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Synthesis and Characterization of ZrO_2 nanoparticles in ionic liquid 1-ethyl-3-methylimidazodium trifluoromethanesulfonate [EmimTfO]

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ABSTARCT

The chemical synthesis of zirconia nanoparticles in ionic liquid 1-ethyl-3-methylimidazodium trifluoromethanesulfonate (EmimOTf) is reported. The nanoparticles obtained were characterized by XRD, SEM/TEM, UV-Vis and IR analytical techniques. The XRD pattern of the sample gathered after centrifugation shows two broad humps at ca. 31.48^o *and* 49.28^o *and weak diffraction peaks at 17.451 and* 78.91^o*. The reflections are assigned to the (100), (111), (022) and (330) planes of monoclinic space group P21/c (14) (JCPDS 86-1449). SEM shows that the precipitates are a mixture of plates, rods and faceted particles. TEM and UV/Vis suggests that nanoparticles have been formed. The infrared spectroscopy shows that molecules of the ionic liquid are adsorbed on the surface of the particles as indicated by absorption bands between ca. 3117 -2880* cm^{-1} *along with the bands between 1575 and 1387* cm^{-1} *assigned to C–H stretching and in-plane vibrations of the imidazolium ring, respectively. The bands between 1263 and 1033* cm^{-1} *can be assigned to aliphatic in-plane vibrations, and the bands between 850 and 520*cm^{-1} *are due to Zr-O bond.*

INTRODUCTION

There is a growing need to synthesize and characterize nano-sized materials due to rapid growth of nanotechnological applications. Among oxide nanoparticles, ZrO_2 nanoparticles are quite attractive, as they offer several advantages such as chemical inertness, excellent thermal stability, high refractive index and high hardness. Consequently, zirconia-based materials have found wide applications as refractories, thermal barrier coatings, toughened ceramics, piezoelectrics, electrolytes, and so on [1–3]. The performance of nanomaterials in many of these applications requires control over the size, the morphology and the surface structure, which is based on the appropriate control of the parameters that influence nucleation and growth. Such control over the growth and morphology of nanomaterials can be achieved by the use of ionic liquids with high degree of self-organization and templating effect.

The use of ionic liquids in the synthesis of inorganic materials has received a great deal of attention[4-8], not only because it is environmentally friendly deriving from its negligible vapour pressure [9-12], but also because very large number of possible combinations of cations and anions allows one to fine-tune the properties of the synthesized product for specific applications. Recently, ionic liquids have been used as solvents, reactants, or templates for the synthesis of inorganic nanomaterials with novel morphologies and improved properties [14-16]. Moreover, ILs can in somecases enable the synthesis of materials that cannot be made via conventional processes [17-28].

There are reports on the preparation of zirconia nanoparticles by by sol–gel methods, homogeneous precipitation, hydrothermal processing, or spray pyrolysis in presence of ligating stabilizing agents as well as by freeze drying using $ZrOCl_2$ solutions [29-43]. In most of these cases, the stabilization of the nanoparticles in the organic medium is difficult without functionalization, which however diminishes the desired advantageous effects of the nanoparticles within the nanocomposite[30-35]. Furthermore, reports of successful preparation of completely homogeneous dispersions of ZrO_2 nanoparticles in conventional organic solvents are scanty [44-47]. In this study, the IL 1-Ethyl-3-methylimidazolium trifluoromethanesulfonate [EmimTfO] is used as a solvent, template as well as stabilizing agent in the synthesis of ZrO_2nanoparticles via chemical reduction of Zr(IV)tetraisopropoxide in the presence of sodium borohydride as reducing agent.

MATERIALS AND METHODS

Materials

The chemicals: IL 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (TfO), sodium borohydride $NaBH_4$, $Zr[OCH(CH3)_2]_4$ were purchased from commercial sources and used as received. Water content in IL was between 0.001 and 0.1% (v/v), as determined by volumetric Karl Fischer titration.

