

**A novel core@double-shell three-layer structure with dendritic fibrous morphology based on Fe<sub>3</sub>O<sub>4</sub>@TEA@Ni-organic framework: A highly efficient magnetic catalyst in the microwave-assisted Sonogashira coupling reaction**

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## ***1. Starting Materials***

N, N-dimethylformamide (DMF), ammonium hydroxide solution (NH<sub>4</sub>OH), triethanolamine (>99.0%), FeCl<sub>2</sub>.4H<sub>2</sub>O (99.99%), FeCl<sub>3</sub>.6H<sub>2</sub>O (99.99%) were supplied by Merck Co. Ltd. (Darmstadt, Germany). Furthermore, 2-aminoterephthalic acid (99.99%) and Ni(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O (99.99%) were purchased from BASF (Ludwigshafen, Germany).

## ***2. Experimental***

### ***2.1. Synthesis of Fe<sub>3</sub>O<sub>4</sub> MNPs***

In order to synthesis Fe<sub>3</sub>O<sub>4</sub> MNPs, a mixture consisting of 3 ml of FeCl<sub>3</sub>.6H<sub>2</sub>O (2 M dissolved in 2 M HCl) and 10.33 ml of ultrapure water was fabricated. In the following, 2 ml of Na<sub>2</sub>SO<sub>3</sub> (1 M) was dropwise added into the former solution under magnetic stirring for one minute. Due to the formation of the complex Fe<sup>3+</sup> with SO<sub>3</sub><sup>2-</sup>, the color of the solution changed from light yellow to red. After the solution's color turned back to light yellow again, 80 ml NH<sub>3</sub>.H<sub>2</sub>O solution (0.85 M) was added into the prior mixture under intense stirring. The black precipitate was rapidly formed. The reaction was allowed to proceed for another 30 min under magnetic stirring to complete the reaction. After magnetic decantation and washing several times with deionized water (to pH < 7.5), the precipitates were dried in a vacuum oven at 60 °C for 12 h, and Fe<sub>3</sub>O<sub>4</sub> MNPs resulted <sup>1</sup>.

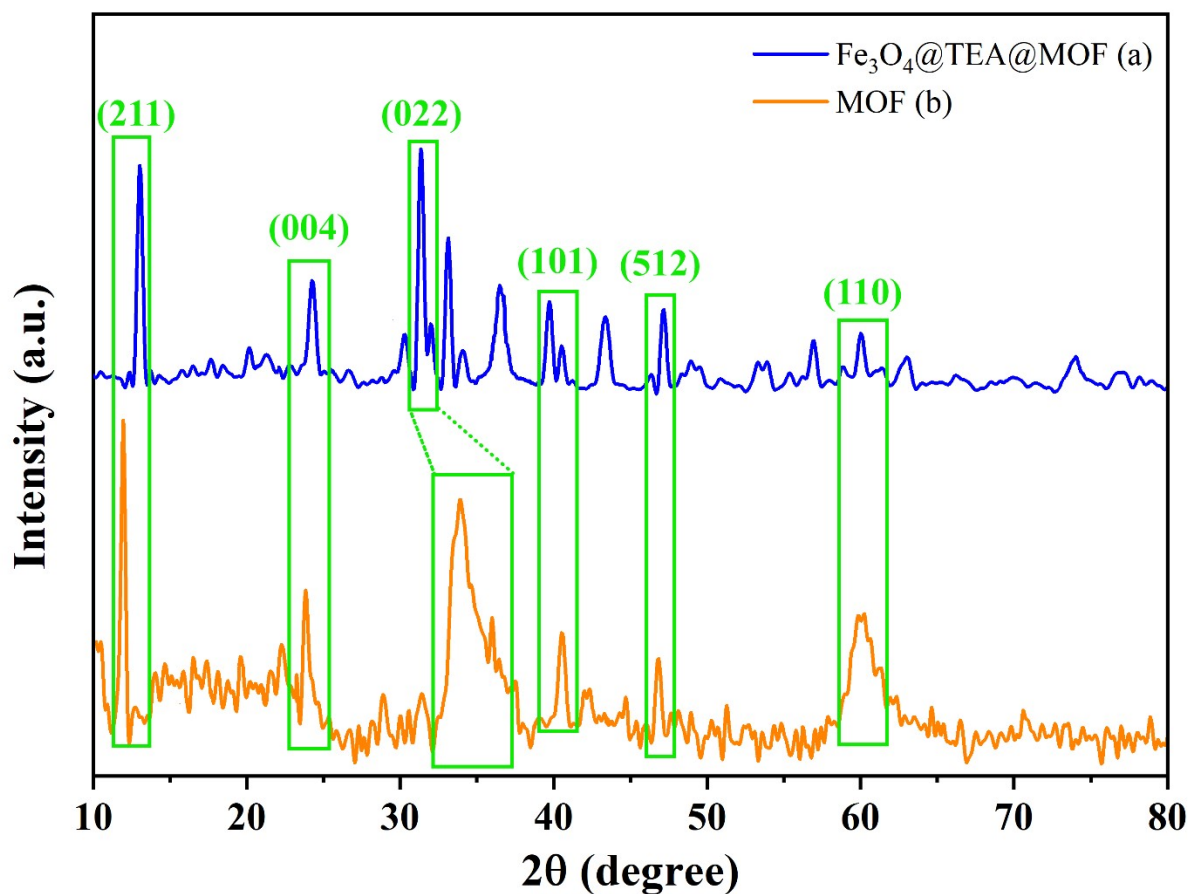
### ***2.2. Synthesis of bare NiNH<sub>2</sub>BDC MOF***

