



# Sol-gel synthesis of nanostructured cobalt oxide in four different ionic liquids

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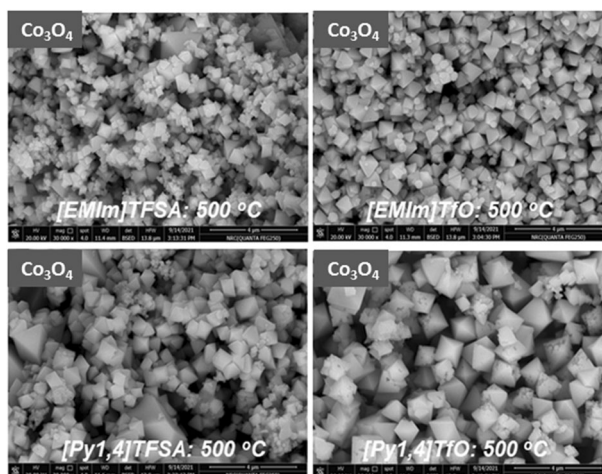
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## Abstract

In this paper we report on the sol-gel synthesis of cobalt oxide in four different ionic liquids with two different cations and anions. The employed ionic liquids are; 1-ethyl-3-methylimidazolium trifluoromethylsulfonate ([EMIm]TfO), 1-butyl-1-methylpyrrolidinium trifluoromethylsulfonate ([Py<sub>1,4</sub>]TfO), 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([EMIm]TFSA), and 1-butyl-1-methylpyrrolidiniumbis(trifluoromethylsulfonyl)amide ([Py<sub>1,4</sub>]TFSA). The influence of the cation and anion of the ionic liquids on the morphology of the synthesized oxides was explored. The results showed that octahedron-shaped Co<sub>3</sub>O<sub>4</sub> nanoparticles with different average sizes depending on the type of the employed ionic liquid. The imidazolium cation was found to play a significant role in reducing the particle size of the synthesized Co<sub>3</sub>O<sub>4</sub> nanoparticles. The samples prepared in the imidazolium-based ionic liquids showed smaller particle sizes than those of the samples prepared in the pyrrolidinium-based ionic liquids. The shape of the particles of the synthesized Co<sub>3</sub>O<sub>4</sub> was not affected by the type of the ionic liquids.

## Graphical abstract

SEM images of sol-gel synthesized cobalt oxide obtained from the ionic liquids [EMIm]TFSA, [EMIm]TfO, [Py<sub>1,4</sub>]TFSA and [Py<sub>1,4</sub>]TfO, and calcined at 500 °C.



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**Keywords** Cobalt oxide · Sol-gel · Ionic liquids · Imidazolium · Pyrrolidinium

### Highlights

- $\text{Co}_3\text{O}_4$  nanoparticles were obtained in the ionic liquids [EMIm]TfO, [Py<sub>1,4</sub>]TfO, [EMIm]TFSA and [Py<sub>1,4</sub>]TFSA via the sol–gel approach.
- Octahydron-shaped  $\text{Co}_3\text{O}_4$  nanoparticles with different average sizes depending on the type of the employed ionic liquid were obtained.
- The imidazolium cation plays a significant role in reducing the particle size of the synthesized cobalt oxide.
- The type of the anion or cation of the employed ionic liquids does not show an obvious influence on the shape of the synthesized cobalt oxide particles.

## 1 Introduction

In recent times, transition metal oxides have attracted considerable interest owing to their distinctive electronic, optical, magnetic, and catalytic properties [1–3]. Diverse methods for the synthesis of transition metal oxides were reported, such as, e.g., sol-gel, hydrothermal, electrodeposition, electrophoretic deposition, direct chemical precipitation, microwave and sonochemical synthesis [4, 5]. Among the synthesis methods, sol-gel is a potential, scalable approach for the synthesis of metal oxides, involving the formation of an amorphous gel from a precursor solution [6].

