Enhanced electrochemical water splitting with chiral molecules coated Fe$_3$O$_4$ nano-particles

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1. Preparation of Fe$_3$O$_4$ nanoparticles

The mono-dispersed Fe$_3$O$_4$ nanoparticles were synthesized by a chemical precipitation method. In a typical synthesis, 0.002 mol FeCl$_3$·6H$_2$O ($\geq$97%, Sigma-Aldrich), 0.001 mol Fe$_2$SO$_4$·7H$_2$O ($\geq$99.5%, BDH Laboratory Supplies, England), and 0.002 mol Sodium citrate dihydrate (Sigma-Aldrich, ≥99%, FG) were dissolved in 20 mL distilled water under continuous magnetic stirring. The solution was transferred into a 50 mL flask with three necks. Under continuous magnetic stirring, 1 mL 10M NaOH solution was added dropwise into the solution. Then, the flask was sealed, and heated at 95°C for 10h (water bath, with condensing reflux) for the chemical precipitation reaction, as illustrated in Scheme S1. When the reaction was finished, the solution was allowed to cool down to room temperature. The nanoparticles were separated from the solution by magnetic separation, washed with distilled water several times, and then re-dispersed into 40 mL distilled water to form an homogeneous dispersion.
2. Attaching chiral and achiral molecules onto Fe₃O₄ nanoparticles

The chiral and achiral molecules used in our work are shown in Table S1. Chiral molecules include D-tryptophan (Sigma Aldrich, purity ≥ 98 %), L-tryptophan (Sigma Aldrich, purity ≥ 98 %), SH-(CH₂)₂-NH-(Ala-Aib)₃-COOH (L-A3, Genemed Synthesis Inc), and SH-(CH₂)₂-NH-(Ala-Aib)₃-COOH (L-A11, Genemed Synthesis Inc). Achiral molecules include SH-(CH₂)₂-COOH (MPA) (Sigma, purity ≥ 99%), and SH-(CH₂)₂-NH-(Aib)₁₀-NH₂ (AIB₁₀) (Genemed Synthesis Inc). All chemicals were used without further purification. D-tryptophan, L-tryptophan, L-A3, L-A11, MPA and AIB₁₀ were dissolved in distilled water to form 1 mM solutions. Namely, 1mM D-tryptophan, 1mM L-tryptophan, 1mM L-A3, 1mM L-A11, 1mM MPA, and 1mM AIB₁₀, respectively.
**Table S1:** Summarization of Chiral and Achiral molecules used in our work

<table>
<thead>
<tr>
<th>Chiral molecules</th>
<th>Molecular formula</th>
<th>Structural scheme</th>
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<tbody>
<tr>
<td>D-tryptophan</td>
<td>C_{11}H_{12}N_{2}O_{2}</td>
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<tr>
<td>L-Tryptophan</td>
<td>C_{11}H_{12}N_{2}O_{2}</td>
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<tr>
<td>L-A11</td>
<td>SH-(CH$_2$)$<em>2$-NH-(Ala-Aib)$</em>{11}$-NH$_2$</td>
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</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Achiral molecules</th>
<th>Molecular formula</th>
<th>Structural scheme</th>
</tr>
</thead>
<tbody>
<tr>
<td>MPA</td>
<td>SH-(CH$_2$)$_2$-COOH</td>
<td><img src="image" alt="MPA" /></td>
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<tr>
<td>AIB$_{10}$</td>
<td>SH-(CH$_2$)$<em>2$-NH-(Aib)$</em>{10}$-NH$_2$</td>
<td><img src="image" alt="AIB$_{10}$" /></td>
</tr>
</tbody>
</table>

Chiral and achiral molecules were linked to Fe$_3$O$_4$ nanoparticles by ultrasonic method. Ultrasonic method has been widely used for the preparation of novel nanostructured materials. The ultrasound effect derives from the acoustic cavitation, which includes the formation, growth, and collapse of bubbles in the solution. Thus, the ultrasonic effect could not only drastically shorten the synthesis time but also improve the uniformity of samples$^{1,2}$.

Herein, in a typical synthesis, 50μL 1mM L-A3 was added into 150 μL Fe$_3$O$_4$ dispersion drop by drop with a 10 μL pipette. The 200 μL mixture were ultrasonically treated for 3h (ultrasonic power 50 W), and then incubated in N$_2$ atmosphere for 20h to achieve equilibrium state. Chiral and achiral molecules are attached robustly onto Fe$_3$O$_4$ NPs due to the hydrogen bonds and the electrostatic interaction between the molecules.
and Fe₃O₄ NPs, as well as high surface activity and surface energy of nanoparticles. In this mixture, the concentration of L-A3 is 0.25 mM, and the Fe₃O₄ NPs attached with L-A3 is named as Fe₃O₄@L-A3. The other nano-particles linked with different molecules are respectively named as Fe₃O₄@L-Tryptophan, Fe₃O₄@D-Tryptophan, Fe₃O₄@MPA, Fe₃O₄@A11, and Fe₃O₄@AIB₁₀.

