RSC Advances

Hydrophilic Ionic Liquid Assisted Hydrothermal Synthesis of ZnO Nanostructures with Controllable Morphology

Mousumi Akter,[a] Md. Arif Faisal,[a] Ajaya Kumar Singh, [b] and Md. Abu Bin Hasan Susan[a,c]*

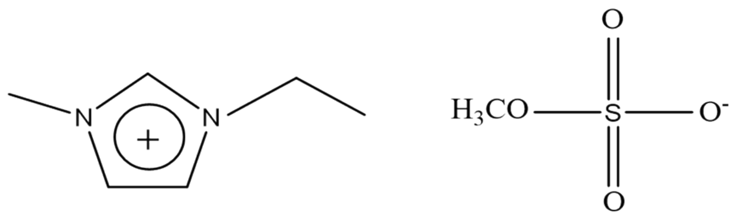
[a]*Department of Chemistry, University of Dhaka, Dhaka 1000, Bangladesh*

[b]*Department of Chemistry, Govt. V. Y. T. PG. Autonomous, College, Durg, Chhattisgarh, 491001, India*

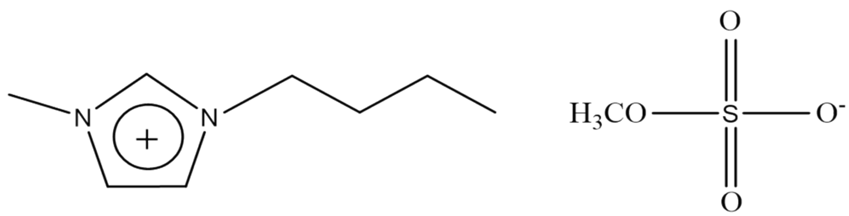
[c]*Dhaka University Nanotechnology Center (DUNC), University of Dhaka, Dhaka 1000, Bangladesh*

†Electronic supplementary information (ESI)

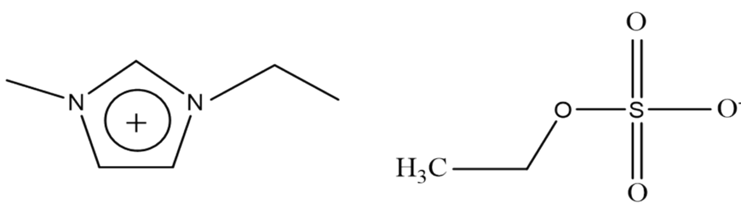
Structure of ILs



1-ethyl-3-methylimidazolium methylsulfate, ($[C_2mim]CH_3SO_4$)



1-butyl-3-methylimidazolium methylsulfate, ($[C_4mim]CH_3SO_4$)



1-ethyl-3-methylimidazolium ethylsulfate, ($[C_2mim]C_2H_5SO_4$)

Fig. S1 Structure of hydrophilic ILs

FTIR spectral analysis

FT-IR spectrum of the synthesized ZnO NPs shows stretching vibration mode of Zn-O band at 456 cm^{-1}. The absorption peak in the range of 3200-3600 cm^{-1} corresponds to the stretching vibration of intermolecular hydrogen bond (O-H) observed due to absorbed surface water molecules in the sample. The intensity of this band diminishes with increasing temperature as the moisture evaporates from the surface of ZnO along with the rising temperature. The stretching modes of vibrations in asymmetric >C=O bond is observed at 1454 cm^{-1} due to the residue of zinc acetate present in the reaction media. Moreover, the absorption band in 700-1100 cm^{-1} is due to the lattice vibration of CO_3^{2-} in the sample. The two weak bonds at 2842 cm^{-1} and 2918 cm^{-1} are observed due to stretching vibration of C-H bond.

