Supporting information

Heterogeneous Fenton-like activity of novel metallosalophen magnetic nanocomposites: Significant anchoring group effect

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Experimental Remarks

All chemicals were analytical grade reagents and used without further purification. FT-IR spectra were recorded on a Nicolet-Impact 400D spectrometer in the range of 400-4000 cm\(^{-1}\). Thermogravimetric analysis (TGA) of powders carried out on Shimadzu 50 under the air flow at a uniform heating rate of 10 °C min\(^{-1}\) in the range of 30-800 °C. Transmission electron microscopy (TEM) measurements were obtained by a 906 E instrument (Zeiss, Jena, Germany). The Fe and Mn content of the catalyst was measured by an inductively coupled plasma optical emission spectrometry (ICP-OES), using a VISTA-PRO ICP analyzer. UV-Vis spectra were recorded on a V670 JASCO spectrophotometer. Magnetic properties measurements were performed using vibrating sample magnetometer (VSM, Lake Shore Cryotronics 7407). Powder X-ray diffraction (XRD) was performed on a Bruker D8-advance X-ray diffractometer with Cu Ka (\(\lambda = 1.5406 \text{ Å}\)) radiation. EDX elemental analysis performed by Scanning Electron Microscope TESCAN Vega Model with EDX detector. GC-MS analysis was performed by Agilent 5975c.

The Preparation of \(\gamma\)-Fe\(_2\)O\(_3\) (MNP)

\(\gamma\)-Fe\(_2\)O\(_3\) MNPs were synthesized by a chemical co-precipitation technique reported previously.\(^1,2\) FeCl\(_2\), 4H\(_2\)O (1.99 g) and FeCl\(_3\),6 H\(_2\)O (3.25 g) were dissolved in deionized water (30 mL) under Ar atmosphere at room temperature. An NH\(_4\)OH solution (0.6 M, 200 mL) was then added dropwise (drop rate = 1 mL min\(^{-1}\)) to the stirring mixture at room temperature to reach the reaction pH to 11. The resulting black dispersion was continuously stirred for 1 h at room temperature and then heated to reflux for 1 h to yield a brown dispersion. The magnetic nanoparticles were then
separated by an external magnet and washed with deionized water until it was neutralized. The as-
synthesized sample was heated at 2 °C min$^{-1}$ up to 250 °C and then kept in the furnace for 3 h to
give a reddish-brown powder.

**Synthesis of silica-coated maghemite nanoparticles (SMNP)**

The silica-coated maghemite nanoparticles were synthesized with minor modifications of
literature.$^3$ 1.7 g of synthesized Fe$_2$O$_3$, suspended in 80 mL methanol and 20 mL deionized water
and sonicated for 1 h at 40 °C. Then aqueous ammonia (25%, 1.8 mL) was added slowly over 10
min and the mixture was heated at 40 °C for 30 min under mechanical stirrer. Then 1 mL of
tetraethylorthosilicate (TEOS) was added slowly to the mixture and then stirred mechanically for
24 h at room temperature. The iron oxide nanoparticles with a thin layer of silica (Fe$_2$O$_3$@SiO$_2$)
were separated by an external magnet and washed two times with ethanol and diethyl ether and
dried under vacuum.

**Preparation of Fe(III)SalophenCl complex**

Fe(III)SalophenCl was prepared as previously described.$^4$ In brief, Salophen ligand was
synthesized by dropwise adding of two equivalents of 2-hydroxybenzaldehyde (20 mmol) in 25
mL ethanol to one equivalent of 1,2-phenylendiamine (10 mmol) in 25 mL ethanol and refluxing
for 1 h that resulted in the yellow precipitate of Salophen. The precipitate cooled down to room
temperature and filtered and washed with cold methanol and water. The FeCl$_3$.6H$_2$O (0.3 mmol)
was mixed with the equivalent amount of Salophen in 10 mL ethanol and heated to 70 °C for 1 h
under argon atmosphere. This resulted solution was cooled down to room temperature and filtrated
off and washed with cool ethanol and dried under vacuum with P$_2$O$_5$.

**Preparation of Mn(III)SalophenCl complex**

Mn(III)SalophenCl synthesized according to the method described previously in the literature.$^5$
0.3 mmol of Salophen ligand is in 10 mL hot absolute ethanol. Then Solid Mn(OAc)$_2$.H$_2$O (0.3
mmol) is added in one portion and the solution is refluxed for 1 h. Approximately 1 mmol of solid
LiCl are then added and, the mixture is heated to reflux for an additional 0.5 h. Cooling the mixture
to 0 °C affords the Mn(III) complex as dark brown crystals that are washed thoroughly with cool ethanol and H₂O and dried under vacuum.

**Fig. S1.** FT-IR spectra of SAPy

**Fig. S2.** FT-IR spectra of Fe(III)SalophenCl
**Fig. S3.** FT-IR spectra of (a) SMNP@SAPy/MnSal, (b) Mn(III)(Salophen)Cl.

**Fig. S4.** EDS Spectrum of the as-prepared (a) SMNP@SAPy/FeSal, (b) SMNP@SAPy/MnSal.
**Fig. S5.** XRD pattern of (a) SMNP@SAPy, (b) SMNP@SAPy/FeSal and (c) SMNP@SAPy/MnSal.

**Fig. S6.** TGA thermograms of SMNP@SAPy/MnSal (B) in comparison with SMNP@SAPy (A).
**Fig. S7.** Hysteresis loops of the as-synthesized (a) bare $\gamma$-Fe$_2$O$_3$, (b) SMNP@SAPy, and (c) SMNP@SAPy/MnSal, at 298 K.

**Fig. S8.** FT-IR spectra of SAET
Fig. S9. FT-IR spectra of MNP (a), SMNP (b), SMNP@SAET (c) and SMNP@SAET/FeSal (d).

Fig. S10. FT-IR spectra of SMNP@SAET/MnSal
Fig. S11. EDS Spectrum of the as-prepared (a) SMNP@SAET/FeSal, (b) SMNP@SAET/MnSal.

Fig. S12. XRD pattern of (a) SMNP@SAET, (b) SMNP@SAET/FeSal, and (c) SMNP@SAET/MnSal.
Fig. S13. TGA thermograms of (a,B) SMNP@SAET/FeSal and (b,B) SMNP@SAET/MnSal in comparison with SMNP@SAET (A in a,b).

Fig. S14. $\ln[\text{RhB}]_0/[\text{RhB}]$ as a function of reaction time for $T = 298, 308, 313, 323$ K.
Fig. S15. $\ln(C_0/C_i)$ as a function of reaction time for RhB, methylene blue (MB), methyl orange (MO) and crystal violet (CV) at $T = 323$ K.
Fig. S16. GC trace and MS spectra of intermediates of RhB degradation in the present system.

Fig. S17. UV-Vis spectral changes of RhB in the present system.

References

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