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Synthesis of Tungsten Oxide in Ionic Liquids Via Sol-Gel and Microwave-Assisted Approaches

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Abstract

The first results for the synthesis of tungsten oxide nanoparticles in four different ionic liquids namely, 1-ethyl-3-methylimidazolium trifluoromethylsulfonate ([EMIm]TfO), 1-butyl-1-methylpyrrolidinium trifluoromethyl sulfonate ([$Py_{1,4}$]TfO), 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([EMIm]TFSA), and 1-butyl-1-methylpyrrolidiniumbis(trifluoromethylsulfonyl)amide ([$Py_{1,4}$]TFSA), are shown. Two different synthesis methods, sol gel and microwave-assisted, were employed in this study. The sol gel as-synthesized samples exhibited different XRD patterns depending on the type of ionic liquids. However, after calcination at 500 ^{o}C, monoclinic phase of tungsten trioxide WO_3 was obtained. The calcined samples obtained in the employed ionic liquids showed very fine particles of WO_3 with sizes in the nanometer regime. The microwave-assisted approach was employed for the synthesis of tungsten oxide in the ionic liquids [EMIm]TfO, and [EMIm]TFSA. In case of the ionic liquid [EMIm]TFSA, tungsten trioxide WO_3 was obtained, whereas hydrogen tungsten oxide H_2WO_4 was obtained using the ionic liquid [EMIm]TfO, which transforms into WO_3 after calcination at 500 ^{o}C.

Keywords: Tungsten oxide, Sol-gel, Microwave, Ionic liquids, Imidazolium, Pyrrolidinium.

1. Introduction

Transition metal oxides have received great attention rowing to their unique chemical and physical properties that lead to several potential applications. Among transition metal oxides, tungsten oxide has attracted considerable attention for its widespread applications

in different fields such as, supercapacitors, Li-ion batteries, sensors, and photocatalysis [1-4]. WO_3 is an intrinsically n-type, wide band-gap semiconductor with a tunable wide energy band gap of 3.0 eV. Moreover, non-stoichiometric tungsten oxides (WO_{3-x}) have received many concerns owing to their enhanced electrical conductivity. Various methods have been employed for the preparation of tungsten oxide such as, chemical precipitation [5], sol–gel [6], solvothermal [1], and spray pyrolysis[8].

Among methods of the synthesis of metal oxides, the microwave-assisted approach represents a rapid and facile approach for the synthesis through simple heating of the precursors in a micro-oven with a wide range of frequency (0.3 to 300 GHz) within a short time with a high degree of morphology control [9]. Microwave energy is a kind of spectrum like visible light, infrared irradiation, and UV irradiation which is directly delivered to the reaction mixture via electromagnetic field/molecular interaction [10]. It can penetrate the material and provide energy; thus, heat can be generated within the volume of the material resulting in volumetric heating. Moreover, this method displays acceleration in reaction rate, yield enhancement, short reaction time, high-purity materials, controlled particle size, fine particle size distribution, and improved physicochemical properties[11]. Indeed, it is an attractive choice for promoting reactions and providing an alternative energy effective heating compared to traditional heating methods. Yani Li; et al. successfully prepared tungsten oxide nanorods by a simple microwave hydrothermal method [12]. The diameter of the obtained nanorods is about 20–50 nm and several micrometers in length while the XRD pattern indicates the formation of hexagonal WO_3. The resulting oxide was investigated for the potential applications of high-

