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Tuning Morphology and Electrocatalytic Activity of Cobalt Ferrite Magnetic Nanoparticles Using Ionic Liquids and Double Salt Ionic Liquids as Soft Templates

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Extended Abstract

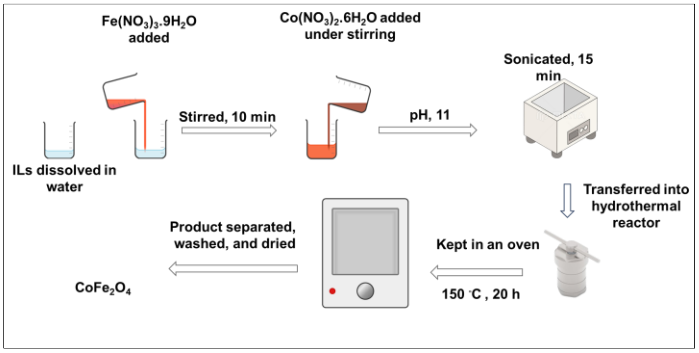

Figure 1: Hydrothermal synthesis of $CoFe_2O_4$.

A bottom-up strategy following a template-based approach to synthesize $CoFe_2O_4$ nanoparticles (NPs) has been a better way to obtain control over morphology and electrocatalytic activity [1]. Ionic liquids (ILs), can control morphologies and be utilized as a soft template to prepare $CoFe_2O_4$ NPs. Ghaemi et al. used octyl-4-aza-1-azoniabicyclo [2.2.2]octane bromide ([C_8dabco]Br) as a template to synthesize different shapes of $CoFe_2O_4$ by varying IL:Fe:Co ratios. ILs affect the resulting morphology and magnetic behavior by controlling the distribution of Co^{2+} cation in octahedral and tetrahedral sites [2]. $CoFe_2O_4$ magnetic NPs are known as efficient oxygen evolution reaction (OER) catalysts due to their improved catalytic activity and durability during electrochemical water splitting under alkaline conditions.

In this study, using a hydrothermal method, as shown in Fig. 1, magnetic $CoFe_2O_4$ NPs were synthesized from cobalt(II) nitrate hexahydrate and iron(III) nitrate nonahydrate. Two imidazolium-based ILs such as 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([C_2mim]CF_3SO_3) and 1-ethyl-3-methylimidazolium methanesulfonate ([C_2mim]CH_3SO_3), having common cation but different anions, were utilized as soft templates. Efforts have been made to identify the mechanism by which the presence of either F or H atoms in the structure of two anions impacts the resulting morphology of $CoFe_2O_4$. Further optimization of the morphology and therefore, the magnetic, optical, and electrocatalytic properties has also been achieved through the use of the double salt ionic liquids (DSILs) [C_2mim]$(CH_3SO_3)_x(CF_3SO_3)_{1-x}$ with different mole ratios.

Using energy dispersive X-ray (EDX) and Fourier transform infrared (FTIR) spectroscopy methods, the successful synthesis of $CoFe_2O_4$ NPs was verified. Fig. 2 shows, the shape of $CoFe_2O_4$ synthesized using [C_2mim]CF_3SO_3 varies from nanospheres to truncated cubic as the concentration of IL changes. $[C_2mim]CH_3SO_3$ exhibits nanospheres and nanocubes with smoother surfaces. DSILs show nanospheres with narrower size distribution throughout the mole ratios. $[C_2mim](CH_3SO_3)_{0.3}(CF_3SO_3)_{0.7}$ yields smaller NPs, with an average particle size of 13 nm. Whereas, when synthesized without ILs, $CoFe_2O_4$ had a particle size of 84 nm. In contrast, smaller NPs with sizes of 19 and 16 nm were obtained for 0.30 M $[C_2mim]CF_3SO_3$ and $[C_2mim]CH_3SO_3$, respectively. This difference was seen as a result of their varying degrees of interaction with NPs. It was accomplished by restricting the growth of particles through the attachment of ILs to the surface of $CoFe_2O_4$ as shown in Fig. 3. Furthermore, different levels of IL concentration exhibit differences in the size of crystallites, which in turn impacts the observed magnetic, optical, and electrocatalytic activities. ILs also play a crucial role in regulating the distribution of cations between tetrahedral and octahedral sites. $[C_2mim]CF_3SO_3$ has a stronger affinity for Fe^{3+} compared to Co^{2+} due to the interaction between the Fe^{3+} ion and the $CF_3SO_3^-$ anion, which contains F. For example, 0.17 M $[C_2mim]CF_3SO_3$ produced $CoFe_2O_4$ with the highest coercivity (H_c) value of 1021 Oe. It also demonstrated the highest remanence (M_r) value of 28 emu g^{-1}, indicating a substantial saturation magnetization (M_s) value of 72 emu g^{-1}. All materials synthesized using $[C_2mim]CH_3SO_3$ show lower magnetic properties. This occurs due to the octahedral site's lower particle size and fewer Fe^{3+}.

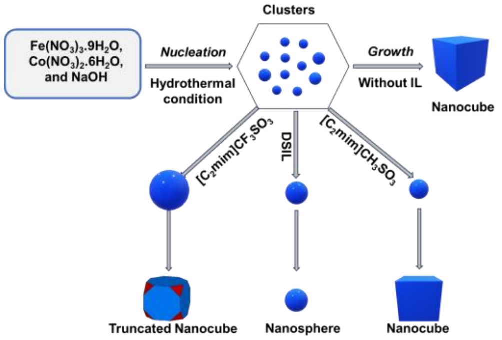

Figure 2: Schematic representation of various shapes of $CoFe_2O_4$ obtained with the variation of ILs.

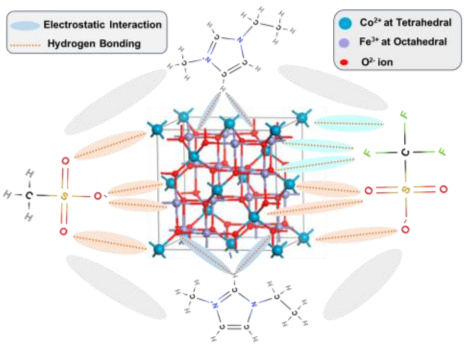

Figure 3: Schematic illustration of probable interaction of DSILs with $CoFe_2O_4$ in controlling morphology.

$CoFe_2O_4$ synthesized in DSILs displays a combination of high and low magnetic properties, showcasing its significant potential in optimizing magnetic properties for specific applications. The optical band gap energy exhibited a range of variation between 2.00 and 2.06 eV. $CoFe_2O_4$ synthesized using 0.45 M of $[C_2mim]CH_3SO_3$, owing to the improved magnetic properties, exhibits improved activity in the OER, which is demonstrated by a low onset overpotential of only 281 mV and a Tafel slope of 99 mV dec^{-1}. These show that ILs and DSILs can tune the structure of $CoFe_2O_4$ to produce optimized nanostructures and magnetic properties, which can enhance the OER activity.

References

[1].Huang Y, Yang W, Yu Y, Hao S, Ordered Mesoporous Spinel $CoFe_2O_4$ ss Efficient Electrocatalyst for the Oxygen Evolution Reaction, Journal of Electroanalytical Chemistry, 840:409-14, 2019.

[2].Ghaemi A, Mohave F, Farhadi A, Takassi MA, Tavakkoli H, Hydrothermal Synthesis of Mesoporous Cobalt Ferrite by Ionic Liquid-Assisted Process; Catalytic Performance, Morphology, and Magnetic Studies, Journal of the Australian Ceramic Society, 57:1321-30, 2021.