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Preparation and properties of titania based ionogels synthesized using ionic liquid 1-ethyl-3-methyl imidazolium thiocyanate

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ABSTRACT

Present study reports the synthesis of titania (TiO_2) based ionogels using ionic liquid (IL) 1-ethyl-3-methyl imidazolium thiocyanate ([EMIM][SCN]) by non-aqueous sol-gel process. Ionogels are characterized using N_2 adsorption-desorption, TGA, DSC, SEM, TEM, XRD, and FTIR. N_2-sorption results show that TiO_2 matrices have meso-pores with uniform pore size distribution. Thermal studies reveal that thermal stability of confined IL decreases while the glass transition temperature (T_g) is found to increase. XRD patterns show that IL containing TiO_2 matrices exhibit amorphous (weak crystalline peaks) nature however after extraction of IL from ionogel, it shows the crystalline (anatase) phase of TiO_2 which has also been found from SAED pattern. SEM micrographs reveal that as the amount of IL is increased, TiO_2 particles are found to agglomerate. FTIR results indicate that the vibrational frequencies of confined IL are found to shift due to interaction of IL molecules with titania pore wall surface.

1. Introduction

Recently, ionogels have received significant attention of researchers and material scientists. Ionogels are a new class of hybrid materials, obtained by the immobilization of ionic liquids in some solid substrate. Ionic liquids (ILs) are low melting temperature ionic salts and generally are in molten state below 100 °C. They possess large number of attractive properties such as high thermal stability, wide electrochemical widow, wide liquidus range, high ionic conductivity etc [1–3]. Therefore, ionogels have become promising materials for the application in various electrochemical devices, such as lithium batteries, fuel cells, dye-sensitized solar cells, etc. [1–7]. Extensive efforts have been made to fabricate ionogels using conducting (carbon nano-tube) and non-conducting inorganic oxide matrices (SiO_2, SnO_2, TiO_2 etc.). Among these, silica has been extensively used to synthesize ionogels and a large number of studies are available on properties of ILs in silica matrices [1,2]. But, the studies on properties of ILs immobilized in TiO_2 and SnO_2 matrices are less studied [8–10]. However, many studies have been reported on the synthesis of TiO_2 using ILs [8,11,12], TiO_2 is still being extensively synthesized with ILs [13–20] due to its various applications.

Titanium dioxide (TiO_2) also known as titania is an important transition metal oxide and has attracted much attention for its various applications such as photo catalysis, solar cell, catalyst support, sensors, corrosion protection, gas sensors, electrode materials for Li ion battery etc. [21–23]. Titanium dioxide has three natural crystalline phases, anatase (tetragonal), rutile (tetragonal) and brookite (orthorhombic) [24,25]. It is well known that anatase phase of TiO_2 is metastable and transforms into rutile phase at higher temperature and also it is chemically and optically active therefore, it is useful for catalysts [21,22]. Specially, the porous anatase phase of TiO_2 has greater importance due to its better catalytic properties [26]. Recently, there has been large emphasis on the synthesis of porous TiO_2 as an effective anode material for Li-ion and Na-ion rechargeable batteries [26–29] as it can be easily synthesized using sol-gel method and anode materials so synthesized has been found to show sufficient discharge capacity. TiO_2 has been prepared using various methods such as hydrothermal, sol-gel, solvothermal etc. [23,26]. But, sol-gel method has been widely used to synthesize porous and crystalline TiO_2 [23,30]. Nanoporous materials such as colloidal mesoporous silica nanoparticles [31], nanoarchitectured porous materials [32], ordered mesoporous materials etc. have attracted great attention of material scientists due to their wide range of interest in commercial applications such as in chemical separations, heterogeneous catalysis, nanoelectronics, chemical sensing, mesoporous solar cells etc [33]. Recently, mesoporous solar cells including dye-sensitized solar cells and perovskite solar cells have become important emerging photovoltaics. These photovoltaics are typically composed of a nanocrystalline anatase TiO_2 active layer [34]. Therefore, nanoarchitectured porous materials have drawn

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much interest due to its soft templated synthesis to prepare nearly all types of nanoarchitectured materials with different compositions [32].

Nakashima and Kimikuza [35] reported the development of hollow TiO_2 microsphere by interfacial sol-gel reactions using ionic liquid [BMIM][PF_6]. Zhou et al. [36] synthesized the mesoporous TiO_2 using IL [BMIM][BF_4]. After these studies, Dionysiou and co-workers [37–40] reported the systematic synthesis and characterization of mesoporous TiO_2 by sol-gel process in the presence of ILs. In another study, Liu et al. [41] reported the synthesis of nanostructured anatase TiO_2 monoliths using IL [BMIM][BF_4] as a template solvent by sol-gel method. Apart from these studies, many studies have been reported on the synthesis of TiO_2 using ionic liquids [16,17,42–44]. However, all these studies were only focused on properties of TiO_2 and their applications. In the present study, synthesis of TiO_2 based ionogels and the properties of confined IL as well as TiO_2 matrix have been reported. It has been observed that the properties such as glass transition temperature, thermal stability and vibrational bands of IL confined in titanium dioxide are changed. Most recently, TiO_2 based ionogel has been synthesized by Li et al. [19] for the application in Li ion battery where they have incorporated IL ([PyR_{1201}][TFSI]) and Li TFSI salt in TiO_2 matrix by non-hydrolytic sol-gel process. They have evaluated the electrochemical performance for the application in Li-metal battery and found acceptable rate performance, high discharge capacity and good capacity retention at 25 °C under the 0.1 C rate. Wu et al., [45,46] have also reported the synthesis of TiO_2 based ionogels using ILs [EMIM][TFSI] and [Py13][TFSI] with salt LiTFSI by non-aqueous sol-gel process for its application in Li-ion rechargeable batteries and reported high discharge capacity. Apart from the above discussed methods for TiO_2 preparation using IL, there are also reports on the synthesis of mesoporous TiO_2 using structure-directing reagent. TiO_2 synthesized using various structural directing reagents is found to exhibit long-ranged 3D nano-size networks, mesoporous and crystalline structure [47–51]. However, IL assisted TiO_2 has been used as electrolyte in electrochemical devices and have been found to show uniform porous structure [16,17,42–44].