Cobalt oxide is one of the important transition metal oxides for its potential application in various fields such as, e.g., catalysis, batteries, gas sensors, electronic devices, and others [7–10]. In this paper nanostructured cobalt oxide via sol-gel method in four different ionic liquids. The simplicity of the sol-gel process, enhances the upscaling of the synthesis of nanostructured metal oxides. Ionic liquids can offer exceptional properties as multifunctional solvents for the synthesis of nanomaterials. Starting from the last decade, ionic liquids have revealed an enormous promise in the preparation of nanomaterials [11–13]. It was proved that ionic liquids can competently serve as stabilizers, templates and crystal growth modifiers [14, 15]. Furthermore, they can offer benign environments for the preparation of metal oxides as the utilization of organic solvents and synthetic stabilizers is usually harmful to the environment. Ionic liquids have extraordinary characteristics making them fascinating materials for a wide variety of applications [16–19]. They exhibit high thermal and electrochemical stabilities, and lower toxicity compared with conventional organic solvents. Moreover, they are nonvolatile and nonflammable, thus, they are considered as superb alternatives to replace volatile, environmentally harmful organic solvents.

Four different ionic liquids, [EMIm]TfO, [Py<sub>1,4</sub>]TfO, [EMIm]TFSA and [Py<sub>1,4</sub>]TFSA, were employed for the synthesis of cobalt oxide via the sol-gel approach. Ionic liquids with different cations and anions were employed in order to explore the influence of the cations and/or anions on

tuning the size and morphology of the synthesized oxides. The employed ionic liquids are commercially available and were previously employed for the synthesis of different metal oxides [11, 14, 20]. To the best of our knowledge, the sol-gel synthesis of cobalt oxide in the employed ionic liquids was not previously reported. The obtained results revealed that the imidazolium cation plays a significant role in reducing the particle size of the synthesized cobalt oxide. The type of the anion or cation of the employed ionic liquids did not have an obvious influence on the shape of the synthesized cobalt oxide particles.

## 2 Experimental

### 2.1 Materials

The employed ionic liquids, [EMIm]TfO, [Py<sub>1,4</sub>]TfO, [EMIm]TFSA and [Py<sub>1,4</sub>]TFSA, were purchased from Io.Li.Tec., Germany. Ammonium hydroxide  $\text{NH}_4\text{OH}$  (Sigma-Aldrich 99.9%) was used to adjust the pH. Anhydrous  $\text{CoCl}_2$  (Alfa 99%) was used as a precursor. Distilled water was used to hydrolyse the precursor solutions. All chemicals were used without further purification.

### 2.2 Synthesis of cobalt oxide

Cobalt oxide was synthesized in the employed ionic liquids via sol gel methods. 1 M  $\text{CoCl}_2$  was prepared in the employed ionic liquids. The precursor solutions (50 ml) were then stirred for about 6 h to obtain harmonized mixtures. The hydrolysis was carried out by a dropwise addition of about 10 ml of distilled water for three hours of continuous stirring to hydrolyse the precursors. The pH was adapted to be 9 using  $\text{NH}_4\text{OH}$  solutions. Subsequently, an emulsion was obtained and then aged for about 6 h to produce a gel. The hydrolysis products were then retrieved via centrifuging and filtration. The samples were washed several times by isopropanol to remove the ionic liquids residues. The samples were left to dry in air and finally calcined at different temperatures to

improve the crystallinity of the synthesized samples and to explore the influence of the temperature on the phase transformation of the synthesized oxides.

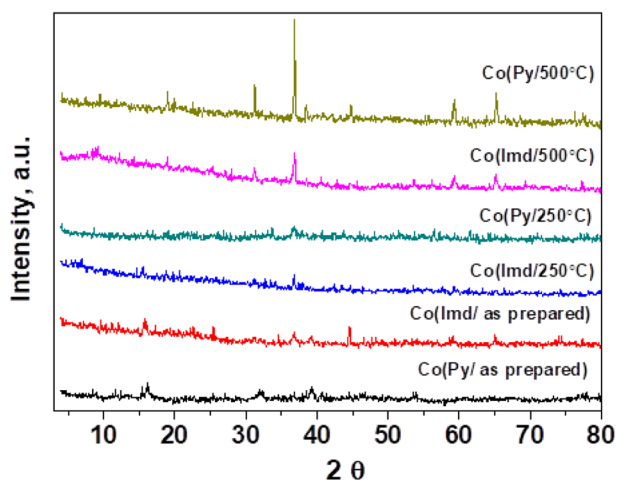
### 2.3 Characterization of the synthesized oxides

The prepared powders were characterized by XRD, TEM, SEM, DTG and Nitrogen gas sorption. The morphology of the prepared samples was investigated by a high-resolution field emission scanning electron microscope (Quanta FEG 250) and a transmission electron microscope. 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  $\text{CuK}\alpha$  radiation. The thermal gravimetric analysis was conducted using a NETZSCH STA 409 PC thermal analyzer. Nitrogen sorption measurements were carried out by an Autosorb-1 (Quantachrome Instruments, Boynton Beach, FL, USA). The surface area of the obtained oxide was estimated by the BET (Brunauer–Emmett–Teller) equation and pore size was determined by the BJH (Barret–Joyner–Hallender) model.