For this purpose, 0.093 g of 2-aminoterephthalic acid ligand (NH<sub>2</sub>BDC) and 0.4 g of Ni(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O were mixed in 20 ml of DMF. Then, the resulting mixture was poured into the Teflon-lined autoclave and was heated for 12 h at 150 °C in the furnace after 1 h of vigorous mechanical stirring. The resulting ocher precipitate was collected by centrifuge and was rinsed several times with distilled water and ethanol, respectively. Finally, the obtained NiNH<sub>2</sub>BDC MOF was dried at 80 °C for 12 h in the oven.

### ***2.3. Synthesis of Fe<sub>3</sub>O<sub>4</sub>-MOF***

For the preparation of the Fe<sub>3</sub>O<sub>4</sub>@MOF, 0.093 g of 2-aminoterephthalic acid ligand (NH<sub>2</sub>BDC) and 0.4 g of Ni(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O were mixed in 20 ml of DMF. After one hour of vigorous mechanical stirring and dissolving of the materials, 0.1 g of Fe<sub>3</sub>O<sub>4</sub> was added to the prepared mixture. The

resulting mixture was poured into the Teflon-lined autoclave and was heated for 12 hours at 150 °C in the furnace.



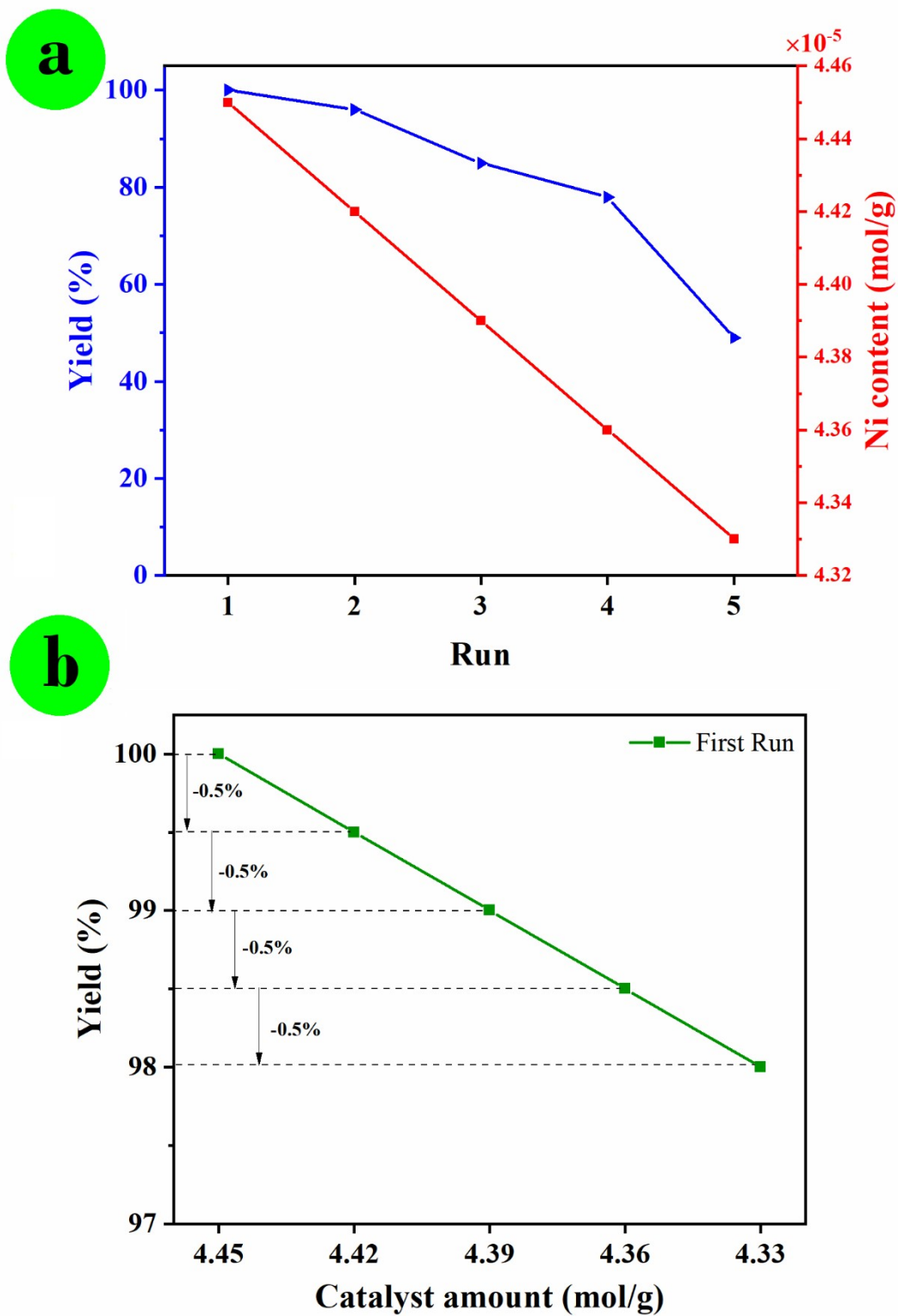
