Supporting information

Ag-doped Nano Magnetic $\gamma$-Fe$_2$O$_3$@DA Core–Shell Hollow Spheres: an efficient and recoverable heterogeneous catalyst for $A^3$, $K^2$ Coupling Reactions and [2+3] cycloaddition

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1. General information

The process for the preparation of the magnetic \( \text{Fe}_2\text{O}_3@\text{DA}/\text{Ag} \) hollow sphere catalyst is schematically described in scheme 1. The nano magnetic \( \text{Fe}_2\text{O}_3@\text{DA}/\text{Ag} \) hollow sphere was prepared from commercially inexpensive available materials and fully characterized using, the corresponding data, provided by FT-IR, FE-SEM, TEM, XRD, TGA, and VSM techniques.

1.1. General details

All chemicals, including \( \text{FeCl}_3\cdot6\text{H}_2\text{O} \), trisodium citrate dihydrate, sodium acetate trihydrate, ethanol, ethylene glycol (EG), PVP, urea, dopamine, \( \text{AgNO}_3 \) and \( \text{NH}_3\cdot\text{H}_2\text{O} \), were analytical grade reagents, purchased from Sigma-Aldrich, and used without further purification. The progress of reaction was monitored by TLC on commercial aluminum-backed plates of silica gel 60 F254, visualized, using ultraviolet light. Melting points were determined in open capillaries using an Electrothermal 9100 without further corrections. \(^1\text{H}\) NMR and \(^{13}\text{C}\) NMR spectra were recorded using a Bruker DRX-400 spectrometer at 400 and 100 MHz respectively. magnetic-\( \text{Fe}_2\text{O}_3@\text{DA}/\text{Ag} \) hollow sphere was characterized by; FT-IR spectra were obtained with potassium bromide pellets in the range of 400–4000 cm\(^{-1}\) using a Shimadzu 8400s spectrometer; X-ray diffraction (XRD) was detected by Philips using Cu-Ka radiation of wavelength 1.54Å; Scanning electron Microscopy, FE-SEM-EDX, analysis was performed using Tescanvega II XMU Digital Scanning Microscope. Samples were coated with gold at 10 mA for 2 min prior to analysis; the magnetic properties were characterized using a vibrating sample magnetometer (VSM, Lakeshore7407) at room temperature. Thermo-gravimetric
analyses (TGA) were analyzed with a LINSEIS modele STS PT 16000 thermal analyzer under air atmosphere at a heating rate of 5 °C min\(^{-1}\).

2. Characterizations of Catalyst

2.1. FT-IR analysis

![FT-IR spectra](image)

**Figure 1.** The FT-IR spectra of (a) h-Fe\(_2\)O\(_3\), (b) h-Fe\(_2\)O\(_3\)@DA and (c) h-Fe\(_2\)O\(_3\)@DA/Ag.
2.2. X-ray diffraction spectra

Figure 2. XRD pattern of (a) h-Fe$_2$O$_3$, (b) h-Fe$_2$O$_3$@DA and (c) h-Fe$_2$O$_3$@DA/Ag

2.3. X-ray diffraction spectra

Figure 3. TGA analysis of (a) h-Fe$_2$O$_3$ and (b) h-Fe$_2$O$_3$@DA/Ag.
2.4. VSM analysis

![Magnetization curves](image)

Figure 4. The magnetization curves of (a) h-Fe$_2$O$_3$, (b) h-Fe$_2$O$_3$@DA and (c) h-Fe$_2$O$_3$@DA/Ag.

2.5. FE-SEM-EDS analysis

![SEM-EDS analysis](image)

Figure 5. The FEG-SEM-EDS analysis of (a,b) h-Fe$_2$O$_3$, (c,d) h-Fe$_2$O$_3$@DA and (e,f) h-Fe$_2$O$_3$@DA/Ag.
2.6. TEM image

Figure 6. The TEM image of h-Fe$_2$O$_3$@DA/Ag.
3. Spectral data for selected compounds

1-(1,3-diphenylprop-2-ynyl)piperidine (table 1, 5a): Pale yellow oily liquid; $^1$H NMR (400 MHz, CDCl$_3$, ppm) $\delta$ 1.45-1.49 (m, 2H), 1.58-1.65 (m, 4H), 2.59 (t, 4H), 4.81 (s, 1H), 7.31-7.40 (m, 6H), 7.53-7.55 (m, 2H), 7.65-67 (d, J=7.6 Hz, 2H).