## 3 Results and discussion

### 3.1 Synthesis of cobalt oxide from the ionic liquids [EMIm]TFSA and [Py<sub>1,4</sub>]TFSA

The synthesis of cobalt oxide in the ionic liquids [EMIm]TFSA and [Py<sub>1,4</sub>]TFSA via sol-gel methods was performed. The synthesized oxide was characterized XRD, TEM, DTG and gas sorption measurements. Figure 1 shows the XRD patterns of the as-synthesized and calcined cobalt oxide obtained in the employed ionic liquids. As seen, the as-synthesized samples exhibit low crystallinity as weak

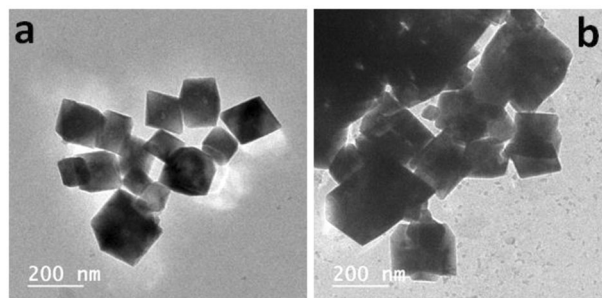


**Fig. 1** XRD patterns of  $\text{Co}_3\text{O}_4$  synthesized from the [EMIm]TFSA and [Py<sub>1,4</sub>]TFSA, and calcined at 250 °C and 500 °C

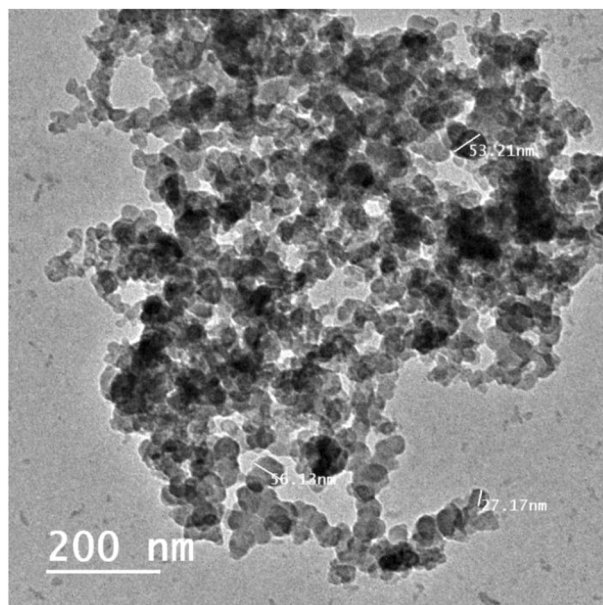
diffraction peaks were recorded. The observed diffraction peaks were assigned to the face centered cubic structure of the spinel tricobalt tetraoxide  $\text{Co}_3\text{O}_4$  (JCPDS No. 74-2120). In the spinel structure of  $\text{Co}_3\text{O}_4$ ,  $\text{Co}^{2+}$  ions occupy the tetragonal sites and  $\text{Co}^{3+}$  ions take the octahedral sites, whereas  $\text{O}^{2-}$  ions are arranged in a cubic close-packed structure [21, 22].

Calcination of the synthesized  $\text{Co}_3\text{O}_4$  at 250 °C leads to inconsiderable improvement in the crystallinity of the samples, Fig. 1. Pronounced diffraction peaks of the spinel  $\text{Co}_3\text{O}_4$  were recorded for the samples calcined at 500 °C.