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performance ethanol sensors under different concentrations of ethanol [13]. Solvothermal method assisted by microwave radiation was conducted to synthesize well-crystallized nano tungsten oxide (WO_3) films with preparation times of 5 and 10 min, at temperatures 150 or 180 ^oC [14].
Another feasible and cost-effective method is sol-gel which can be effectively employed for the synthesis of tungsten oxide [6-7].
The fabrication of nanostructured WO_3 particles with the assistance of the ionic liquids 1-butyl-3-methyl imidazolium chloride and 1-carboxymethyl-3-methylimidazolium chloride in benzyl alcohol solution was reported [13]. Generally, ionic liquids were widely utilized in the synthesis of nanomaterials as they offer environmentally benign conditions and can act as stabilizers and crystal growth modifiers [16-20]. Tungsten trioxide was also synthesized in absolute ethanol and glacial acetic acid via a hydrothermal route with the addition of small amount of ionic liquid 1-butyl-3-methyl tetrafluoroborate [21].
In the present paper, the synthesis of tungsten oxide via sol-gel in the ionic liquids; [EMIm]TfO, [$Py_{1,4}$]TfO, [EMIm]TFSA and [$Py_{1,4}$]TFSA was investigated. The microwave-assisted approach was also employed for the synthesis of tungsten oxide in the ionic liquids [EMIm]TfO, and [EMIm]TFSA. To the best of our knowledge, the synthesis of tungsten oxide via sol gel or microwave-assisted methods using the employed ionic liquids was not previously reported. We aim at demonstrating the capability of employing the different ionic liquids for the synthesis of tungsten oxide via sol-gel and microwave-assisted approaches.

2. Experimental

2.1. Materials

Four different ionic liquids were employed in this study; [EMIm]TfO, [$Py_{1,4}$]TfO, [EMIm]TFSA and [$Py_{1,4}$]TFSA. The ionic liquids were purchased from Io.Li.Tec., Germany. To adjust the pH, ammonium hydroxide NH_4OH (Sigma-Aldrich 99.9%) was utilized. As a precursor, WCl_6 (*Alfa* 99 %) was employed. The precursor solutions were hydrolyzed by distilled water.

2.2.So-gel synthesis of tungsten oxide

1 M WCl_6 solutions were prepared in the employed ionic liquids. Afterwards, the precursor solutions were hydrolyzed by the addition of about 10 ml of distilled water with continuous stirring for about 4 hours. The pH of the solution was adjusted to 9 using NH_4OH solutions, and then the solutions were left to form a gel. The formed products were centrifuged and washed several times with isopropanol.

2.3. Microwave-assisted synthesis of tungsten oxide

The microwave-assisted approach was employed for the synthesis of tungsten oxide. 1 M solutions of WCl_6 were prepared in the employed ionic liquids and the pH was adjusted by to 9 by ammonia solution. The ionic liquid/precursor solutions were then heated using a domestic microwave oven with a microwave power of 300 W for 5 minutes. The products were reclaimed by centrifuging and then washed several times with isopropanol to get rid of the remaining ionic liquids.

2.4. Characterization of the synthesized oxides

The prepared oxide was characterized by XRD, and SEM. The morphology of the prepared samples was investigated by a high-resolution field emission scanning electron microscope (Quanta FEG 250). The XRD measurements were performed using a Philips-diffractometer Model PW 2013, the Netherlands, operating at 35 kV and 20 mA with a source of CuKα radiation.

3. Results and Discussion -

3.1. Sol-gel synthesis of tungsten oxide from the employed ionic liquids

Tungsten oxide was synthesized via sol-gel methods in the employed ionic liquids, [EMIm]TfO, [$Py_{1,4}$]TfO, [EMIm]TFSA and [$Py_{1,4}$]TFSA. The synthesized oxide was characterized by XRD and SEM. Fig. 1 shows the XRD patterns of the as-prepared samples obtained in the four ionic liquids. The as-prepared products show good crystallinity as pronounced diffraction peaks were recorded. The as-prepared samples show different XRD patterns depending on the type of ionic liquids. The XRD patterns of the samples obtained in the ionic liquids [$Py_{1,4}$]TFSA and [EMIm]TFSA reveal the formation of tungsten oxide hydrate $WO_3.(H_2O)_{0.5}$ (JCPDS 36-1143). However, the XRD patterns of the as-prepared samples obtained in the ionic liquids [$Py_{1,4}$]TfO and [EMIm]TfO show the characteristic diffraction peaks of hydrogen tungsten oxide (JCPDS 01-0583), indicating the formation of H_2WO_4.

