

Supplemental Material

Green asymmetric synthesis of binol *via* oxidative cross-coupling in the presence of L-cysteine@Fe₃O₄ nanoparticles

Akram Ashouri*, Behzad Nasiri, Somayeh Pourian, Hazhir Moghaddami Fard#, Omid Mohammadi#, Arezu Moradi#

Equal contribution (in alphabetic order)

Department of Chemistry, Faculty of Science, University of Kurdistan, 66177-15175, Sanandaj, Iran.

Email: a.ashouri@uok.ac.ir

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1. Characterization of the L-cysteine@Fe₃O₄

1.1. FT-IR spectrum

The FT-IR analyses were conducted to confirm the presence of L-cysteine on Fe₃O₄ after immobilization. In Figure 1, a broad absorption around 3400 cm⁻¹ confirms the presence of the -NH and -OH functional groups in the L-cysteine@Fe₃O₄ nanoparticles. Two peaks observed at 1623 and 1184 cm⁻¹ indicate the stretching vibrations of COO⁻ groups. A very weak absorption at 1290 cm⁻¹ is attributed to the C-N stretching. The disappearance of the S-H group absorption at 2555 cm⁻¹ in the spectra of L-cysteine@Fe₃O₄ nanoparticles suggests the attachment of L-cysteine molecules to the Fe₃O₄ magnetic nanoparticles occurs via the S-H group, forming a covalent Fe-S bond on the Fe₃O₄ substrate (586 cm⁻¹)¹.

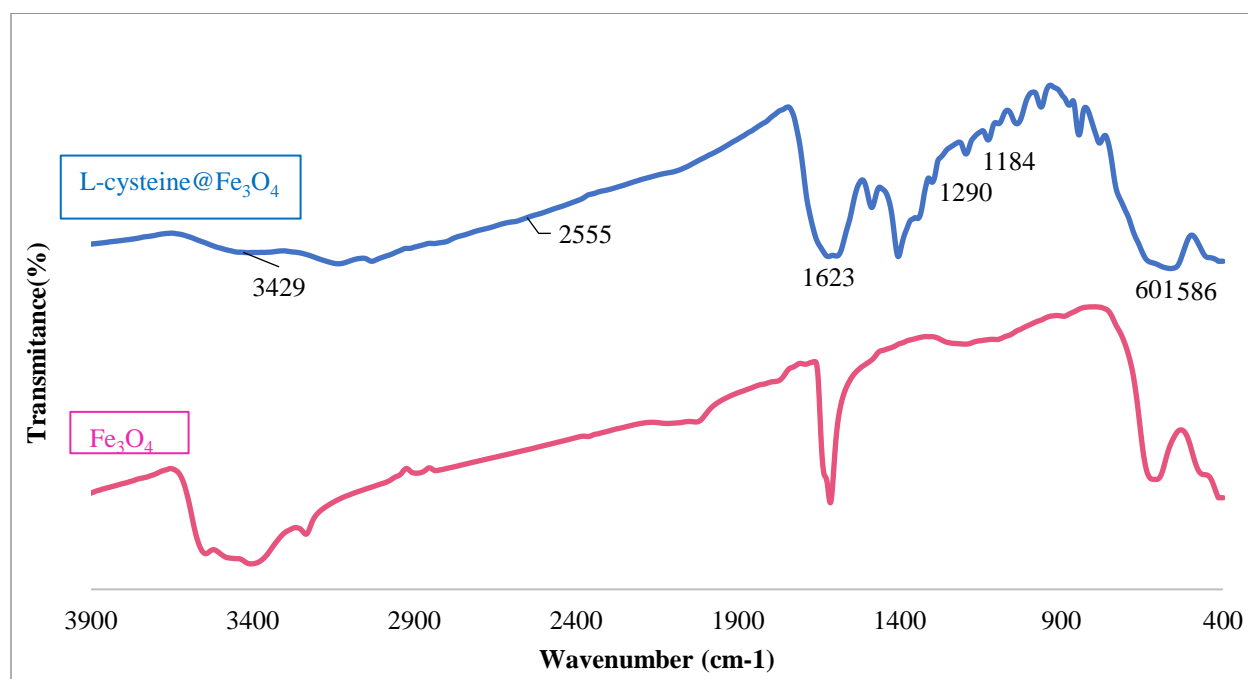


Figure 1. FT-IR spectrum of Fe₃O₄ and L-cysteine@Fe₃O₄ nano catalyst

1.2. EDAX spectrum

In the next step, to confirm the elements present in L-cysteine@Fe₃O₄ nanoparticles, the EDAX spectrum was examined, indicating the presence of carbon, oxygen, nitrogen, iron, and sulfur.