3. Preparation of the Anode electrode

The fluorine-doped tin oxide (FTO) glasses used in this work were purchased from Sigma-Aldrich, with surface resistivity of 7 Ω/sq. Before deposition, the FTO coated glasses are thoroughly cleaned in boiling acetone for 10 min and then in boiling ethanol for another 10 min. In a typical coating process, 30 μL Fe₃O₄@L-A3 dispersion was spin-coated to form a 1*1 cm² working area on a 1*2 cm² FTO glass, as illustrated in Figure S1 and S2. The FTO glass deposited with Fe₃O₄@L-A3 was then dried at 40°C for 12 h in the air.

![Figure S1](image_url): (a) Scheme and (b) SEM images of Fe₃O₄@L-A3 nanoparticles coated on FTO glass to form a 1*1 cm² working area on a 1*2 cm² FTO glass.
Figure S2: SEM images of Fe₃O₄@L-A3 NPs (a) Fe₃O₄@L-A3 NPs layer on FTO glass (b-d) Fe₃O₄@L-A3 NPs layer.

4. Stability study of Anode coated with chiral and achiral Fe₃O₄ NPs

![Graph](image)

Figure S3: Stability study of the anode coated by Fe₃O₄@L-A3 NPs (chiral) and Fe₃O₄@AIB₁₀ NPs (achiral) under 1.241 V voltage (vs NHE). Electrochemical measurements were conducted in a 0.1 M KOH solution (pH 13) as the electrolyte solution, and calomel electrode as the reference. E(NHE) = E (vs. Calomel) + E°(Calomel), where E°(Calomel)=0.241 V.
The stability tests were conducted under 1.241 V (vs NHE) for 100 min, in a 0.1 M KOH solution (pH 13) as the electrolyte solution, and calomel as a reference electrode.

5. Characterization Details

5.1 Crystal structure, size and morphology characterization

X-ray diffraction (XRD) patterns of the samples were recorded on a Sealed Cu-anode tube (line source) Rigaku ULTIMA III (2kW) theta-theta vertical diffractometer equipped with CBO. The SEM images were recorded using a Zeiss Sigma 500 electron microscope.

The XPS spectra were measured by an AXIS-Ultra DLD spectrometer (KRATOS), equipped with a dual, hemispherical /spherical analyzer that enables spectroscopy and mapping at improved lateral resolution, down to 3µm. The dispersion of the NPs was deposited on Au surface and dried in vacuum for 48 h.

5.2 Electrochemical characterization

The electrochemical measurements are carried out in 0.1 M KOH solution (pH 13) using a Pt wire as the counter electrode and calomel as the reference electrode. The photo-electrochemical measurements were performed using linear sweep voltammetry (LSV) in the potential range from -0.01 V to 2.0 V vs. calomel electrode, with a scan rate of 20 mV/s. Photo-current was measured under visible-light irradiation (power 8W), and dark current was detected without light irradiation.

5.3 H₂O₂ detection

The formation of H₂O₂ was measured by spectrophotometric titration of the used electrolytes, with the o-tolidine as redox indicator and 0.1 M Na₂SO₄ as solvent. If H₂O₂ was produced, a yellow color appeared with an absorption peak at about 436 nm. This peak is characteristic for the complete two-electron oxidation product of o-tolidine formed by the reaction with hydrogen peroxide. The detection steps are as follows. (1) Carrying out water splitting reaction under 1.8 V (vs calomel) for 2 h. (2) Take out 4 mL electrolytes near anode by 1 mL pipette, then add 1 mL o-tolidine and mix them by vibrating. (3) After 30 min, measure the absorption spectra of the solution by a Varian Cary 50 Bio UV/ Visible spectrophotometer.
6. Hydrogen production

Figure S4. Three cycles of H₂ production rate at constant potential 1.4 V vs NHE, in 0.1 M KOH electrolyte (pH=13) at room temperature.

Figure S4 shows three cycles of H₂ production over the Fe₃O₄, Fe₃O₄@L-A3 and Fe₃O₄@AIB10. Each cycle lasted for 60 min in 0.1 M KOH electrolyte (pH=13) at room temperature. Fe₃O₄@L-A3 exhibited higher H₂ production rate than bare Fe₃O₄ and Fe₃O₄@AIB10 in each cycle, indicating the CISS effect played important role in reducing the reaction barrier of water splitting. Moreover, the results show that Fe₃O₄, Fe₃O₄@L-A3 and Fe₃O₄@AIB10 all exhibited robust catalytic activity for hydrogen producing, implying that the catalyst are stable during the catalytic reactions.
7. Circular dichroism (CD) spectra of samples

![Circular Dichroism (CD) spectra of samples](image)

**Figure S5:** CD spectra of L-Tryptophan (Black dotted line), Fe₃O₄@L-Tryptophan (Black solid line) D-Tryptophan (Red dotted line), Fe₃O₄@D-Tryptophan (Red solid line)

![Circular Dichroism (CD) spectra of samples](image)

**Figure S6:** (a) CD spectra of L-A11 (Black line) solution and Fe₃O₄@L-A3 (Red line) (b) CD spectra of Fe₃O₄@MPA (Red line) and Fe₃O₄@AIB10 (Black line).