**Figure 1S.** XRD pattern of (a)  $\text{Fe}_3\text{O}_4@\text{TEA}@\text{MOF}$  and (b) bare MOF

**Table 1S.** The catalytic activity of each substance in the Sonogashira coupling reaction <sup>a</sup>.

Entry	Substance	Time (h:min)	Yield (%)	Description
1	Fe <sub>3</sub> O <sub>4</sub>	01:10	42	Easy separation, agglomeration
2	Fe <sub>3</sub> O <sub>4</sub> @TEA	02:00	Trace*	Easy separation, uniform distribution
3	Fe <sub>3</sub> O <sub>4</sub> @TEA@MOF	00:07	100	Easy separation, uniform distribution
4	Fe <sub>3</sub> O <sub>4</sub> -MOF	00:35	74	Easy separation, irregular distribution
5	MOF	00:50	70	Difficult separation

\* Because of the absence of any metal in the structure

<sup>a</sup> Reaction condition: Phenylacetylene (0.25 mmol), iodobenzene (0.25 mmol), Cs<sub>2</sub>CO<sub>3</sub> (0.5 mmol), microwave-assisted (540 W), substance amount: 2 mg



**Figure 2S.** The yield and Ni content amount in the reusability test (a), the yields of different catalysts with specified Ni amount in the Sonogashira coupling reaction.

## References

- 1 A. Marandi, E. Nasiri, N. Koukabi and F. Seidi, *Int. J. Biol. Macromol.*, 2021, **190**, 61–71.