and carbon derivatives like graphene oxide [11], metal sulphide composite like CuS/CoS [12] and CuS/PbS [13], nanosulfide/carbon composite [14], GO/CuS composite [15], GO/CoS composite [16], NiS [17], MoS_2[18]. MoO_3 so far has not been considered as counter electrode in QDDSCs, but is used in DSSCs [19]. We herein, Probabaly first time report use of α-MoO_3-carbon composite as counter electrode, which employs a cost effective and facile method of preparation as compared to the existing CE Materials.

Molybdenum oxide (MoO_3) is a wide band gap n-type Semiconductor material and one of the transition metal oxides. Some of the MoO_3 compounds are thermodynamically stable having orthorhombic phase (α-MoO_3), metastable phase of monoclinic & hexagonal respectively (β-MoO_3 and h-MoO_3). Among them, α-MoO_3 has attracted more attention because the orthorhombic α-MoO_3 has a layered structure, containing two layers of octahedral MoO_6, held together by double covalent bonding and Van der Waal's forces. Some of the reserchers reported synthesis of MoO_x-C composite by various methods. Ko et.al. have reported synthesis of ant cave structured microballs of MoO_2-C composite by using Ultrasonic spray pyrolysis method using molybdenum salt, polystyrene nanobeads and sucrose at 900 °C in N_2 atmosphere and MoO_2–C microballs were oxidized at 300 °C under an

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RESEARCH ARTICLE

Studies on the Fe^{3+} Doping Effect on Structural, Optical and Catalytic Properties of Hydrothermally Synthesized TiO_2 Photocatalyst

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Abstract: Pure TiO_2 and Fe^{3+}-TiO_2 nanoparticles have been prepared by a simple hydrothermal method with different Fe^{3+} concentrations. The synthesized nanoparticles are analysed to determine its structural, optical, morphological and compositional properties using X-ray diffraction, Raman, UV-DRS, photoluminescence, Mossbauer, XPS, TEM and SEM/EDS. The EDS micrograph confirms the existence of Fe^{3+} atoms in the TiO_2 matrix with 0.85, 1.52 and 1.87 weight percent. The crystallite size and band gap decrease with increasing Fe^{3+}concentration. The average particle size obtained from TEM is 7-11 nm, in good agreement with XRD results. Raman bands at 640 cm^{-1}, 517 cm^{-1} and 398 cm^{-1} further confirm pure phase anatase in all samples. XPS results show the proper substitutions of a few sites of Ti^{4+} ions by Fe^{3+} ions in the TiO_2 host lattice. The intensity of PL spectra for Fe^{3+}-TiO_2 shows a gradual decrease in the peak intensity with increasing Fe^{3+} concentration in TiO_2, and it indicates a lower recombination rate as the Fe^{3+} ion concentration increases. These nanoparticles are further studied for its photocatalytic activities using malachite green dye under UV, visible and sunlight.

Keywords: Hydrothermal synthesis, Fe^{3+}-TiO_2, properties, visible light photocatalyst, nanoparticles.

1. INTRODUCTION

Nanocrystalline titanium dioxide (TiO_2) is a widely used semiconductor material for photocatalytic applications due to its outstanding properties such as high stability, low-cost and abundance. In addition to its high catalytic activity, it has effective applications in solar cells, photoconductors, coatings, fillers, pigments, gas sensors, optics, cosmetics, biomaterials and self-cleaning materials [1-5]. Industries such as textile, paper, printing and dying produce a large amount of toxic and non-biodegradable dye effluents which enter into the environment. Hence this work focuses on the removal of these toxic dyes using photocatalytic methods with TiO_2 photocatalyst. The photocatalytic degradation of a dye involves formation of electrons (e^-) and holes (h^+) on the surface of catalyst, their serving as redox sources which react with adsorbed reactants, leading to the destruction of pollutants [2, 6-7]. Anatase TiO_2 has a band gap of 3.2 eV, thus its photocatalytic property can be activated under the UV light ($\lambda < 400$ nm). The energy produced by sunlight in the visible region is less than the UV region [8, 9].