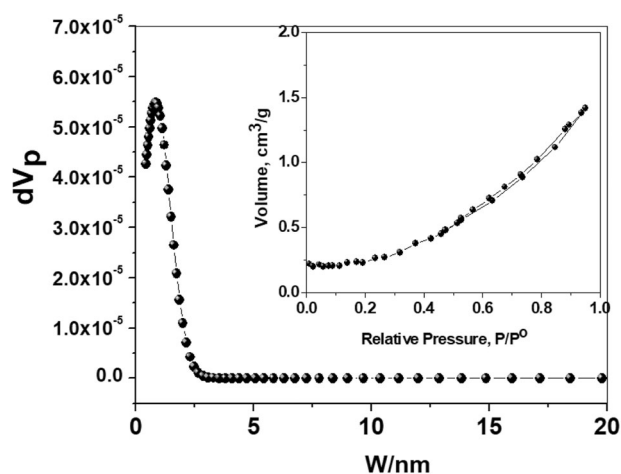
The morphology of the synthesized  $\text{Co}_3\text{O}_4$  in both [EMIm]TFSA and [Py<sub>1,4</sub>]TFSA ionic liquids was investigated by transmission electron microscopy (TEM). In case of [EMIm]TFSA, octahedron-shaped  $\text{Co}_3\text{O}_4$  nanoparticles with an average size of about 90 nm were obtained, Fig. 2. However, in case [Py<sub>1,4</sub>]TFSA smaller  $\text{Co}_3\text{O}_4$  nanoparticles with an average diameter of about 30 nm were obtained, Fig. 3. This signifies the influence of the type of ionic liquid on tuning the size of the synthesized  $\text{Co}_3\text{O}_4$  nanoparticles.



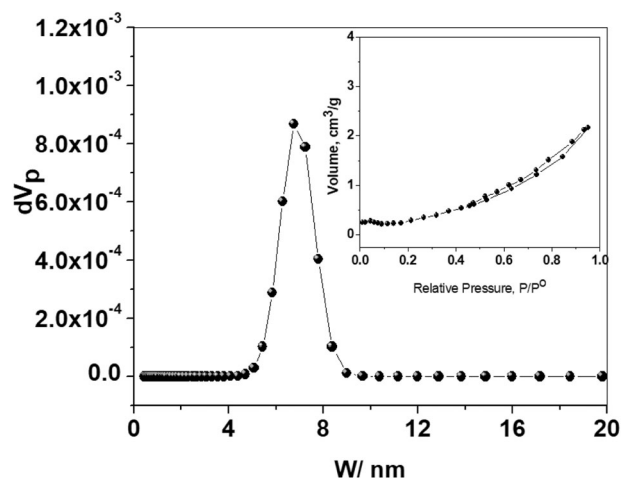
**Fig. 2** TEM images of  $\text{Co}_3\text{O}_4$  prepared in [EMIm]TFSA and calcined at (a) 250 °C and (b) 500 °C



**Fig. 3** TEM image of  $\text{Co}_3\text{O}_4$  prepared in the ionic liquid [Py<sub>1,4</sub>]TFSA calcined at 250 °C

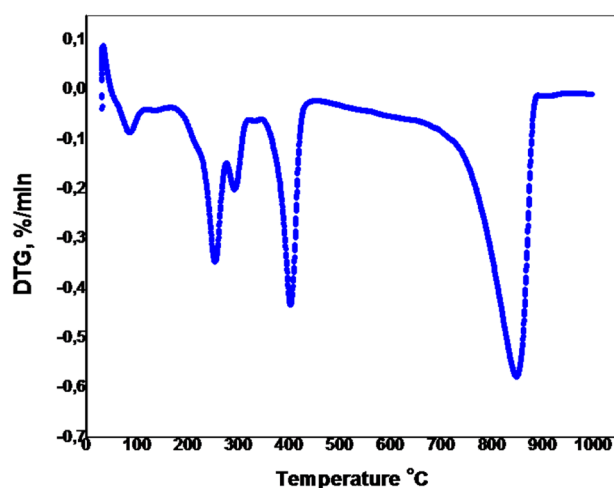


**Fig. 4** Pore size distribution of  $\text{Co}_3\text{O}_4$  prepared in the ionic liquid [EMIm]TFSA and calcined at  $500^\circ\text{C}$ . Inset: Nitrogen gas adsorption-desorption isotherm of the synthesized  $\text{Co}_3\text{O}_4$



**Fig. 5** Pore size distribution of  $\text{Co}_3\text{O}_4$  prepared in the ionic liquid [Py<sub>1,4</sub>]TFSA and calcined at  $500^\circ\text{C}$ . Inset: Nitrogen gas adsorption-desorption isotherm of the synthesized  $\text{Co}_3\text{O}_4$