1-(3-phenyl-1-(thiophen-2-yl)prop-2-ynyl)piperidine (table 1, 5g): Yellow solid; mp 50-51 ºC (Lit.$^1$ 52-53 ºC); $^1$H NMR (400 MHz, CDCl$_3$, ppm) $\delta$ 1.48-1.52 (m, 2H), 1.63-1.70 (m, 4H), 2.62-2.71 (m, 4H), 5.03 (s, 1H), 7.00 (dd, J$^1$=J$^2$=3.6 Hz, 1H), 7.25-7.30 (m, 1H), 7.31 (d, J=4.4 Hz, 2H). 7.36-7.38 (m, 3H), 7.54-7.57 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm) $\delta$ 24.4, 26.1, 50.6, 58.2, 85.3, 86.9, 123, 125.3, 125.8, 126.2, 128.2, 128.3, 131.8, 144.
1-(3-phenyl-1-(4-(3-phenyl-1-(piperidin-1-yl)prop-2-ynyl)phenyl)prop-2-ynyl)piperidine (table 1, 5h): White solid; mp 157-159 °C (Lit.\textsuperscript{1} 158-160 °C); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, ppm) \(\delta\) 1.47 (m, 2H), 1.59-1.63 (m, 4H), 2.59 (m, 4H), 4.81 (s, 1H), 7.33-7.35 (m, 3H), 7.52-7.55 (m, 2H), 7.63 (s, 2H).

1-(1-(naphthalen-3-yl)-3-phenylprop-2-ynyl)piperidine (table 1, 5i): Yellow oil; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, ppm): \(\delta\) 1.47-1.51 (m, 2H), 1.60-1.67 (m, 4H), 2.64 (t, 4H), 4.97 (s, 1H), 7.36-7.40 (m, 3H), 7.48-7.52 (m, 2H), 7.58-7.61 (m, 2H), 7.79 (dd, \(J^1=J^2=8.4\) Hz, 1H), 7.85-7.91 (m, 3H), 8.11 (s, 1H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}, ppm) d 24.4, 26.2, 50.8, 62.5, 86, 88.1, 123.3, 125.8, 125.9, 126.7, 127.2, 127.5, 127.7, 128.1, 128.12, 131.8, 132.9, 133.1, 136.3.
N,N-diethyl-1,3-diphenylprop-2-yn-1-amine (table 1, 5r): Pale yellow oily liquid; 
$^1$H NMR (400 MHz, CDCl$_3$, ppm) δ 1.04 (m, 6H), 2.36-2.62 (m, 4H), 5.19 (s, 1H), 7.15-7.27 (m, 4H), 7.29-7.38 (m, 3H), 7.39-7.41 (m, 2H).

4-(3-phenylprop-2-ynyl)morpholine (table 1, 6c): yellow oil; $^1$H NMR (400 MHz, CDCl$_3$, ppm) δ 2.64-2.67 (m, 6H), 3.52 (s, 3H), 3.69-3.71 (m, 1H), 3.77-3.79 (m, 6H), 7.28-7.31 (m, 4H), 7.43-7.46 (m, 2H).

1-(1-cyclohexyl-3-phenylprop-2-ynyl)pyrrolidine (table 1, 6i): Colorless liquid; $^1$H NMR (400 MHz, CDCl$_3$, ppm) δ 1.05-1.36 (m, 5H), 1.56-1.63 (m, 2H), 1.75-1.79 (m, 6H), 1.82-2.10 (m, 4H), 2.5-2.98 (m, 4H), 3.36-3.38 (d, J = 7.6 Hz, 1H), 7.14-7.33 (m,
3H), 7.50-7.63 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$, ppm) δ 24.9, 26.9, 27.1, 28.3, 32.7, 33, 42.9, 51.1, 61.1, 86.1, 88.9, 125.9, 128.9, 129.8, 132.6.