Nanoparticle synthesis

In a typical synthesis, 19.38m g (0.05 mmol) of Zr[OCH(CH3)2]4 was added to 1301.2mg of IL EmimTfO. The mixture was sonicated for 10 min. Then 3.78m g (0.1 mmol) of $NaBH_4$ was added at ambient conditions. The resulting colorless solution was heated to 140^oC for 12 h. Before isolating the precipitate by centrifugation, a small fraction of the colloidal dispersion was removed for UV/Vis and IR, measurements. The centrifuged product was washed with ethanol and dried under vacuum at room temperature for 12 h.

Characterization

X-ray diffraction

Wide angle X-ray diffraction (XRD) was done on an ENRAF-Nonius FR 590 diffractometer with a Cu Ka X-ray tube fitted with an Inel CPS 120 hemispherical detector ranging from 1 to 120_ 2h. Data analysis was performed via EVA.

Spectroscopy

FTIR spectra of the solid samples were also recorded with KBr pellets in the same spectral range on a Thermo Nicolet Nexus 670 spectrometer at 2 cm-1 resolution. UV/Vis spectroscopy was done on an Agilent 8453 spectrometer using 10-mm quartz cuvettes containing the nanoparticle dispersion either in the as-synthesized dispersion or redispersed particles in ethanol at room temperature.

Electron microscopy

TEM images were acquired on a Zeiss EM 912 operated at 120 kV. One droplet of the suspension was applied to a 400-mesh carbon-coated copper grid and left to dry in air.

RESULTS AND DISCUSSIONS

Nanoparticles have been synthesized via the decomposition of zirconium isopropoxide in ionic liquid 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (TfO). The reaction was performed under reducing conditions in the presence of $NaBH_4$ and at elevated temperatures to obtain homogeneous reaction mixtures.

Figure 1 shows a typical X-ray diffraction (XRD) pattern of the as synthesized product. The XRD shows that nanoparticles of zirconium oxide are obtained in pure phase. The reflections are assigned to the (100), (111), (022) and (330) planes of monoclinic space group $P_{21}/c(14)$ (JCPDS 86-1449) .. The reflections are very broad and thus indicate that the particles are rather small and poorly-crystallized. SEM shows that the precipitates are a mixture of nanoplates, nanorods and faceted particles (Fig.2). Furthermore, the particle sizes are not uniform, but range from a few 100 nm to tens of micrometers. The plates are at the larger end of the sizes . SEM is therefore consistent with XRD, as the large plates are dominated by (111) facets. The presence of the rodlike particles accounts for the presence of the other reflections in the XRD pattern. SEM also reveals a qualitative difference between the samples grown at different temperature. At 120^{o}C nanorods are the predominant species. With increasing, temperature (at 140^{o}C) predominantly platelike particles form. This shows that the temperature has qualitative influence on the mineralization.

In Figure 3, the TEM image of the sample grown at 140^{o}C is presented. TEM suggests that these particles could form via the aggregation of smaller particles as particles with a diameter of ca. 15–30 nm can be observed. The TEM suggests that the particles are in fact larger structures that form via the growth of small plate-like particle.

Figure 4 shows the FTIR spectrum of ZrO_2 nanoparticles after isolation, while Figure 5 gives the UV/Vis spectra of the products. IR spectroscopy shows that even after centrifugation and washing, quite a number of bands appear. The bands between ca. 3117 -2880 cm^{-1} along with the bands between 1575 and 1,387 cm^{-1} can be assigned to C–H stretching and *in-plane* vibrations of the imidazolium ring, respectively. The bands between 1263 and 1033 cm^{-1} can be assigned to aliphatic *in-plane* vibrations, and the bands between 850 and 520cm^{-1} are due to Zr-O bond. Therefore molecules of the ionic liquid are adsorbed on the surface of the particles thus providing an electrosteric colloid-type protection [46-48] of the nanostructured particles formed. According to DLVO (Derjaungin-Landau-Verwey-Overbeek) theory [51-53], ILs provides an electrostatic protection in the form of a '*protective shell*' for nanoparticles, so that no extra stabilizing molecules or organic solvents are needed[49-50]. The strong hydrogen bonding interaction formed between the C(Emim)+)-H-OZrO accounts for the broad absorption band at 3519cm^{-1}[41]