Figures 4 and 5 show the pore size distribution and nitrogen adsorption-desorption isotherms (insets) of  $\text{Co}_3\text{O}_4$  samples prepared in the ionic liquids [EMIm]TFSA and [Py<sub>1,4</sub>]TFSA, respectively, and calcined at  $500^\circ\text{C}$  for 3 h. The sample prepared in [EMIm]TFSA shows an average pore diameter of about 0.75 nm with a total pore volume of  $2.19 \times 10^{-3} \text{ cm}^3 \text{ g}^{-1}$ . However, the sample prepared in [Py<sub>1,4</sub>]TFSA show an average pore diameter of about 6.75 nm and a total pore volume of  $3.34 \times 10^{-3} \text{ cm}^3 \text{ g}^{-1}$ . The nitrogen adsorption-desorption isotherms of the two samples are similar as they exhibit Type II isotherms according to the IUPAC classification [23]. A slight hysteresis loop in the  $p/p^0$  range of 0.5 to 1 was observed, indicating the presence of mesopores. The BET surface areas of the samples prepared in [EMIm]TFSA and in



**Fig. 6** Differential thermal gravimetric of  $\text{Co}_3\text{O}_4$  synthesized from [Py<sub>1,4</sub>]TFSA

[Py<sub>1,4</sub>]TFSA were found to be 1.11 and  $1.55 \text{ m}^2 \text{ g}^{-1}$ , respectively. In general, the surface area of the prepared samples is relatively low with a slight increase in the surface area of the sample prepared in [Py<sub>1,4</sub>]TFSA. Also, the total pore volume of the sample prepared in [Py<sub>1,4</sub>]TFSA is higher than that of the sample prepared in [EMIm]TFSA. This can be ascribed to the higher porosity of sample prepared in [Py<sub>1,4</sub>]TFSA compared with the sample prepared in [EMIm]TFSA.

The thermal behaviour of the synthesized  $\text{Co}_3\text{O}_4$  was investigated. Figure 6 shows the DTG curve of the  $\text{Co}_3\text{O}_4$  prepared in the ionic liquid [Py<sub>1,4</sub>]TFSA. The DTG was measured in the temperature range from  $25^\circ\text{C}$  to  $1000^\circ\text{C}$ . As shown in the thermogram of Fig. 6, four pronounced peaks were observed. The thermal process was recorded in the temperature range of  $25\text{--}150^\circ\text{C}$  which can be ascribed to the evaporation of the physically adsorbed water. The second process was observed in the temperature range  $200\text{--}350^\circ\text{C}$  that can be associated with the removal surface hydroxyl groups. The peak observed at about  $400^\circ\text{C}$  is attributed to the thermal decomposition of the ionic liquid residues trapped in the synthesized oxide. A pronounced loss in the weight was observed in the temperature range from  $700$  to  $950^\circ\text{C}$  resulting from the thermal decomposition of  $\text{Co}_3\text{O}_4$  into CoO [24, 25] according to the following equation:

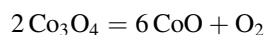


Figure 7 shows the differential thermal gravimetric analysis DTG of  $\text{Co}_3\text{O}_4$  synthesized from the ionic liquid [EMIm]TFSA. The sample of  $\text{Co}_3\text{O}_4$  prepared in the ionic liquid [EMIm]TFSA almost exhibits a similar thermal behaviour to that of the sample prepared in [Py<sub>1,4</sub>]TFSA. However, the peak of the thermal decomposition of  $\text{Co}_3\text{O}_4$  to CoO is not obvious as in the sample prepared in [Py<sub>1,4</sub>]



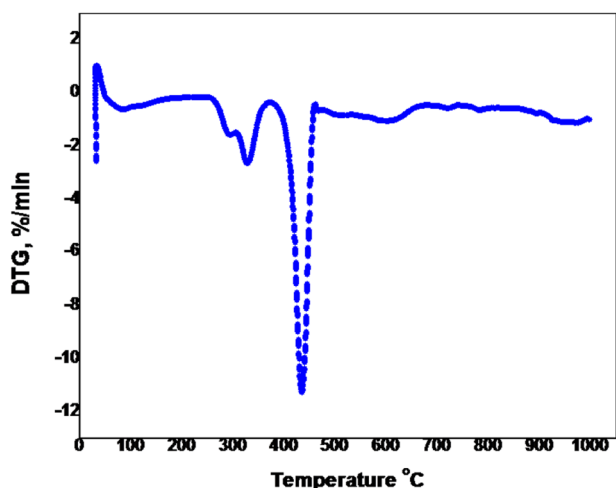


Fig. 7 Differential thermal gravimetric analysis of  $\text{Co}_3\text{O}_4$  synthesized from [EMIm]TFSA

