



Elegant Explorations of Ionic Liquids in the Expeditious Synthesis of Fe₃O₄ Nanoparticles

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ABSTRACT

Ionic Liquids (ILs) are becoming an innovative and attractive synthesis medium for inorganic nano-materials, allowing more efficient, environmentally benign and sustainable preparation of high quality nano-materials. The present study explores the potentials of imidazolium ionic liquids as a stabilized reaction medium in the synthesis of metal oxide nanoparticles. Furthermore, a detail explanation regarding the methods of modifying surfaces with ILs of varying chain length for the formation of Fe₃O₄ nanoparticles have been addressed.

Keywords: Ionic Liquids (ILs), Metal oxide nanoparticles, Co-precipitation.

INTRODUCTION

Transition metal nanoparticles are critical for a wide range of potential applications in science and industry, including sensors and catalysts.¹⁻⁵ Several physical and chemical approaches were used to form metal oxide nanoparticles of Ru, Rh, Ir, Mn, Fe, Zn, Cu and Co.⁶⁻¹¹ Magnetite NPs, an important family of nanoparticles, has been extensively used as a catalyst,¹² adsorbent,¹³ and sensor.¹⁴ As a result, regulated synthesis, as well as the generation of stabilized metal nanoparticles, is critical.¹⁵ To develop new

methods an era of green synthesis approach is gaining great attention in upcoming research and development on materials science and technology. Ionic liquids (ILs) have been increasingly used and researched in recent years as reaction media, for catalysis,¹⁶ biocompatible protein stabilization,¹⁷ surfactant,¹⁸ environmentally friendly chemical processes,¹⁹ micro-extraction technique,²⁰ electrochemical non-enzymatic detection of sulfite in food samples,²¹ dye-sensitized solar cells,²² in biomedical and pharmaceutical applications²³ and so on. Furthermore because of their particular physical and chemical properties, they can be



used to synthesize nanoparticles²⁴ and to form colloidal nanocrystals (NCs).²⁵ Because their electrostatic stability, ILs have the potential to be used in the synthesis of inorganic nanomaterials²⁶ and nanoflakes.²⁷ Metal oxide nanoparticles are protected from electrostatic charge by the strong polarity, high dielectric constant, and supramolecular network of ionic liquids, according to the Derjaguin, Landau, Verwey and Overbeek (DLVO) theory. As a result, imidazolium ionic liquids ILs were utilized as an electrostatic stabilizer, reaction solvent and capping agent for various nano-materials to regulate their size or shape. Metal Nanoparticles (MNPs) in ILs were synthesized using various methods.²⁸⁻²⁹ ILs were employed to effectively control metal oxide nanoparticle shape, avoid inter-particle aggregation, and optimize particle production. The easiest and most efficient way to create metal oxide nanoparticles at the desired level is with Room-temperature ionic liquids (RTILs) assistance. Ionic liquids have the ability to stabilize metal oxide nanoparticles.^{30,31,32,33} According to Dupont *et al.*,³⁴ imidazolium cations present in ILs form a protective layer that stabilizes NP surfaces by providing steric and electronic protection against aggregation. Herein, we describe a smart and aptly developed incorporation of ILs (1-Propyl-3-methylimidazolium bromide [C3mim][Br], 1-Butyl-3-methylimidazolium bromide [C4mim][Br] and 1-Hexyl-3-methylimidazolium bromide [C6mim][Br]) and unconventional methods of synthesis offers additional value to be drawn from the broad matrix of available property combinations. These supramolecular liquids therefore facilitate new and rapid universal manufacturing techniques that provide solutions to the present complications associated with nano-manufacturing, and beyond that will open completely new horizons and possibilities for controlling the growth and assembly of nanostructures.

EXPERIMENTAL

Materials

1-methyl imidazole, 1-propyl bromide, 1-butyl bromide, 1-hexyl bromide purchased from Sigma Aldrich, FeSO₄·7H₂O, FeCl₃·6H₂O and NaOH purchased from Avra Chemicals. All chemicals and solvents were obtained from commercial sources and were used without further purification.