The photocatalytic activity of TiO_2 can be increased by shifting its band gap less than 3.2 eV in

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Synthesis, Characterisation of Barium Calcium Zirconate by Combustion Method

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ABSTRACT : BaxCa1-x Zro3 (0.1<x<.5) have been prepared by combustion method. The structural and morphological properties were investigated for calcium barium zirconate. The synthesized powders of various compositions were sintered at 900 ^{0}c for five hours with the heating rate 5^0 per min.XRD and SEM properties of different powders were studied.XRD shows prominent peaks at 25 and 30, which becomes more prominent at x=0.5. SEM images show porous natures of powder. Nano size particles were obtained.

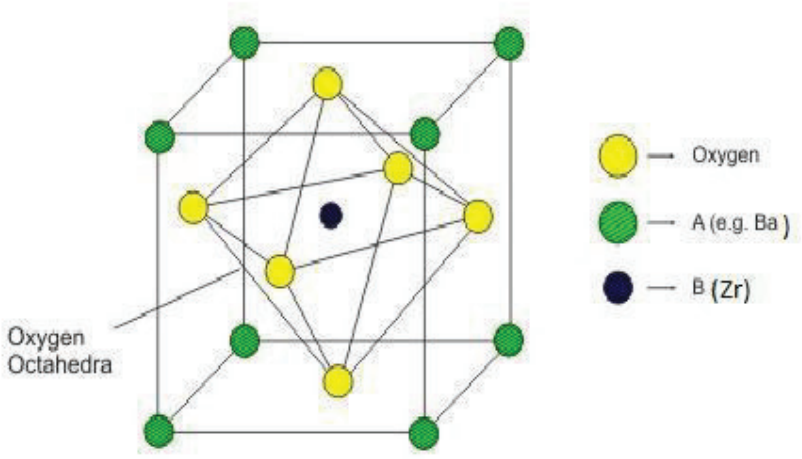
INDEX TERMS : Combustion, XRD, SEM

I. INTRODUCTION

Inorganic perovskite-type oxides are fascinating nonmaterials because of their wide applications in catalysis, fuel cells, and electrochemical sensing. They exhibit attractive physical and chemical characteristics such as electronic conductivity, electrically active structure, the oxide ions mobility through the crystal lattice, variations on the content of the oxygen, thermal and chemical stability, and super-magnetic, photo catalytic, thermoelectric, and dielectric properties. Pervoskite oxides exhibit an array of electrical properties and a variety of solid-state phenomena from insulating, semiconducting, metallic, and superconducting characters; therefore, they are very fascinating to be studied and applied in a large scale. (1) Many of ABO3 pervoskite are cubic or nearly cubic in structure in their ideal form; however, one or more phase transitions may be achieved particularly at low temperature.(1)

The ceramic material belongs to the family pervoskite with general ABO3 type structure that exhibits different electric and magnetic properties such as ferromagnetism and superconductivity (2)

Pervoskite of type ABO3 has the structure as, B site atom is at the centre of the cube. A site atom is at the corners of the cube and o atoms are at the centre of the face. As shown in figure



ABO_3

Barium zirconium titanate ceramics are attractive candidates for dynamic random access memories and tunnable microwave devices. Such a lead free, envoirnment friendly materials are known to exhibit relaxor behaviour in bulk materials with increase in Zr content.The interest in high strain materials is incresing for electromechanical transducers and various related applications.(3)

CaZrO3 possesses an orthorhombic structure of slightly domed octohedra. It undergoes polymorph transformation from Orthorhombic CaZrO3to cubic CaZrO3 at 2750^{0}c .(4) Scientists are focused on CaO-ZrO2 system as a main research topic.Most of investigations are aimed the synthesis and characterisation of CaO stabilised ZrO2 solid solution,very little attension is paid to study of CaZrO3 Phase .Although for several decades the existence of CaZrO3 in CaO-ZrO2 equilibrium diagrame is known.(5).CaZrO3 is potential candidate for use of mechanical filters, coatings and electrical applications such as resonators and capacitors(4). CaZrO3 is orthombic pervoskite consist of slightly deformed (ZrO6)octohedra and (CaO8).(6) CaZrO3has wide