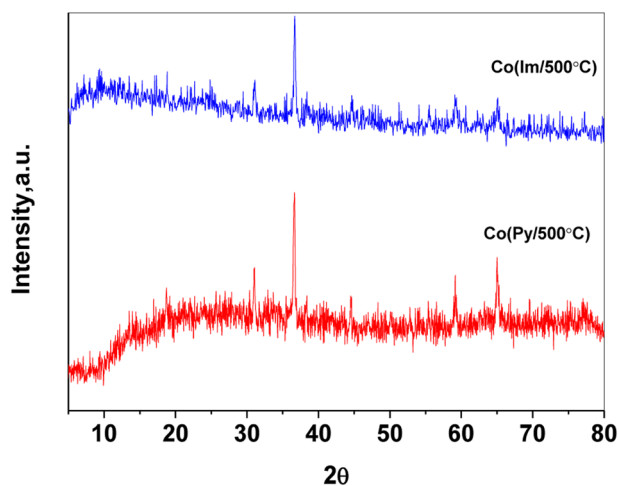


Fig. 8 XRD patterns of  $\text{Co}_3\text{O}_4$  synthesized from the ionic liquid [EMIm]TfO and [Py<sub>1,4</sub>]TfO, and calcined at 500 °C

TFSA. This might indicate the higher thermal stability of  $\text{Co}_3\text{O}_4$  prepared in [EMIm]TFSA. It was previously reported that the thermal stability of sol-gel synthesized metal oxides using ionic liquids can be significantly enhanced [11, 26]. The transformation of the anatase phase of  $\text{TiO}_2$ , synthesized in the ionic liquid [EMIm]TFSA, to rutile phase was occurred at higher temperatures [26]. Thus, the observed thermal stability of  $\text{Co}_3\text{O}_4$  synthesized in the ionic liquid [EMIm]TFSA is not surprising.

### 3.2 Synthesis of cobalt oxide from the ionic liquids [EMIm]TfO and [Py<sub>1,4</sub>]TfO

Cobalt oxide has been prepared in the ionic liquids [EMIm]TfO and [Py<sub>1,4</sub>]TfO via sol-gel methods. The synthesized oxide was characterized XRD and TEM. Figure 8 shows the XRD patterns of the synthesized cobalt oxide obtained in