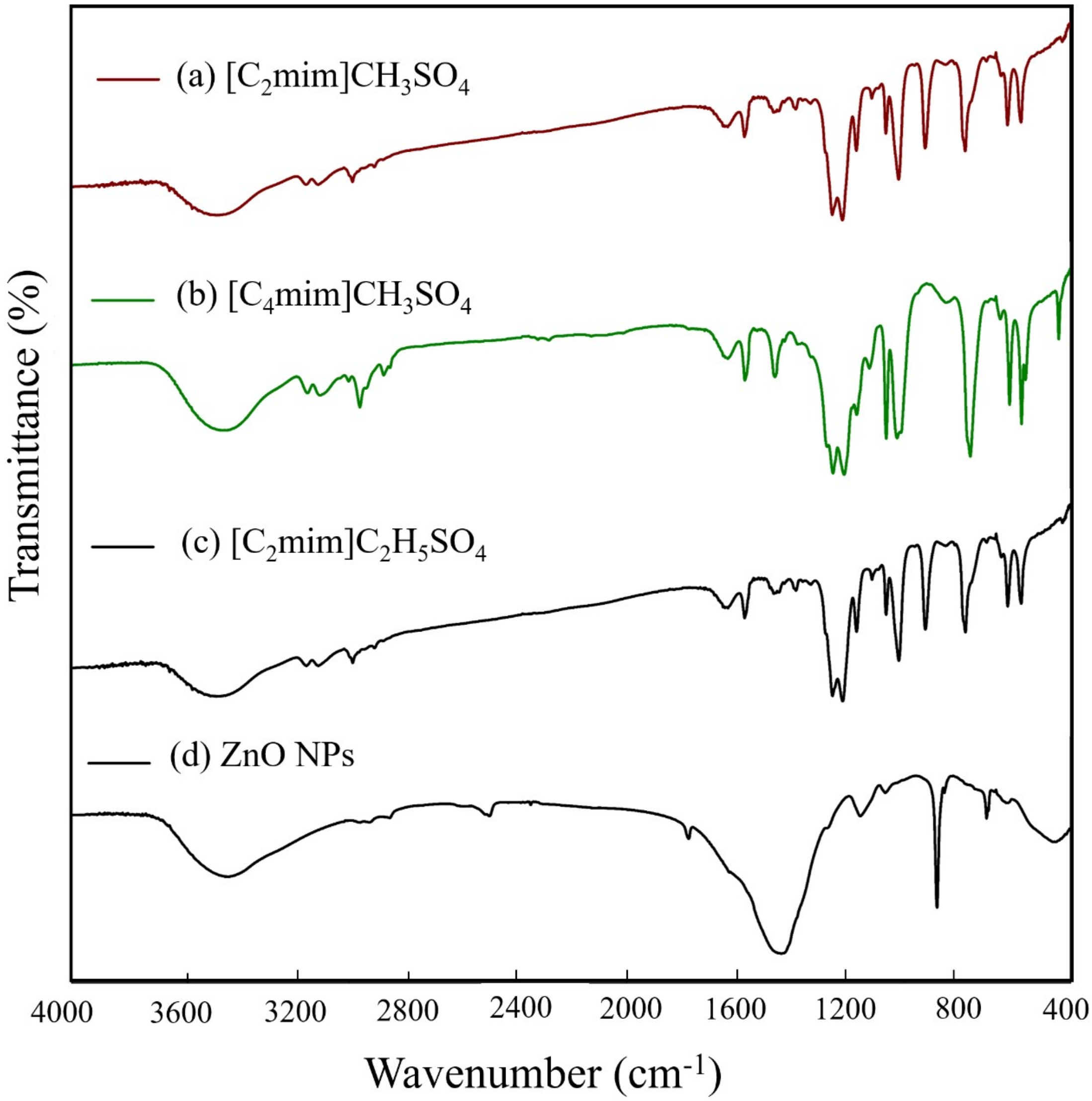


Fig. S2 FTIR spectra of ZnO NPs synthesized in presence of (a) $[C_2mim]CH_3SO_4$, (b) $[C_4mim]CH_3SO_4$, (c) $[C_2mim]C_2H_5SO_4$, and (d) no IL.

The strong absorption band in the range of 1050-1217 cm^{-1}, is observed due to the stretching mode of vibration in >C-N bond. The weak absorption band at 1645 cm^{-1}, is caused by the stretching vibration of >C=N bond in the IL. The assignments of the bands are consistent with the literature.[1] These suggest the presence of ILs adsorbed in the ZnO surface as well as confirmation of distinct products with a certain IL.

XRD pattern

The ZnO-NPs crystallite size (D) was calculated from the highest intense peak (101) using the Debye–Scherrer equation (Table S1).

$$D = \frac{k\lambda}{\beta \cos\theta}$$

where, k is the proportionality constant (k = 0.9); λ is the X-ray wavelength coming from Cu-Kα; β is the FWHM of the diffraction peak in radians; θ is the Braggs' angle in degrees.

Table S1 The average crystallite size of ZnO nanostructures using different ILs as templates.

Template	***Crystallite size (nm)***
Without IL	29.43
$[C_2mim]CH_3SO_4$	25.86
$[C_2mim]C_2H_5SO_4$	28.20
$[C_4mim]CH_3SO_4$	23.08

Table S2 The relative intensities of first three peaks in XRD pattern.

Template	***I/I$_o$ (%)*** *(where I$_o$ is for (101))*		***(100)/(002)***
	(100)	***(002)***	
Without IL	59.72	43.16	1.384
$[C_2mim]CH_3SO_4$	61.42	63.79	0.963
$[C_4mim]CH_3SO_4$	59.22	59.31	0.998
$[C_2mim]C_2H_5SO_4$	59.16	57.46	1.029

Analysis of band gap energy

Kubelka-Munk method: The value of the optical band gap, E_g can be determined using the fundamental absorption, which corresponds to electron excitation from the valance band to the conduction band.

The E_g of samples has been determined by the following relation:

$$\alpha h\nu = A(h\nu - E_g)^n$$

where, A is an energy-independent constant and E_g is the optical band gap, The n value for the specific transition can be experimentally determined from the best linear fit in the absorption spectra using the different equations. The optical band gap of the NPs was determined from the plots of $(F(R)h\nu/t)^2$ as a function of photo energy $h\nu$. Extrapolating the linear portions of these plots to the x axis (photon energy) *i.e.* $h\nu = 0$, values of the E_g is obtained for NPs.[2-4]

Table S3 Band gap energy of ZnO NPs synthesized using different templates.

Template	*Band gap energy,* E_g *(eV)*
Without IL	3.17
0.5% $[C_2mim]CH_3SO_4$	2.63
1.0% $[C_2mim]CH_3SO_4$	2.90
1.0% $[C_2mim]C_2H_5SO_4$	3.05
2.5% $[C_2mim]C_2H_5SO_4$	3.00
1.0% $[C_4mim]CH_3SO_4$	2.97
2.5% $[C_4mim]CH_3SO_4$	3.20

Notes and references

1 G. Xiong, U. Pal, J. G. Serrano, K. B. Ucer, and R. T. Williams, *Phys. Status. Solidi*, 2006, **3**(10), 3577–3581.

2 R. López and R. Gómez, *J. Sol-Gel Sci. Technol*. 2012, **61**, 1–7.

3 P. Kubelka and F. Munk, *Z. Tech. Phys.*, 1931, **12**, 593-601.

4 P. Kubelka, *J. Opt. Soc. Am*., 1948, **38** ,448-457.