Figure S5 and Figure S6 are the circular dichroism (CD) spectra of the samples. As shown in Figure S5 and Figure S6 (a), Fe₃O₄@L-Tryptophan, Fe₃O₄@D-Tryptophan, and Fe₃O₄@AIB10 all exhibit wide CD peaks. Fe₃O₄@MPA and Fe₃O₄@AIB10 did not exhibit CD signals, as seen in Figure S6 (b).
These results present that the chiral molecules, L-Tryptophan, D-Tryptophan and L-A11, induced the chirality of Fe₃O₄ nanoparticles. This effect of induced chirality in NPs, as a result of the adsorption of chiral molecules, is well documented both for metal and semiconducting NPs⁴-⁵ and is demonstrated here for the Fe₃O₄ NPs.⁶,⁷ In contrast, Fe₃O₄@MPA and Fe₃O₄@AIB10 have no CD peaks because MPA and AIB10 molecules are achiral and they could not induce the chirality of Fe₃O₄ nano-particles.

7. XPS spectra of samples

Figure S7: XPS spectra of Fe₃O₄, Fe₃O₄@L-A3, and Fe₃O₄@AIB10

The samples were deposited on a Au surface, and dried in vacuum 48 h before conducting XPS characterization. Figure S7 is the XPS survey spectra of samples. Figure S7 shows that the surface of the samples are mainly composed of Fe, O and C elements. The Au elements come from the Au surface.

L-A3 and AIB10 molecules contain nitrogen and sulfur, as illustrated in Table S1. Their amount is much less than C, O and Fe, so their signals in Figure S7 are not as obvious. Nonetheless, we present their S 2p (Figure S8), C 1s spectra (Figure S9) and N 1s spectra (Figure S10) to show more details of chiral and achiral molecules coated on Fe₃O₄ nanoparticles.

As shown in Figure S8, the S elemental signals of Fe₃O₄@L-A3 and Fe₃O₄@AIB10 stem from their thiol (-SH) groups. The peaks around 162 eV are assigned to the Fe-S bonding⁸, indicating the L-A3 and AIB10 molecules were linked with Fe₃O₄ nanoparticles by the interaction of Fe and S elements. The peaks at 164 and 165.0 eV belonging to the C-S-C structure.
The peaks at 169 and 170 eV belong to oxidized sulfur groups like SO$_3$$^-$ and SO$_4$$^-$, indicating that the S elements are partially reacted with oxygen elements on Fe$_3$O$_4$ surfaces.

**Figure S9:** The XPS spectra in the region of S 2p of Fe$_3$O$_4$, Fe$_3$O$_4$@L-A3, and Fe$_3$O$_4$@AIB10
**Figure S10:** C 1s XPS spectra of Fe$_3$O$_4$, Fe$_3$O$_4$@L-A3, and Fe$_3$O$_4$@AIB10

**Figure S11:** N 1s XPS spectra of Fe$_3$O$_4$, Fe$_3$O$_4$@L-A3, and Fe$_3$O$_4$@AIB10
Figure S10 and Figure S11 show the C 1s and N 1s spectra of Fe$_3$O$_4$, Fe$_3$O$_4$@L-A3, and Fe$_3$O$_4$@AIB10. They present that the L-A3 and AIB-10 molecules were linked on the surface of Fe$_3$O$_4$ nanoparticles. In Figure S10, the –C-N groups come from the backbone of L-A3 and AIB10 molecules. In Figure S11, the 400 eV peak could be attributed to the N$_2$ absorbed on the surface of Fe$_3$O$_4$ nanoparticles. The 400.5 and 400.7 eV peaks originated from the –N-H groups of Fe$_3$O$_4$@L-A3 and Fe$_3$O$_4$@AIB10. Compared with Fe$_3$O$_4$@AIB10, the C 1s peaks and N 1s peaks are shifted to higher binding energy, indicating stronger chemical binding between L-A3 and Fe$_3$O$_4$.

8. Gas Chromatography spectrum

The Gas Chromatography spectra were detected on HP 6890 Series GC system, with thermal conductivity detector (GC-TCD) and Helium as carrier gas.

![Gas Chromatography spectrum](image)

**Figure S12:** Gas Chromatography spectrum of hydrogen produced from water splitting reaction with Fe$_3$O$_4$@L-A3 as catalyst
Figure S13: Gas Chromatography spectrum of CO$_2$ reference

Figure S14: Gas Chromatography spectrum of air reference

Figure S12 is the Gas Chromatography spectrum of H$_2$ produced during photoelectrochemical water splitting with Fe$_3$O$_4$@L-A3 as anode. The O$_2$ and N$_2$ peaks in Figure S13 result from air. Figure S13 and Figure S14 are the Gas Chromatography spectrum of CO$_2$ and air, references respectively.

References