Methods

Fourier-transform infrared spectroscopy (FT-IR)

FT-IR spectrum of synthesized metal oxide NPs was observed by Perkin Elmer-Spectrum RX-IFTIR.

X-ray Diffractometer (XRD)

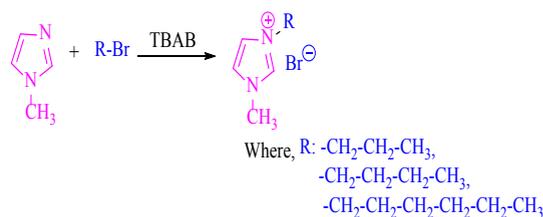
Crystallite diffraction peaks of synthesized metal NPs was observed by Powder X-ray Diffractometer (X'Pert Pro, PANalytical Netherlands).

Field Emission Scanning Electron (FE-SEM)

Morphology of the synthesized metal oxide NPs was studied by Field Emission Scanning Electron Microscope (SU 8010 Series, Hitachi, Japan).

Synthesis of imidazolium ionic liquids:

Through a water condenser, a stirred mixture of 1-methyl imidazole (30mmol, 2.46 g) and an alkyl halide (30mmol, (propyl bromide, 03.68 g), (butyl bromide, 4.1106 g), (hexyl bromide, 4.65 g)) was slowly added to the molten tetrabutylammonium bromide (TBAB). The reaction mass was extracted with ethylmethyl ketone (50 mLx5) after the reaction mixture had finished adding all the ingredients. The reaction mass quickly split into two immiscible phases after being added to. These phases were then separated using a separating funnel. In order to get tetrabutylammonium bromide for reusing, the ethylmethyl ketone was distilled off after the ionic liquid phase had been transported to a vacuum oven for drying.³⁵

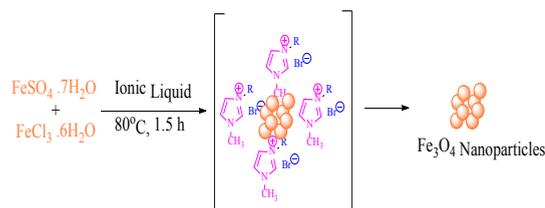


Scheme 1. Synthesis of 1-alkyl-3-methylimidazolium bromides

Synthesis of Magnetite (Fe₃O₄) nanoparticles using ionic liquid

The magnetite nanoparticles were prepared via the chemical co-precipitation method by the following 0.11 g of FeSO₄·7H₂O and 0.22 g of FeCl₃·6H₂O, with the molar ratio of ferric ion to ferrous ion in the solution of 2:1, were dissolved in 30 mL of deionized water. Then 4mmol IL and 1N NaOH were added to

the solution under vigorous stirring at 80°C. The solution color changed from yellow-orange to black rapidly. The magnetite nanoparticles were filtered and thoroughly washed with deionized water several times. Finally, Fe₃O₄ samples were dried in oven at 150°C for 2 hours.



Scheme 2. Synthesis of Fe₃O₄ nanoparticles using ionic liquid

RESULTS AND DISCUSSION

Our investigations began with the synthesis, characterization of ionic liquids, and iron oxide nano-particles using modern analytical characterization methods such as X-ray, scanning electron microscopy, and FT-IR. The results obtained for the characterization of the iron oxide nano-particles are discussed briefly in the following sections.

Optimization of reaction parameters

In this study, certain imidazolium ionic liquids were used in order to synthesize iron metal oxide nanoparticles.