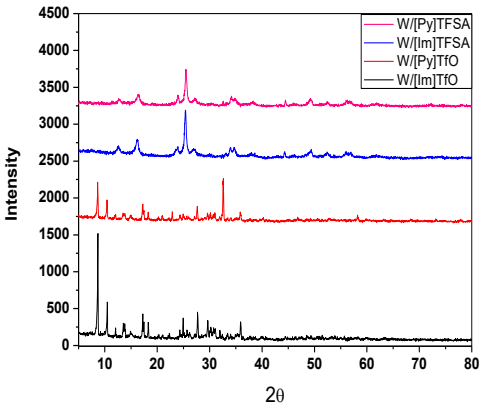

Fig. 1. XRD patterns of the as-prepared tungsten oxide prepared in the employed ionic liquids.

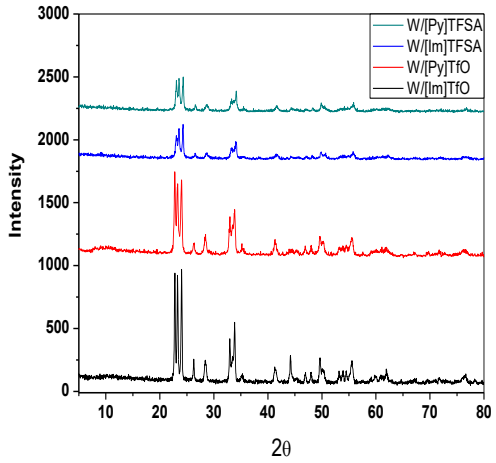

Fig. 2 XRD patterns of tungsten oxide prepared in the employed ionic liquids and calcined at 500 ºC.

The as-synthesized samples obtained in the employed ionic liquids were calcined at 500 ºC. The XRD patterns of the calcined samples are shown in Fig. 2. As seen, all samples exhibit similar XRD patterns and all diffraction peaks are indexed to the monoclinic phase of tungsten trioxide WO_3(JCPDS no. 43-1035).

The morphology of the as-synthesized and calcined tungsten oxide samples obtained from the four ionic liquids were investigated by SEM, Fig. 3. As seen the as-synthesized sample obtained from the ionic liquid [EMIm]TfO shows particles agglomeration (Fig. 3a) and after calcination at 500 oC (Fig. 3e) nanoparticles of sizes ranging from 50 to 100 nm were clearly seen. The SEM micrograph of the sample obtained from the ionic liquid [$Py_{1,4}$]TfO shows coarse, irregular particles (Fig. 3b) while small needles like particles are seen in the SEM micrograph of the calcined sample (Fig. 3f). The as-synthesized samples obtained in both ionic liquids [EMIm]TFSA (Fig. 3c) and [$Py_{1,4}$]TFSA (Fig. 3g) show a similar morphology as the agglomeration of particles were obtained and after calcination at 500 oC, very fine particles with sizes in the nanometer regime are clearly seen, Fig. 3g and Fig. 3h.

3.2. Microwave-assisted synthesis of tungsten oxide from the ionic liquids [EMIm]TFSA and [EMIm]TfO

Tungsten oxide was synthesized via microwave-assisted route in the ionic liquids [EMIm]TFSA and [EMIm]TfO. The two ionic liquids have the same imidazolium cation and different anions to check whether the anion of the ionic liquid has an impact on the phase formation and growth of the synthesized tungsten oxide. Fig. 4 demonstrates the XRD patterns of the as-synthesized and calcined tungsten oxide samples obtained from [EMIm]TFSA and [EMIm]TfO.