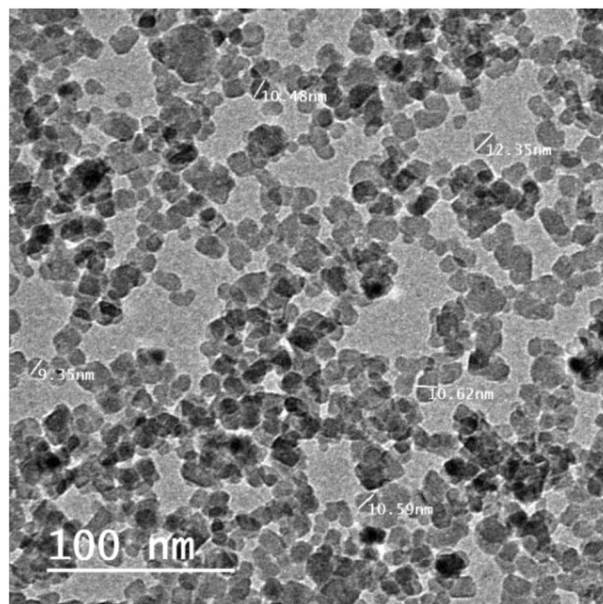


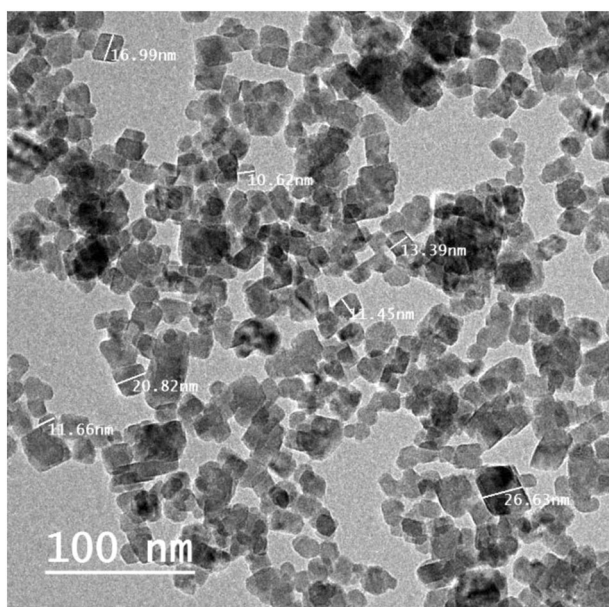
Fig. 9 TEM image of  $\text{Co}_3\text{O}_4$  prepared in the ionic liquid [EMIm]TfO and calcined at 500 °C

the two ionic liquids and calcined at 500 °C. The XRD patterns of the as-synthesized samples (not shown) showed amorphous behaviour. The crystallinity of the samples were improved after calcination at 500 °C, Fig. 8. The recorded diffraction peaks were assigned to the face centered cubic structure of the spinel tricobalt tetraoxide  $\text{Co}_3\text{O}_4$  (JCPDS No. 74-2120).

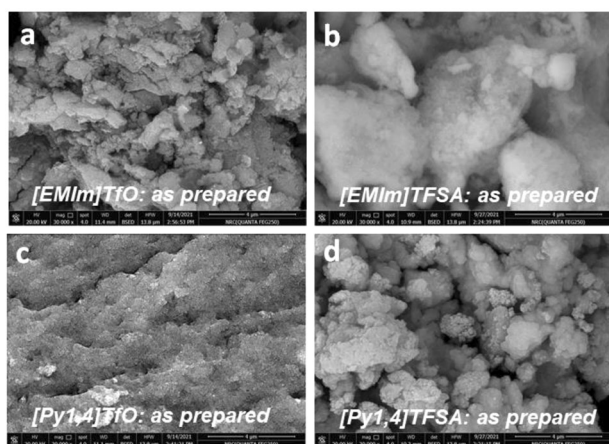
The  $\text{Co}_3\text{O}_4$  samples calcined at 500 °C were characterized by TEM to explore the morphology of the obtained oxide. The obtained oxide in both ionic liquids, [EMIm]TfO and [Py<sub>1,4</sub>]TfO shows a similar morphology as cubic nanoparticles with an average diameter of about 10 nm, in case of [EMIm]TfO, and 15 nm, in case of [Py<sub>1,4</sub>]TfO, were obtained, Figs. 9 and 10, respectively. The average diameter of the particle size of  $\text{Co}_3\text{O}_4$  obtained in the employed TfO-based ionic liquids is a bit lower than that of the particle size of  $\text{Co}_3\text{O}_4$  obtained in the TFSA-based ionic liquids. This reveals the influence of the TfO anion on reducing the particle size of the synthesized  $\text{Co}_3\text{O}_4$ . Furthermore, the shape of the particles of the synthesized  $\text{Co}_3\text{O}_4$  is not affected by the type of the ionic liquids.

### 3.3 Exploring the influence of the ionic liquids on the morphology of the synthesized oxides

The influence of the cations and anions of the ionic liquids on the morphology of the synthesized  $\text{Co}_3\text{O}_4$  nanoparticles was investigated. Four different ionic liquids, [EMIm]TFSA, [Py<sub>1,4</sub>]TFSA, [Py<sub>1,4</sub>]TfO and [EMIm]TfO, with two different anions and cations were employed in the synthesis of the oxides in order to explore the influence of anions and



**Fig. 10** TEM image of  $\text{Co}_3\text{O}_4$  prepared in the ionic liquid  $[\text{Py}_{1,4}]\text{TfO}$  and calcined at  $500^\circ\text{C}$