This was also confirmed by the elemental map (Figure 2) ².

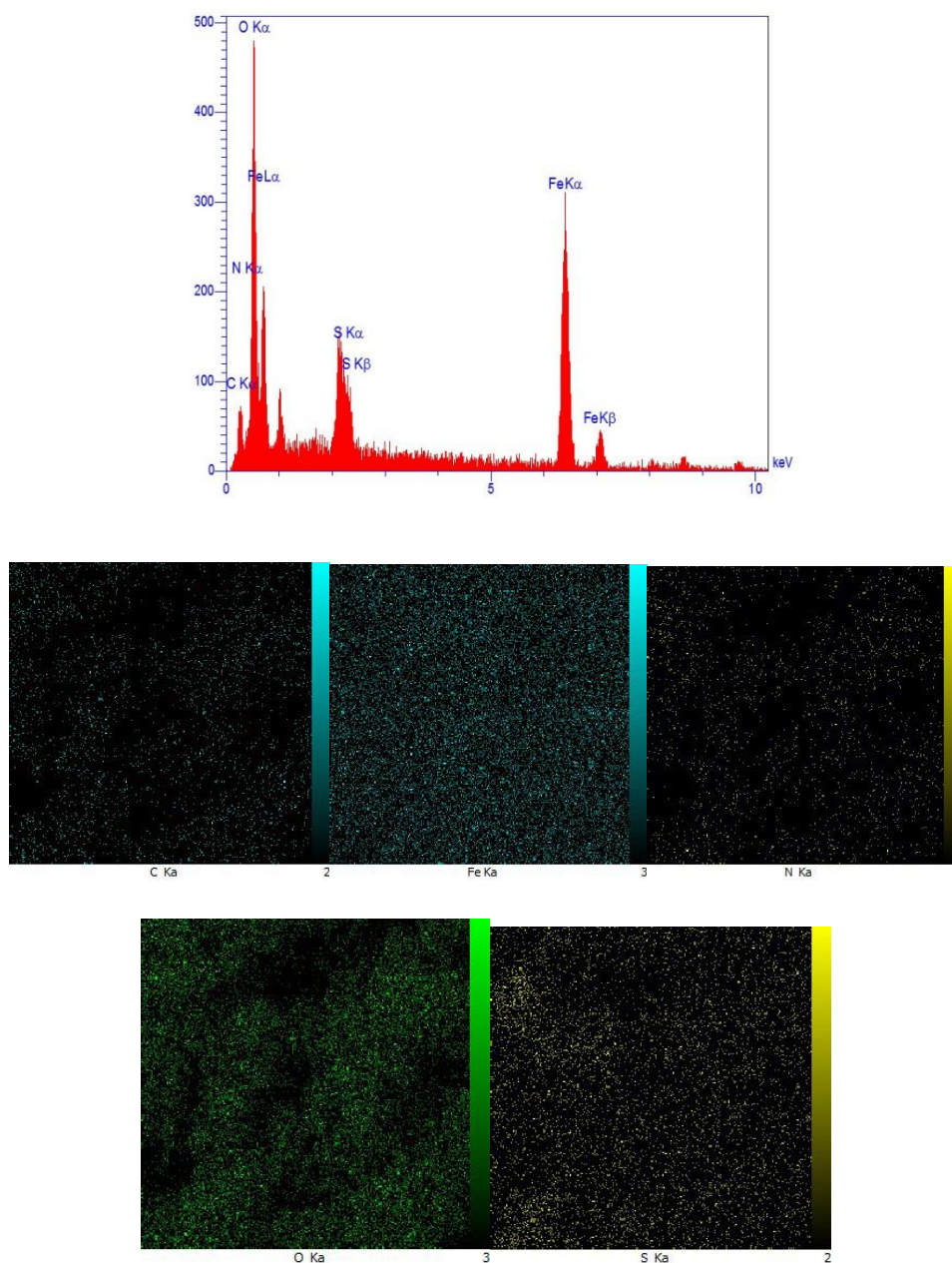


Figure 2. EDAX spectrum of L-cysteine@Fe₃O₄ nanoparticles

1.3. SEM images

The morphology of Fe_3O_4 and L-cysteine@ Fe_3O_4 magnetic nanoparticles was investigated by SEM technique (Figure 3a and 4b). Based on the images, the spherical and uniform dispersion of magnetic nanoparticles in three dimensions is observed. When L-cysteine is deposited onto the Fe_3O_4 nanoparticles, the morphology does not change significantly but is more aggregated.