UV/Vis spectroscopy shows two prominent features. Between ca. 200 and 240 nm, a rather intense and broad absorption band is visible and a second, much weaker absorption is visible between ca. 280 and 300 nm. The absorption between 200 and 240 nm is assigned to the imidazoliumcation, which dominates the spectrum, again even after extensive washing. The second, much weaker absorption maximum can be assigned to the nanoparticles. UV/Vis spectroscopy thus confirms the formation of nanoparticles.

In conclusion, nanoparticles of zirconium oxide have been prepared in ionic liquid EmimTfO. The ionic liquid plays a dual role of solvent and stabilizing agent.

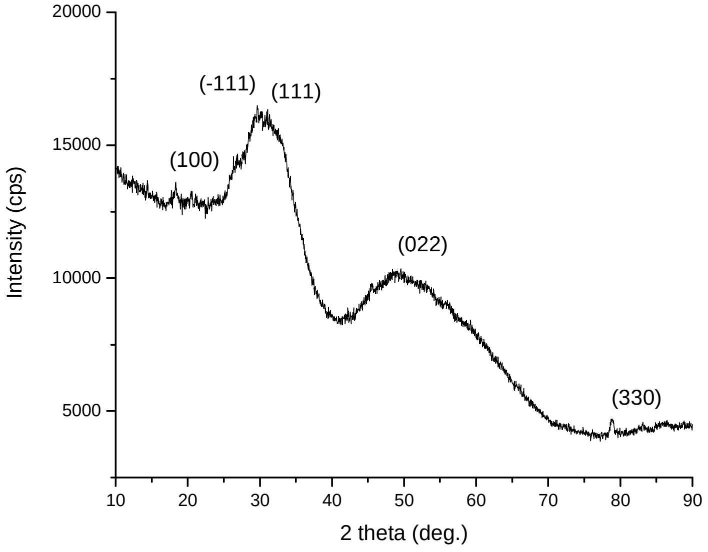

Figure 1. XRD pattern of ZrO_2 nanostructure in ionic liquid EmimOTf

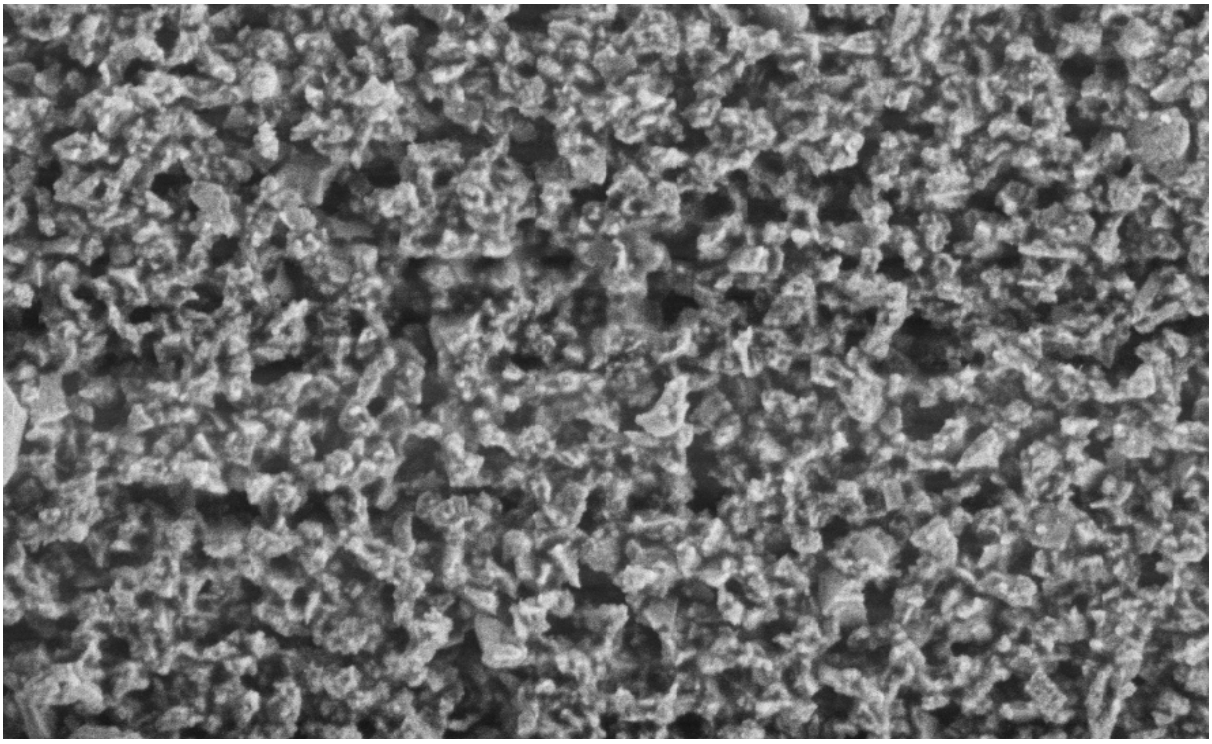

Figure 2.SEM image of the nanostructured ZrO_2. Scale bar is 2µm