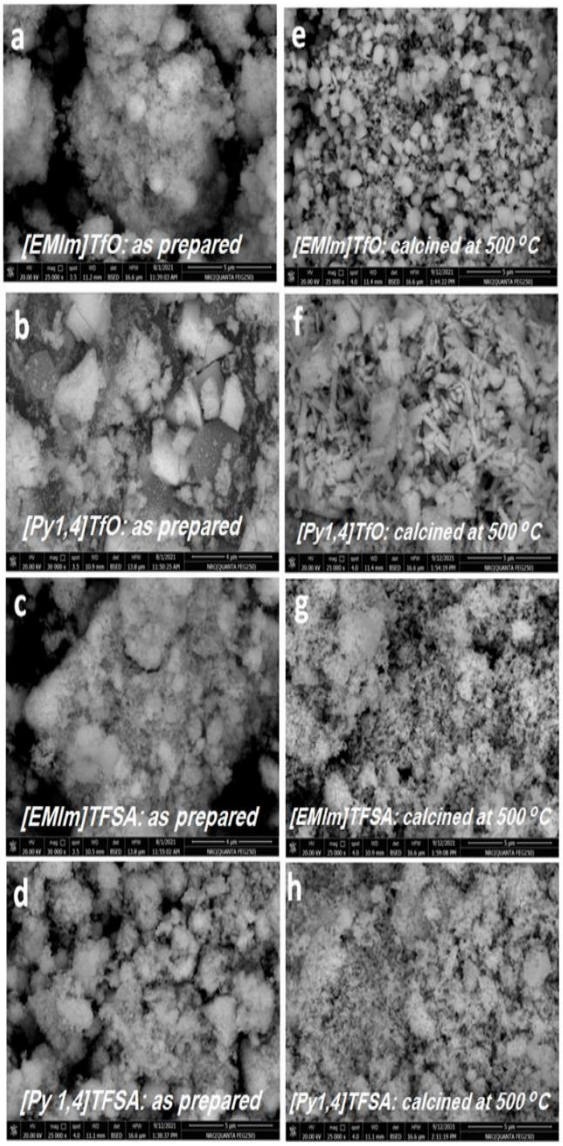

Fig. 3 SEM images of sol-gel synthesized tungsten oxide: As synthesized from (a) [EMIm]TfO, (b) [$Py_{1,4}$]TfO, (c) [EMIm]TFSA and (d) [$Py_{1,4}$]TFSA: Calcined at 500 oC (e) [EMIm]TfO, (f) [$Py_{1,4}$]TfO, (g) [EMIm]TFSA and (h) [$Py_{1,4}$]TFSA.

The as-synthesized sample obtained from [EMIm]TFSA exhibits poor crystallinity as weak, broad diffraction peaks were recorded. The peaks are well indexed to the monoclinic phase of tungsten trioxide WO_3(JCPDS no. 43-1035). Calcination of the as-prepared sample at 500 ºC improves the crystallinity of the sample well-defined, and broad diffraction peaks of the monoclinic phase of WO3 are observed. The broadening of the diffraction peaks indicates the lower particle size of the synthesized oxide. Interestingly, the sample obtained in the ionic liquid [EMIm]TfO shows different diffraction patterns as the recorded peaks assigned to hydrogen tungsten oxide (JCPDS 01-0583), indicating the formation of H_2WO_4. The sol gel synthesized sample using the ionic liquid [EMIm]TfO exhibited similar XRD patterns (as

shown in Fig. 1). This indicates that the type of the anion of the ionic liquid can influence the phase composition of the synthesized tungsten oxide. After calcination at 500 ºC, H_2WO_4 transforms to WO3 as revealed from the XRD patterns of the calcined sample, Fig. 4. The morphology of the synthesized tungsten oxide samples was investigated. Fig. 5 shows the SEM images of the as-synthesized and calcined samples obtained from the ionic liquids [EMIm]TFSA and [EMIm]TfO. The SEM image of the as-synthesized WO3 obtained from [EMIm]TFSA shows aggregations of small particles, Fig. 5a, and after calcination at 500 ºC coarse, layered particles are formed. The SEM image of H2WO4 obtained from the ionic liquid [EMIm]TfO shows homogenous particles with sizes in the micrometer regime, Fig. 5b, and on calcination coarse particles, Fig. 5d, containing nanosized particles are observed, as shown in the SEM of Fig. 5e.