4-(1-phenylhex-1-yn-3-yl)morpholine (Table 1, 6m): Yellow oil; $^1$H NMR (400 MHz, DMSO-$d$_6, ppm) δ 0.97 (m, 3H), 1.45-1.75 (m, 4H), 2.67–2.70 (m, 2H), 2.79–2.83 (m, 2H), 3.82-4.13 (m, 1H), 4.15-4.17 (m, 4H), 7.46–7.50 (m, 3H), 7.62–7.64 (m, 2H).

1-(1-(2-p-tolylethynyl)cyclohexyl)piperidine (Table 2, 8e): Yellow oil; $^1$H NMR (400 MHz, CDCl$_3$, ppm) δ 1.39-1.93 (m, 16H), 2.17-2.20 (m, 2H), 2.53 (s, 3H), 2.73-2.83 (m, 2H), 7.26-7.27 (m, 3H), 7.46-7.48 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm) δ 21.32, 23.4, 24.4, 25, 26.7, 37.6, 47.9, 58.8, 85.4, 92.1, 123, 127.6, 128.3, 133.
4-(1-(2-phenylethynyl)cyclohexyl)morpholine (Table 2, 8f): Pale yellow oily liquid; 

$^1$H NMR (400 MHz, CDCl$_3$, ppm) $\delta$ 1.28-1.30 (m, 1H), 1.52 (m, 2H), 1.63-1.67 (m, 3H), 1.73 (br.s, 2H), 2.03-2.05 (m, 2H), 2.74 (br.s, 4H), 3.78 (br.s, 4H), 7.27 (m, 3H), 7.44-7.45 (m, 2H), $^{13}$C NMR (100 MHz, CDCl$_3$, ppm) $\delta$ 22.7, 25.7, 35.4, 46.6, 58.8, 67.4, 86.4, 89.8, 123.4, 127.7, 128.1, 131.7.

![Image of 4-(1-(2-phenylethynyl)cyclohexyl)morpholine](image1)

4-(1-(4-fluorophenyl)ethynyl)cyclohexyl)morpholine (Table 2, 8i): Yellow oil; $^1$H NMR (400 MHz, DMSO-$_d_6$, ppm) $\delta$ 1.26-1.34 (m, 1H), 1.57-1.62 (m, 2H), 1.69-1.78 (m, 3H), 1.80-1.86 (m, 2H), 2.00-2.02 (m, 2H), 2.78 (s, 4H), 3.70 (br.t, J = 4.2 Hz, 4H), 6.97-7.00 (t, J = 8.6 Hz, 2H), 7.32-7.40 (m, 2H).

![Image of 4-(1-(4-fluorophenyl)ethynyl)cyclohexyl)morpholine](image2)

5-Phenyl-1H-tetrazole (Table 3, 9a): White solid; mp 213–215 °C (Lit.$^2$ 214–215 °C); $^1$H NMR (400 MHz, DMSO-$_d_6$, ppm) $\delta$ 7.68 (s, 3H, Ph), 7.92 (s, 2H, Ph); $^{13}$C NMR (100 MHz, DMSO-$_d_6$, ppm) $\delta$ 126.6, 128.6, 130.3, 134.6, 155.

![Image of 5-Phenyl-1H-tetrazole](image3)
5-(4-Nitrophenyl)-1H-tetrazole (Table 3, 9b): Yellow solid; mp 218–219 °C (Lit.\textsuperscript{2} 220-222 °C); \textsuperscript{1}H NMR (400 MHz, DMSO-\textit{d}_{6}, ppm) δ 8.30 (d, 2H, \textit{J} 8.4, Ph), 8.39 (d, 2H, \textit{J} 8.8, Ar-H); \textsuperscript{13}C NMR (100 MHz, DMSO-\textit{d}_{6}, ppm) δ 127.6, 129.1, 131, 149.5.