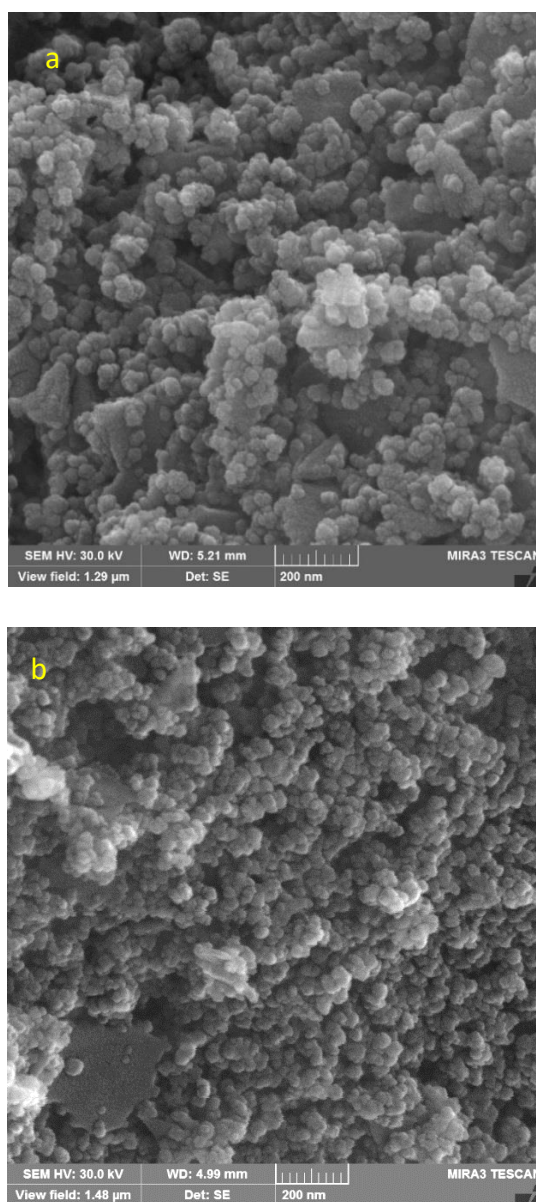


Figure 3. SEM image of synthesized (a) Fe_3O_4 and (b)L-cysteine@ Fe_3O_4 nanoparticles

1.4. XRD spectrum

The XRD technique was used to identify the crystal properties, phase, and size of synthesized L-cysteine@Fe₃O₄ nanoparticles. According to Figure 5, diffraction peaks at 2θ values of 30.4°, 35.7°, 43.3°, 54.8°, 57.5°, and 62.8° corresponded to crystal planes (220), (311), (400), (422), (511), and (440), which are attributed to the structure of Fe₃O₄. This aligns with the reported pattern for Fe₃O₄ nanoparticles (JCPDS No. 79-0418)³, indicating that the surface coating of magnetite with L-cysteine did not alter its composition after the grafting of L-cysteine. The calculated crystalline size from the Scherrer equation is about 22.8 nm for L-cysteine@Fe₃O₄ (Figure 4)².

