Sustainable Preparation of Sun-light Active α-Fe$_2$O$_3$ Nanoparticles using Iron containing Ionic Liquids for Photocatalytic Applications

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Supporting Information

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Annexure S1: Synthesis of ILs, [Cₙmim][Cl]

Synthesis of ILs, [Cₙmim][Cl] (n = 4, 8 and 16) was done using method reported in literature with slight modifications. The synthesized ILs have been characterised using ¹H-NMR spectroscopy. The characterization data for ILs is provided as Annexure S1 and Figure S1-S3 (Supporting Information). ¹H-NMR spectra were recorded on Bruker Ascend 400 spectrometer (AVANCE III HD console) using CDCl₃ as solvent.

Synthesis of iron containing ionic liquids (MILs)

Iron (metal) containing MILs were synthesized using the method reported in literature with slight modification. Equimolar amount of [Cₙmim][Cl] (n = 4, 8 and 16) with FeCl₃·6H₂O were stirred in round bottom flask for 4-5 hours using dichloromethane as solvent at room temperature. The product is dried using sodium sulphate while the solvent was evaporated through rotary evaporator resulting in a formation of [Cₙmim][FeCl₄] (n = 4, 8 and 16). The obtained MILs were washed twice with diethyl ether and distilled water followed by vacuum drying at 80°C for 24 h for removal of moisture. The synthesized MILs shows characteristic peaks of [FeCl₄]⁻ in Raman and UV-visible spectra, (Figure S4 and S5, Supporting Information, respectively), confirming the formation of [Cₙmim][FeCl₄].

Characterization of [Cₙmim][Cl] ILs

¹H NMR and mass spectroscopy data for synthesized ILs:

[C₄mim][Cl]: ¹H NMR (400 MHz, CDCl₃, δ-ppm) 0.876 (t, 3H, CH₃), 1.245 ( m, 2H, (-CH₂-CH₃)), 1.903 (q, 2H, (N⁺-CH₂-CH₂⁻)), 4.132 (s, 3H, N-CH₃), 4.316 (t, 3H, N⁺-C₂H₅-CH₂⁻), 7.290 (d, 1H, N-CH-CH-N⁺), 7.416 (d, 1H, N-CH-CH-N⁺), 10.67 (s, 1H, N-CH-CH-N⁺).

[C₈mim][Cl]: ¹H NMR (400 MHz, CDCl₃, δ-ppm) 0.872 (t, 3H, CH₃), 1.288 ( br m, 2H, (-CH₂-CH₃)), 1.904 (q, 2H, (N⁺-CH₂-CH₂⁻)), 4.129 (s, 3H, N-CH₃), 4.318 (t, 3H, N⁺-CH₂-CH₂⁻), 7.332 (d, 1H, N-CH-CH-N⁺), 7.477 (d, 1H, N-CH-CH-N⁺), 10.55 (s, 1H, N-CH-N⁺).
[C_{16}mim][Cl]: $^1$H NMR (400 MHz, CDCl$_3$, δ-ppm) 0.879 (t, 3H, CH$_3$), 1.245 ( br m, 2H, (-CH$_2$-CH$_3$)), 1.903 (q, 2H, (N$^+$-CH$_2$-CH$_2$-)), 4.132 (s, 3H, N-CH$_3$), 4.316 (t, 3H, N$^+$-CH$_2$-CH$_2$-), 7.290 (d, 1H, N-CH-CH-N$^+$), 7.416 (d, 1H, N-CH-CH-N$^+$), 10.67 (s, 1H, N-CH-N$^+$).