The closure scrutiny of Table 1 reveals

Table 1: Optimization of reaction parameters

NPs	Entry	NaOH(M)	FeSO ₄ ·7H ₂ O(g)	FeCl ₃ ·6H ₂ O(g)	IL(mmol)	Temperature(°C)	Yield (g)	%Practical Yield	
Fe ₃ O ₄	1	1M	0.11	0.22	0	80	0.08	87.9	
	Without ILs								
	2	1M	0.11	0.22	1	80	0.072	79.1	
	3	1M	0.11	0.22	2	80	0.078	85.7	
	4	1M	0.11	0.22	4	80	0.081	89.0	
	5	1M	0.11	0.22	6	80	0.068	74.7	
	1-Propyl-3-methylimidazolium bromide [C3mim][Br]								
	6	1M	0.11	0.22	1	80	0.068	74.7	
	7	1M	0.11	0.22	2	80	0.0789	86.7	
	8	1M	0.11	0.22	4	80	0.089	97.8	
	9	1M	0.11	0.22	6	80	0.078	85.7	
	1-Butyl-3-methylimidazolium bromide [C4mim][Br]								
	10	1M	0.11	0.22	1	80	0.0659	72.4	
11	1M	0.11	0.22	2	80	0.072	79.1		
12	1M	0.11	0.22	4	80	0.0841	92.4		
13	1M	0.11	0.22	6	80	0.0831	91.3		

that the concentration of ionic liquid plays a subtle role in the synthesis of metal oxide nanoparticles. The experimental data in hand envisaged that the practical yield of the resulting nanoparticles is to be increased up to 4mmol concentration of IL but there is no significant impact after 4mmol was found. Therefore, 4mmol IL concentration is chosen for metal oxide nanoparticle synthesis.

In the next, effect of temperature on the magnitude of the reaction has been advanced by performing certain experiments and the experimental data is tabulated in Table 2. The data obtained manifests that 80°C is the most suitable condition of temperature to facilitate the synthesis of Fe₃O₄ NPs.

FT-IR analysis of Fe₃O₄ NPs

FT-IR spectroscopy was used to identify the NPs generated through Co-precipitation employing Fe²⁺/Fe³⁺ precursors in an ionic liquid. In Fig. 1(d) the major phase of the synthesized particles, magnetite, was validated at low frequencies by a prominent absorption band that was centered between 480 and 620 cm⁻¹, with the peak assigned to the vibration and torsional modes of the Fe-O bonds. Broad peaks in the spectrum that appeared around 1636 and 3474 cm⁻¹ were attributed, respectively, to H₂O's stretching and bending vibrations of the -OH bond. Due to the aliphatic C-H of the methylene in the ionic liquid, there are stretching vibrations at 2850-2920 cm⁻¹.³⁶⁻³⁷

Table 2: Effect of Temperature on the yield of the reaction

NPs	Entry	NaOH (M)	FeSO ₄ ·7H ₂ O (g)	FeCl ₃ ·6H ₂ O (g)	IL(mmol)	Temperature (°C)	Yield (g)	%Practical Yield	
Fe ₃ O ₄	Without ILs								
	1	1M	0.11	0.22	0	30	0.05	54.9	
	2	1M	0.11	0.22	0	40	0.052	57.1	
	3	1M	0.11	0.22	0	60	0.062	68.1	
	4	1M	0.11	0.22	0	80	0.08	87.9	
	5	1M	0.11	0.22	0	100	0.078	85.7	
	1-Propyl-3-methylimidazolium bromide [C3mim][Br]								
	6	1M	0.11	0.22	1	30	0.038	41.7	
	7	1M	0.11	0.22	1	40	0.057	62.6	
	8	1M	0.11	0.22	1	60	0.068	74.7	
	9	1M	0.11	0.22	1	80	0.072	79.1	
	10	1M	0.11	0.22	1	100	0.072	79.1	
	1-Butyl-3-methylimidazolium bromide [C4mim][Br]								
	11	1M	0.11	0.22	1	30	0.045	49.4	
	12	1M	0.11	0.22	1	40	0.052	57.1	
	13	1M	0.11	0.22	1	60	0.062	68.1	
	14	1M	0.11	0.22	1	80	0.068	74.7	
	15	1M	0.11	0.22	1	100	0.067	73.6	
	1-Hexyl-3-methylimidazolium bromide [C6mim][Br]								
	16	1M	0.11	0.22	1	30	0.043	47.2	
17	1M	0.11	0.22	1	40	0.049	53.8		
18	1M	0.11	0.22	1	60	0.052	57.1		
19	1M	0.11	0.22	1	80	0.0659	72.4		
20	1M	0.11	0.22	1	100	0.0659	72.4		