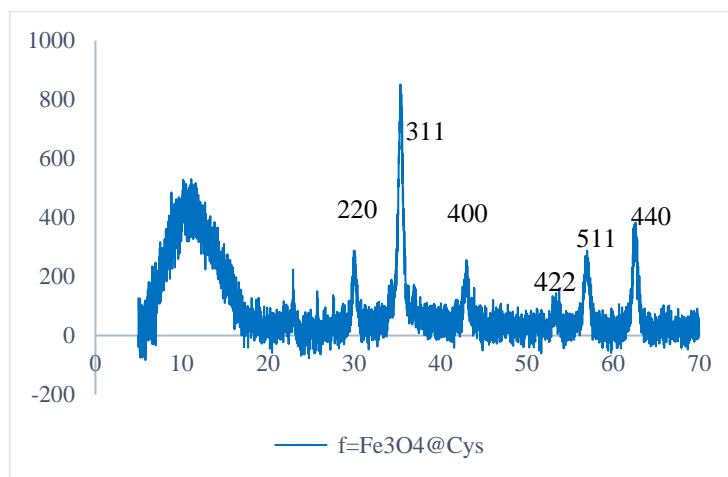


Figure 4. XRD spectrum of L-cysteine@Fe₃O₄ nanoparticles

1.5. TGA Spectrum

The thermal behavior of the catalysts was studied using the TGA technique. The curve in Figure 5 shows a significant weight loss of L-cysteine@Fe₃O₄ nanoparticles, indicating their high thermal instability. The first and second weight losses below 250°C are due to water evaporation on the surface and trapped water in the catalyst's crystalline structure. The third weight loss between 250 and 450°C is attributed to the decomposition of the organic layer of L-cysteine. According to TGA, the total weight loss was around 10%, indicating the loading percentage of cysteine on Fe₃O₄.²

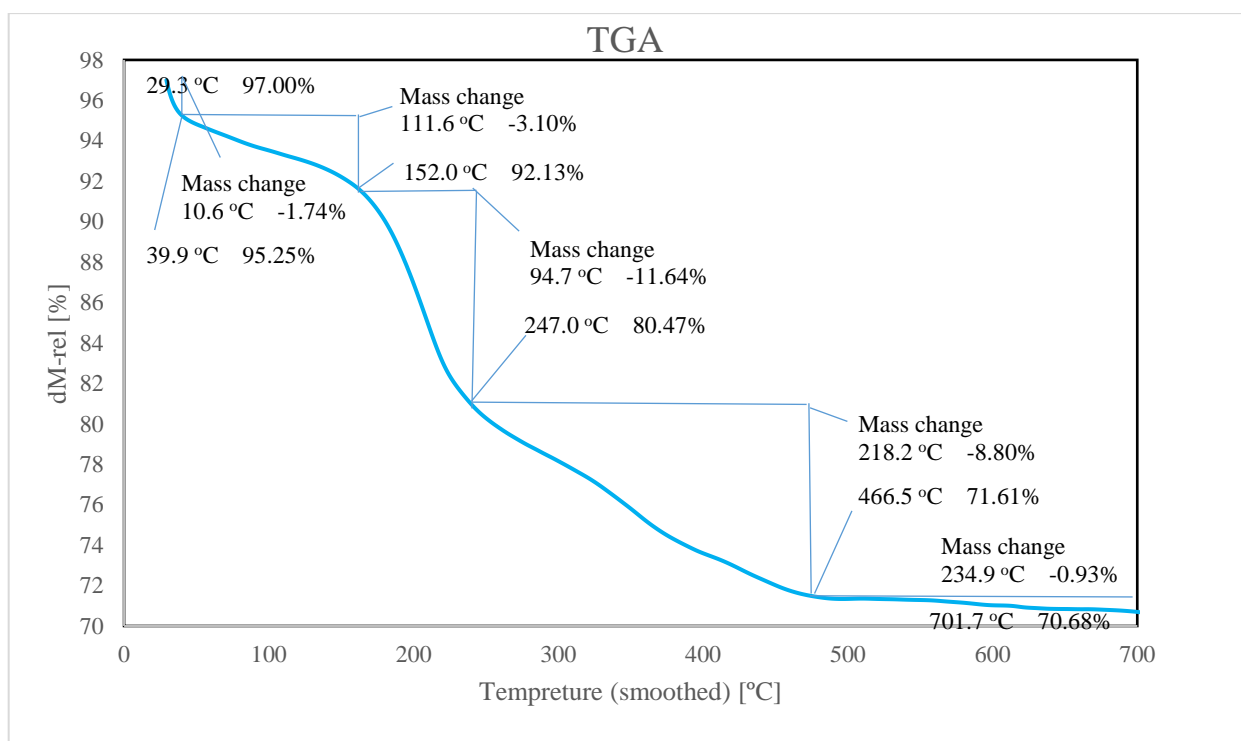


Figure 5. TGA Spectrum of L-cysteine@Fe₃O₄ nanoparticles

1.6. VSM curves

The magnetization curves of nanocatalysts at 300 K measured the magnetic properties of L-cysteine@Fe₃O₄ nanoparticles. The saturation magnetization (σ_s) of the nanoparticles was found to be 43.6 emu/g and 39.4 emu/g, respectively, confirming the magnetic nature of the prepared nanoparticles (see Figure 6). Therefore, the obtained results confirm that L-cysteine was successfully grafted onto the surface of Fe₃O₄.