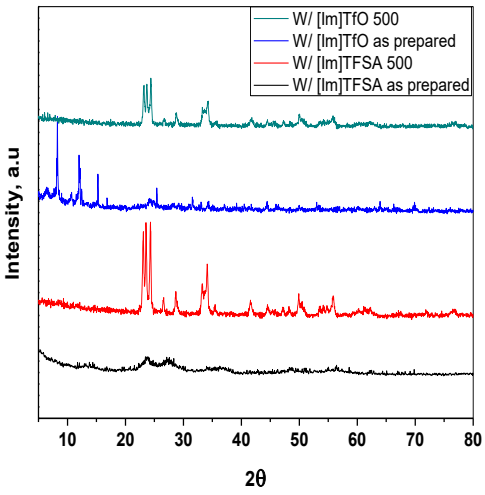

Fig. 4 XRD patterns of the as-prepared and calcined (500 ºC) tungsten oxide synthesized from the ionic liquids [EMIm]TfO and [EMIm]TFSA.

4. Conclusions

The sol-gel synthesis of nanostructured tungsten oxide was carried out in the ionic liquids [EMIm]TFSA, $[Py_{1,4}]$TFSA, $[Py_{1,4}]$TfO and [EMIm]TfO. The XRD patterns of the samples obtained in the ionic liquids $[Py_{1,4}]$TFSA and [EMIm]TFSA showed the formation of tungsten oxide hydrate $WO_3.(H_2O)_{0.5}$. However, the XRD patterns of the as-prepared samples obtained in the ionic liquids $[Py_{1,4}]$TfO and [EMIm]TfO revealed the formation of hydrogen tungsten oxide H_2WO_4. After calcination at 500 ºC, monoclinic phase of tungsten trioxide WO_3 was obtained. The calcined samples obtained in the employed ionic liquids showed very fine particles of$WO_3$with sizes in the nanometer regime. Tungsten oxide was also synthesized via the microwave-assisted approach in the ionic liquids [EMIm]TfO, and [EMIm]TFSA. In case of the ionic liquid [EMIm]TFSA, Tungsten trioxide WO_3 was obtained using the ionic liquid [EMIm]TFSA, whereas hydrogen tungsten oxide H_2WO_4 was obtained using [EMIm]TfO, which transforms into WO_3 after calcination at 500 ºC.

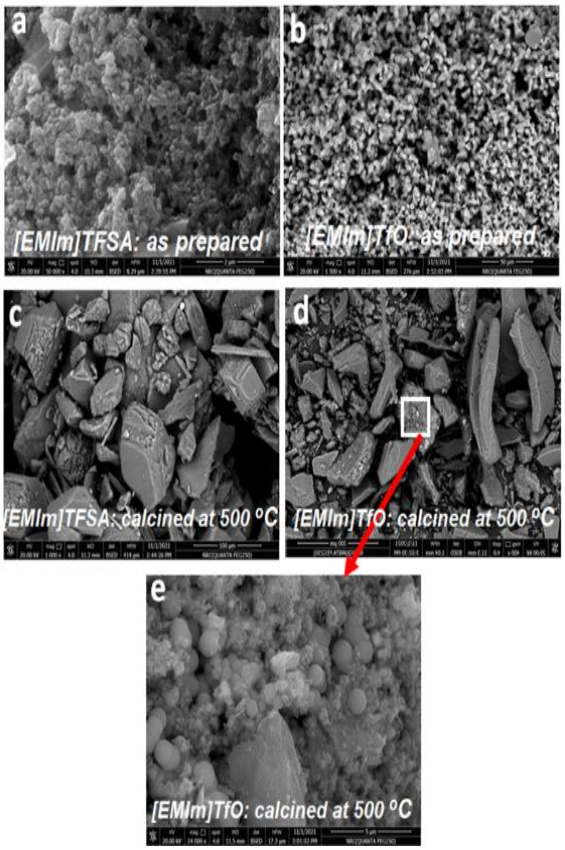

Fig.5. SEM images of tungsten oxide: As synthesized from (a) [EMIm]TFSA and (b) [EMIm]TfO: Calcined at 500 ºC (c) [EMIm]TFSA, (d) [EMIm]TfO and (e) Zoom in in the area shown in the SEM image d.

5. Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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