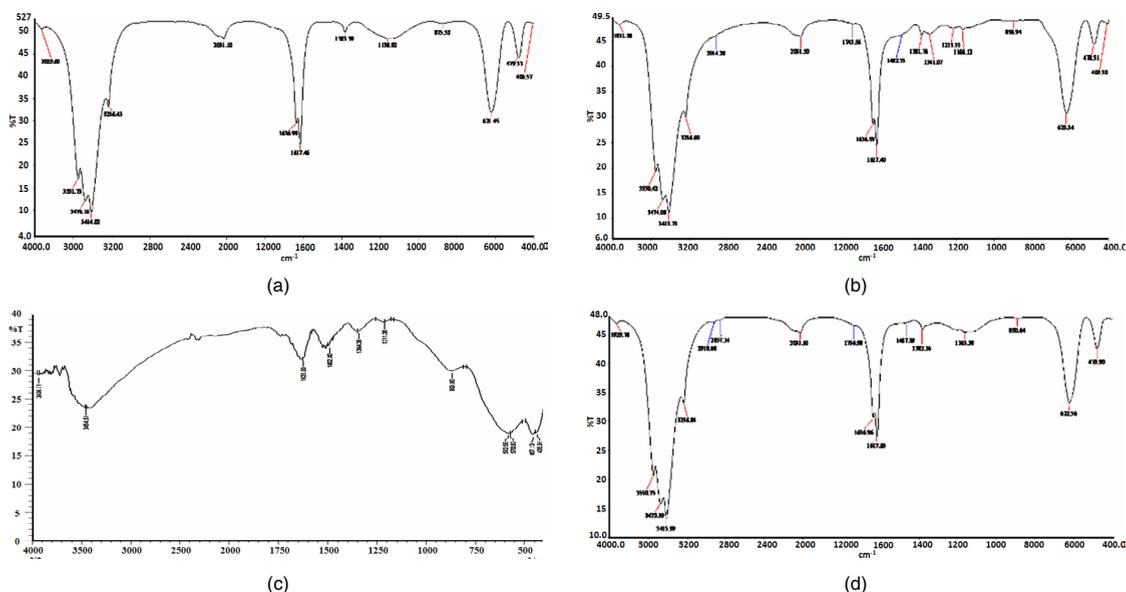


Fig. 1. FT-IR spectrum of Fe₃O₄ NPs, (a) Fe₃O₄ NPs synthesized without ionic liquid, (b) with [C3mim][Br] ionic liquid, (c) with [C4mim][Br] ionic liquid and (d) with [C6mim][Br] ionic liquid

XRD analysis of Fe₃O₄ NPs

The crystalline structure of the produced Fe₃O₄ NPs has been confirmed by the XRD investigation. Diffraction peaks at 30.49, 35.85, 43.52, 57.45, and 63.07 were matched to 220, 311, 400, 422, 511 and 440 planes respectively,

in the Fe₃O₄ XRD pattern shown in Fig. 2 [Fig.b] The JCPDS Card 01-071-6336 (Joint Committee on Powder Diffraction Standards) and the diffraction peaks are in good agreement, which amply demonstrates that the produced Fe₃O₄ NPs are crystalline in nature.³⁸The Debye

Scherrer equation was used to get the average crystallite size.