From the above discussions, it can be seen that the properties of IL in TiO_2 matrix are still very less reported. Therefore, to know the properties of IL in TiO_2 matrix as well as synthesis of porous TiO_2 with uniform pore size is important. In the present study, we have synthesized TiO_2 based ionogels using IL 1-ethyl-3-methyl imidazolium thiocyanate ([EMIM][SCN]) by non-hydrolytic sol-gel process. Ionogels have been characterized using different experimental techniques e.g. BET, TGA, DSC, SEM, TEM, XRD, and FTIR. N_2-sorption measurement shows that the TiO_2 matrices have mesoporous structure with uniform pore size distribution. TGA results exhibit the decrease in thermal stability of IL in TiO_2 matrices. From the DSC results, we have observed the change in glass transition temperature of IL upon immobilization in TiO_2 matrices. SEM micrographs indicated that as the amount of IL is increased, TiO_2 matrices become stable. XRD results confirm the synthesis of TiO_2 and also exhibit that as prepared TiO_2 samples are in amorphous phase, however after removal of IL, it shows the anatase crystalline phase of TiO_2. FTIR results show the change in vibrational bands of IL due to the interaction of IL molecules with titanium dioxide pore wall surface.

2. Materials and methods for preparation of ionogels

2.1. Chemicals

Tetraethyl orthotitanate (TEOT; 98%) and ionic liquid, 1-ethyl-3-methyl imidazolium thiocyanate ([EMIM] [SCN]) were purchased from Sigma-Aldrich. Formic acid (GR Grade) was purchased from Merck, Germany. Before use, the IL was heated at a temperature of 100 °C for 12 h followed by vacuum drying at a pressure of $\sim 10^{-3}$ torr to remove traces of water.

2.2. Synthesis of titanium dioxide (TiO_2) based ionogels

Titanium dioxide and ionogels (IL, [EMIM] [SCN], confined TiO_2 matrix) were prepared by non-hydrolytic sol-gel process. For this, tetraethyl orthotitanate (TEOT) as a titania precursor was mixed with formic acid and IL at a TEOT/HCOOH/IL molar ratio of 1:8:x where (x = 0.0, 0.3, 0.5, and 0.7 mol). After mixing TEOT/HCOOH/IL, gelation process was started and it was found that all the samples took gelation time about 1 to 5 min. The chemical reactions involved in the non-hydrolytic sol-gel process [45] for the synthesis of TiO_2 based ionogels using precursor TEOS are given below:

(i) Carboxylation

$$Ti(OC_2H_5)_4 + 4HCOOH \rightarrow Ti(OOCH)_4 + 4C_2H_5OH \quad (1)$$

(ii) Esterification

$$HCOOH + C_2H_5OH \rightarrow H_2O + C_2H_5OOH \quad (2)$$

(iii) Hydrolysis

$$Ti(OOCH)_4 + 4H_2O \rightarrow Ti(OH)_4 + 4HCOOH \quad (3)$$

(iv) Condensation

$$Ti(OH)_4 + Ti(OOCH)_4 \rightarrow 2TiO_2 + 4HCOOH \quad (4)$$

Further, these samples were left for two weeks for ageing. Finally the samples (ionogels) are obtained in the powder form. The synthesized samples are described as T-0, T-1, T-2 and T-3 having 0.0, 0.3, 0.5 and 0.7 mol% of IL, respectively.

2.3. Characterization techniques

The pore parameters (BET surface area, pore volume and pore size) were measured on a Gemini VII 2390t from Micromeratics Instrument corporation at 77 K. Before the measurement, ionic liquid was extracted from the ionogel samples by using procedure as reported in the literature elsewhere [52,53]. For which, ionogels were washed in acetone for several times followed by ultrasonic irradiation in water for 5 min to ensure the removal of IL. After extracting IL from the samples T-1, T-2 and T-3, these samples are described as WT-1, WT-2 and WT-3, respectively. Further, samples were subjected to vacuum drying at 100 °C for 24 h. After that, all the samples (T-0, WT-1, WT-2 and WT-3) were degassed under flow of dry N_2 for 24 h at 60 °C prior to N_2-physisorption study. The thermal properties of samples were analyzed using thermogravimetric analysis (Mettler Toledo TGA/DSC 1 analyzer) and differential scanning calorimetry (Mettler Toledo DSC-1) and resulting data were evaluated with STARe software. For the TGA measurements all the samples were put in alumina (Al_2O_3) pan at a heating rate of 10 °C/min under N_2 atmosphere. However, for the DSC measurements, samples were kept in 40 μL hermetically sealed aluminum pan with pinhole at the top of the pan. The samples inside the DSC-furnace were exposed under continuous flow of N_2 atmosphere. The DSC measurements were carried out using temperature programmme that includes a first heating cycle from 25 °C to 100 °C at a rate of 20 °C/min and holding it there for 30 min to remove traces of water. Then, the sample was cooled from 100 °C to −120 °C at a cooling rate of −20 °C/min, followed by an isotherm of 30 min at −120 °C and further, the DSC thermogram was recorded by heating the sample at a rate of 10 °C/min from −120 °C to 100 °C. Final, data was collected after repeating the