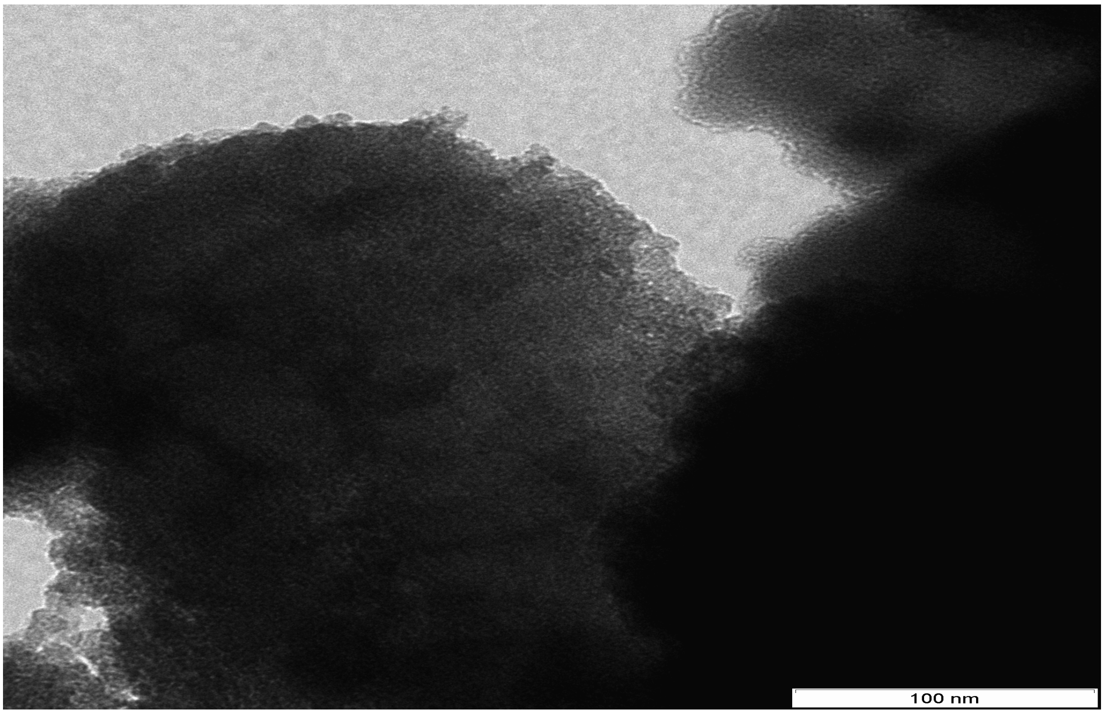

Figure 3. TEM of the nanoparticles of ZrO_2 grown in IL EMIMOTf

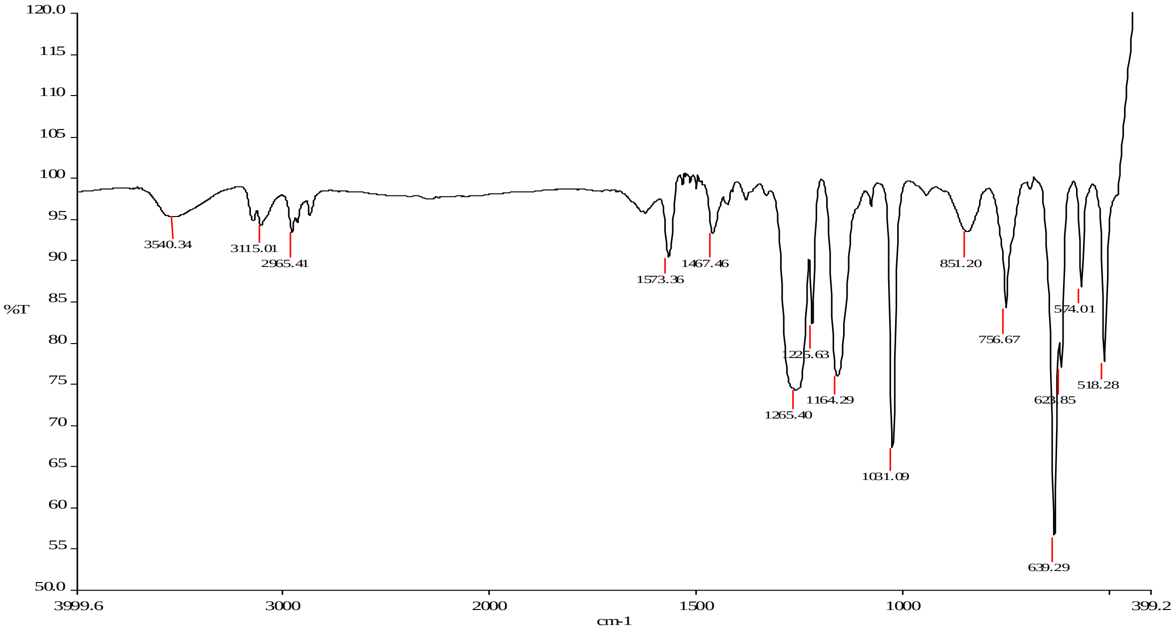

Figure 4. Infrared spectrum of sample grown in IL EmimOTf

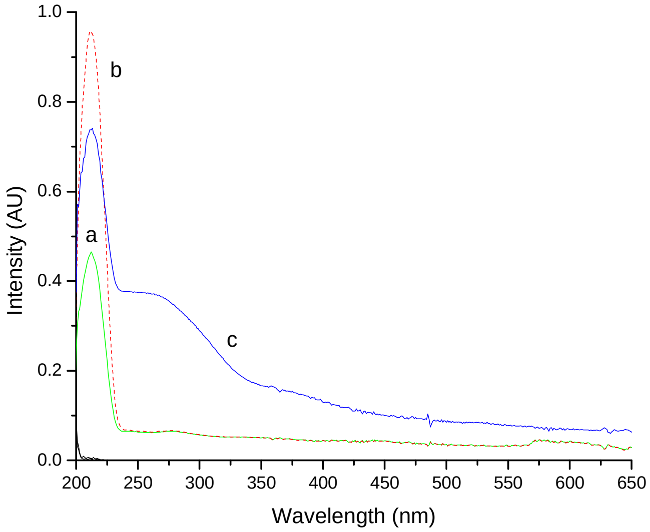

Figure 5. UV-Vis spectra of nanostructure ZrO_2 in IL EmimOTf. Samples gathered after 5hr of heating at (a)120°C, b) 140°C and c) 140°C after 12hr

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