$$D = K\lambda/\beta \cos\theta$$

Where, D is average particle size (nm),

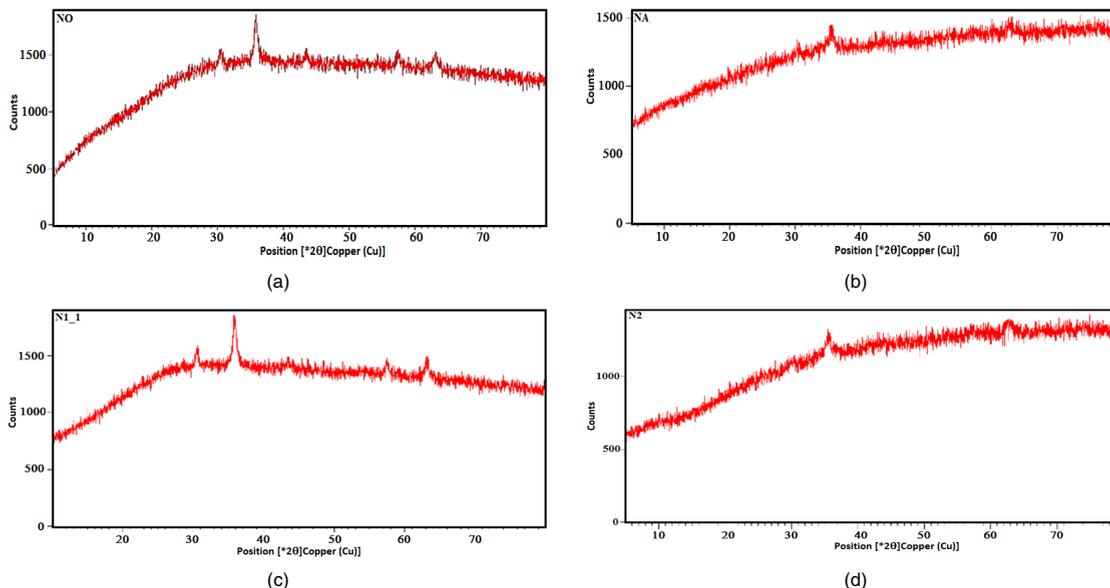


Fig. 2. XRD spectrum of Fe_3O_4 NPs, (a) Fe_3O_4 NPs synthesized without ionic liquid, (b) with [C3mim][Br] ionic liquid, (c) with [C4mim][Br] ionic liquid, (d) with [C6mim][Br] ionic liquid

Morphology of Fe_3O_4 nanoparticles

Figure 3 shows SEM pictures of metal oxide nanoparticles made with various imidazolium ionic solutions. Fe_3O_4 nanoparticles are all sphere-like formations, as can be seen. While Fe_3O_4 nanoparticles prepared with imidazolium ionic liquid exhibit very moderate dispersion (Fig. 3b, 3c, and 3d), those prepared without ionic liquid exhibit significant agglomeration (Fig. 3a). Therefore, [C6mim][Br], one of the three imidazolium ionic liquids used in the study, could offer both steric and electrostatic stability. It reduces the possibility of close particle interactions producing big particle sizes.³⁹

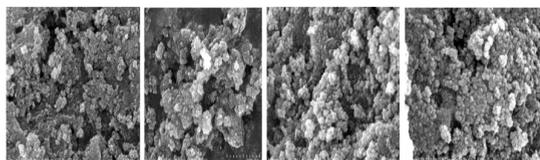


Fig. 3. FE-SEM images of Fe_3O_4 nanoparticles

K is constant as equal to 0.94, is wavelength of X-ray radiation. β is full-width at half maximum (FWHM) of peak in radians and θ is diffraction angle (degree). The calculated average crystallite size of green synthesized Fe_3O_4 NPs is found to be in the range of 11-13nm.

CONCLUSION

In conclusion, we have shown a simple and efficient co-precipitation technique for the one step production of Fe_3O_4 NPs utilizing imidazolium ionic liquid. Our findings show that employing ionic liquid during synthesis resulted in lower particle sizes than doing so without.

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Conflict of Interest

The authors declare that there is no conflict of interest related to this article.

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