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\text{N} \\
\text{N} \\
\text{N}
\end{array} \]

5-(4-Methylphenyl)-1H-tetrazole (Table 3, 9c): White solid; mp 249-251 °C (Lit.\textsuperscript{2} 247-249 °C); \textsuperscript{1}H NMR (250 MHz, DMSO-\textit{d}_{6}, ppm) δ 2.35 (s, 3H, CH\textsubscript{3}), 7.37 (d, 2H, \textit{J} 7.6 Hz, Ph), 7.90 (d, 2H, \textit{J} 7.5 Hz, Ph).

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\text{N} \\
\text{N} \\
\text{N} \\
\text{Cl}
\end{array} \]

5-(3-Chlorophenyl)-1H-tetrazole (Table 3, 9g): White solid; mp 138-140 °C (Lit.\textsuperscript{3} 137-139 °C); \textsuperscript{1}H NMR (250 MHz, DMSO-\textit{d}_{6}, ppm) δ 7.55 (m, 2H, Ph), 7.96 (d, 1H, \textit{J} 7.6, Ph), 7.99, (s, 1H); \textsuperscript{13}C NMR (62.9 MHz, DMSO-\textit{d}_{6}, ppm) δ 125.4, 126.2, 126.4, 130.7, 131.1, 133.9, 154.6.

\[ \begin{array}{c}
\text{Cl} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{Cl}
\end{array} \]

5-(4-Chlorophenyl)-1H-tetrazole (Table 3, 9h): White solid; mp 251-253 °C (Lit.\textsuperscript{2} 251-252 °C); \textsuperscript{1}H NMR (400 MHz, DMSO-\textit{d}_{6}, ppm) δ 7.61 (d, 2H, \textit{J} 8.4, Ph), 8.09 (d, 2H, \textit{J} 8.8, Ph).
5-(4-Hydroxyphenyl)-1H-tetrazole (Table 3, 9j): White solid; mp 235 °C (Lit.\(^2\) 233-234 °C); \(^1\)H NMR (400 MHz, DMSO-\(d_6\), ppm) \(\delta\) 6.91 (d, 2H, \(J\) 8.4, Ph), 7.58 (d, 2H, \(J\) 8.4, Ph), 10.11 (s broad, OH); \(^13\)C NMR (100 MHz, DMSO-\(d_6\), ppm) \(\delta\) 116.1, 117.4, 128.8, 153.2, 159.8.

4-(1H-tetrazol-5-yl)-benzonitrile (Table 3, 9k): White solid; mp 257-259 °C (Lit.\(^4\) 258-260 °C); \(^1\)H NMR (250 MHz, DMSO-\(d_6\), ppm) \(\delta\) 8.06 (d, 2H, \(J\) 7.1, Ph), 8.19 (d, 2H, \(J\) 8.6, Ar-H); \(^13\)C NMR (62.9 MHz, DMSO-\(d_6\), ppm) \(\delta\) 113.3, 118.1, 127.6, 128.7, 133.1, 155.2, 162.2.

2-(1H-tetrazol-5-yl)pyridine (Table 3, 9l): White solid; mp 210-213 °C (Lit.\(^5\) 211-212 °C); \(^1\)H NMR (400 MHz, DMSO-\(d_6\), ppm) \(\delta\) 7.75 (s, 1H, Ph), 8.07 (s, 1H, Ph), 8.20 (d, 1H, \(J\) 8.4 Ph), 8.63 (s, 1H).
4-(1H-tetrazol-5-yl)pyridine (Table 3, 9m): White solid; mp 256-258 °C (Lit.\(^6\) 256-258 °C); \(^1\)H NMR (250 MHz, DMSO-\(d_6\), ppm) \(\delta\) 8.10 (d, 2H, \(J\) 6.0, Ph), 8.77 (d, 2H, \(J\) 6.5, Ph); \(^{13}\)C NMR (62.9 MHz, DMSO-\(d_6\), ppm) \(\delta\) 120.9, 121.3, 133.8, 149.9, 165.7.
3.1. Copies of 1H and 13C NMR for selected products

Figure 7. $^1$H NMR spectrum of (table 1, 5a)
Figure 8. $^1$H NMR, Expand spectrum of (table 1, 5a)
Figure 9. $^1$H NMR, spectrum of (table 1, 5g)
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Figure 46 $^{13}$C NMR spectrum of (table 3, 9m)
4. References