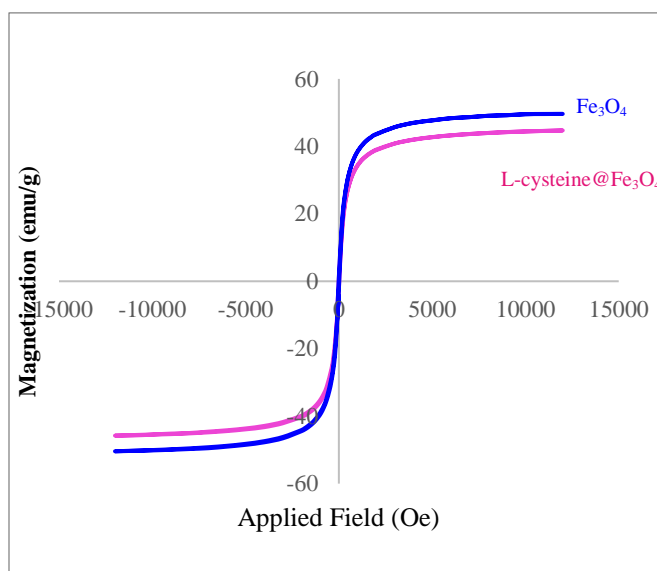


Figure 6. VSM curves of L-cysteine@Fe₃O₄ nanoparticles

1.8. HPLC chromatogram

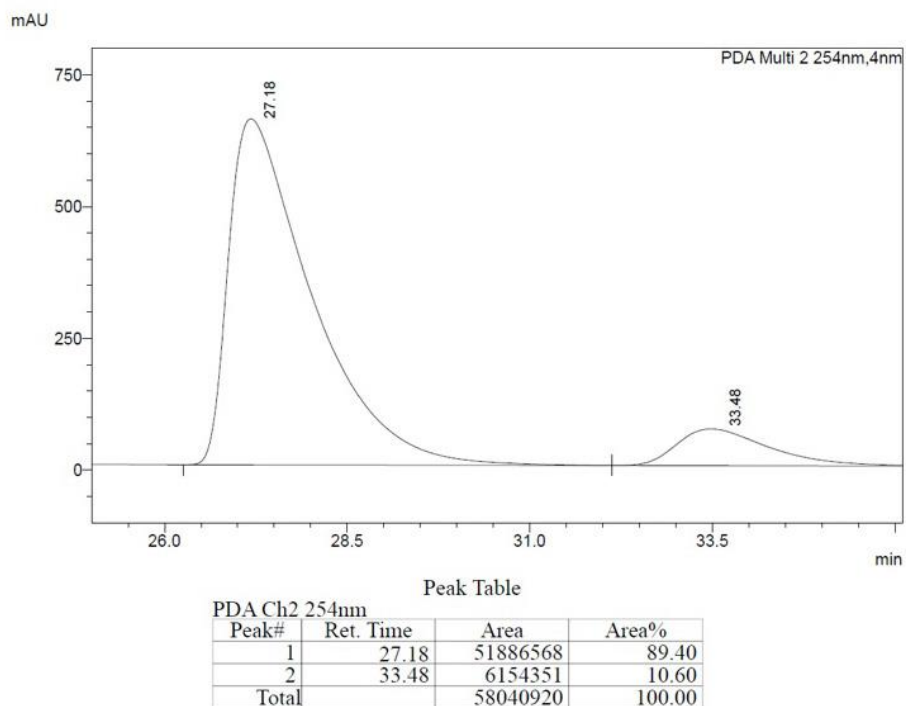


Figure 8. The HPLC chromatogram of obtained S-binol

2. References

1. Sarkar, T.; Brahma, D.; Gupta, A. N. **2024**, *Microchem J* 196: 109541.
<https://doi.org/https://doi.org/10.1016/j.microc.2023.109541>
2. Bashir, A.; Pandith, A. H.; Malik, L. A.; Qureashi, A.; Ganaie, F. A.; Dar, G. N. **2021**, *s J Environ Chem Eng* 9: 105880.
<https://doi.org/https://doi.org/10.1016/j.iece.2021.105880>
3. Guo, L.; Liu, G.; Hong, R.-Y.; Li, H.-Z. *Mar. Drugs* **2010**, 8(7), 2212-2222;
<https://doi.org/10.3390/md8072212>