**Figure S1:** $^1$H NMR spectra of [C$_4$mim][Cl].

**Figure S2:** $^1$H NMR spectra of [C$_8$mim][Cl].
Figure S3: $^1$H NMR spectra of [C$_{16}$mim][Cl].
Figure S4: Raman spectra of [C\textsubscript{16}mim][FeCl\textsubscript{4}] as representative, showing the three characteristic peaks at 112, 333 and 390 cm\textsuperscript{-1}, which is in accordance with the literature reports.\textsuperscript{4}

Figure S5: Absorbance spectra [C\textsubscript{16}mim][FeCl\textsubscript{4}] as representative, showing the characteristic peaks 247 and 366 nm, which is in accordance with the literature reports.\textsuperscript{5}
Figure S6: FT-IR spectra of MIL and synthesized $\alpha$-Fe$_2$O$_3$, after removal of MIL, have no absorption peak corresponding to MIL, indicating complete removal of MIL after washing.

Figure S7: Energy dispersive X-ray spectroscopy (EDAX) spectra of prepared $\alpha$-Fe$_2$O$_3$ NPs.
Figure S8: Tauc plot to measure (A) direct band gap and (B) indirect band gap of synthesised α-Fe$_2$O$_3$ NPs.

Figure S9: Mössbauer spectra of (A) α-Fe-4; and (B) α-Fe-8.
Table S1: Characteristic parameters of synthesized α-Fe₂O₃ NPs calculated from XRD, UV-Visible and TEM measurements.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\theta$</th>
<th>$d_{104}$ / Å</th>
<th>$\beta$ / Å</th>
<th>$D^a$ / nm</th>
<th>Band gap$^c$ / eV</th>
<th>Band gap$^d$ / eV</th>
<th>$D^b$ / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Fe-4</td>
<td>33.40</td>
<td>2.679</td>
<td>3.8×10⁻³</td>
<td>40.0</td>
<td>2.12</td>
<td>1.42</td>
<td>95.5</td>
</tr>
<tr>
<td>α-Fe-8</td>
<td>33.30</td>
<td>2.687</td>
<td>4.4×10⁻³</td>
<td>34.4</td>
<td>2.10</td>
<td>1.61</td>
<td>44.5</td>
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<tr>
<td>α-Fe-16</td>
<td>33.28</td>
<td>2.689</td>
<td>4.6×10⁻³</td>
<td>32.1</td>
<td>2.25</td>
<td>1.86</td>
<td>35.5</td>
</tr>
</tbody>
</table>

$\theta$ is the X-ray diffraction angle, $d_{104}$ is the interplaner distance for (104) plane, $\beta$ is the half-line width, $D^a$ and $D^b$ are the crystallite sizes obtained from XRD and TEM measurements respectively, $c$ and $d$ refer to direct and indirect band gap, respectively.
Table S2: Mössbauer parameters of α-Fe₂O₃ NPs obtained from Mössbauer spectra recorded at room temperature

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Iron Sites</th>
<th>(H_{hf}) / Tesla</th>
<th>(\Delta) / mm/s</th>
<th>(\delta) / mm/s</th>
<th>Relative area (R_A) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Fe-4</td>
<td>Sextet</td>
<td>51.63</td>
<td>-0.219</td>
<td>0.30</td>
<td>98.04</td>
</tr>
<tr>
<td></td>
<td>Doublet</td>
<td>–</td>
<td>0.859</td>
<td>0.42</td>
<td>1.96</td>
</tr>
<tr>
<td>α-Fe-8</td>
<td>Sextet</td>
<td>51.59</td>
<td>-0.217</td>
<td>0.36</td>
<td>98.7</td>
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<tr>
<td></td>
<td>Doublet</td>
<td>–</td>
<td>0.539</td>
<td>0.31</td>
<td>1.3</td>
</tr>
<tr>
<td>α-Fe-16</td>
<td>Sextet</td>
<td>51.47</td>
<td>-0.219</td>
<td>0.35</td>
<td>99.6</td>
</tr>
<tr>
<td></td>
<td>Doublet</td>
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<td>0.275</td>
<td>0.20</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Standard error in \(H_{hf}, \Delta\) and \(\delta\) is ±0.002, ±0.006 and ±0.003, respectively

References