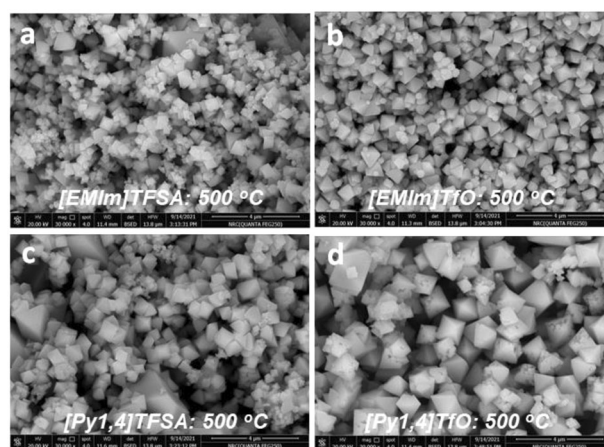


**Fig. 11** SEM images of as-synthesized cobalt oxide obtained from (a)  $[\text{EMIm}]\text{TfO}$ , (b)  $[\text{EMIm}]\text{TFSA}$ , (c)  $[\text{Py}_{1,4}]\text{TfO}$  and (d)  $[\text{Py}_{1,4}]\text{TFSA}$

cations on the synthesized oxides. Imidazolium and pyrrolidinium cations with trifluoromethylsulfonate and bis(trifluoromethylsulfonyl) amide anions were the ionic liquids constituents.

The four ionic liquids were employed in the sol gel synthesis of cobalt oxide. The morphology of the as-synthesized and calcined cobalt oxide was investigated to explore the influence of cation and anion of the ionic liquids on the particle shape. Figure 11 shows the SEM images of the as-synthesized cobalt oxide.

All SEM micrographs have the same magnification for better comparison. In all SEM images of the as-synthesized cobalt oxide, no well-defined, isolated particles are observed and only coarse particles aggregations are seen. The trapped



**Fig. 12** SEM images of sol-gel synthesized cobalt oxide, calcined at  $500^\circ\text{C}$  obtained from (a)  $[\text{EMIm}]\text{TFSA}$ , (b)  $[\text{EMIm}]\text{TfO}$ , (c)  $[\text{Py}_{1,4}]\text{TFSA}$  and (d)  $[\text{Py}_{1,4}]\text{TfO}$

ionic liquids in the powder, which could not be completely removed by washing, might conceal the particles. After getting rid of the ionic liquid residues on calcination, nanosized square pyramid-shaped  $\text{Co}_3\text{O}_4$  particles are clearly seen, Fig. 12. All  $\text{Co}_3\text{O}_4$  oxide samples prepared in the employed ionic liquids exhibit the same morphology but with different particle sizes. The samples prepared in imidazolium based ionic liquids show smaller particle sizes than those of the samples prepared in the pyrrolidinium based ionic liquids. This signifies the significant role of the cation of the ionic liquids on the size of the particles of the synthesized cobalt oxide. Imidazolium cations might be adsorbed on the growing nuclei preventing their further growth. The morphology of the synthesized  $\text{Co}_3\text{O}_4$  particles obtained from the TFSA-based ionic liquids is a bit similar to that of the synthesized  $\text{Co}_3\text{O}_4$  particles from TfO-based ionic liquids. This might indicate that the type of the anion or cation of the employed ionic liquid does not play a significant role on the shape of the synthesized  $\text{Co}_3\text{O}_4$  oxide particles.

## 4 Conclusion

Cobalt oxide was synthesized via sol-gel methods in the employed ionic liquids. Four different ionic liquids,  $[\text{EMIm}]\text{TFSA}$ ,  $[\text{Py}_{1,4}]\text{TFSA}$ ,  $[\text{Py}_{1,4}]\text{TfO}$  and  $[\text{EMIm}]\text{TfO}$ , with two different anions and cations were employed in the synthesis of the oxides in order to explore the influence of anions and cations on the synthesized oxides. The synthesized oxides were characterized by XRD, SEM, TEM, DTG and nitrogen gas sorption measurements. The results showed that the imidazolium cation plays a significant role in reducing the particle size of the synthesized oxides. The samples prepared in the imidazolium-based ionic liquids showed smaller particle sizes than those of the samples

prepared in the pyrrolidinium-based ionic liquids. The type of the anion or cation of the employed ionic liquids does not play a significant role on the shape of the synthesized  $\text{Co}_3\text{O}_4$  oxide particles.

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## Compliance with ethical standards

**Conflict of interest** The authors declare no competing interests.

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