Supporting information

Novel multi-walled carbon nanotubes decorated with gold nanoparticles graft poly(2-methacryloyloxyethyl ferrocenecarboxylate) organic-inorganic nanohybrids:
Preparation, characterization and electrochemical sensing applications

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1. Modification of MWCNTs

Considering the hydrophobicity of MWCNTs, modification was performed so as to enlarge the micropores on the tube wall of MWCNTs, and thus improve the loading efficiency of Au NPs on the surface of MWCNTs in aqueous phase. Common modification methods include concentrated HNO₃, concentrated H₂SO₄, mixed acid, strong oxidizing H₂O₂, KMnO₄, thiophenol and HF etc. Researches manifested that modification of MWCNTs by thiophenol and HF could form C-S and C-F bonds and thus achieved better modification effect. In this study, HF was used to modify MWCNTs, and details were as follows: 0.2 g MWCNTs was dispersed in 40 ml acetone, and rinsed through ultrasonication for about 30-60 min, and then vacuum filtrated and dried under vacuum at 80 °C for 24 h. The modified MWCNTs was ultrasonicated for about 30-60 min in 1.0 mol l⁻¹ NaOH aqueous solution and immersed for 5 h. The modified MWCNTs solution was vacuum filtrated, and then rinsed with deionized water until neutrality, and finally dried under vacuum at 80 °C for 24 h. The final product was obtained by ultrasonating for ca 30 min in a 50 ml 5wt% HF solution and then continuously immersing for 8 h with stirring, vacuum filtrating, and then rinsing with deionized water until neutrality, and finally dried under vacuum at 80 °C for 24 h.

2. Preparation of MWCNTs@Au nanocomposites

Preparation of MWCNTs@Au nanocomposites was performed as per an in situ reduction method at a mass ratio of MWCNTs to Au of 1:1, 1:2 and 1:4 (w/w). Unless otherwise specified, the amount of Au was calculated according to the mass percentage of Au in HAuCl₄·3H₂O (ca 48%) thereinafter. In detail, the modified MWCNTs of 0.05 g were dispersed in 92 ml deionized water in a 250 ml beaker, and ultrasonicated for about 1 h. Afterwards, 10 ml 1% (0.25 mmol) HAuCl₄·3H₂O aqueous solution at MWCNTs:Au=1:1 (w/w) and 5 ml 0.05 M (0.25 mmol) TCD aqueous solution at
Au:TCD:NaBH$_4$=1:1:1.2 (mole ratios) were added into the MWCNTs dispersion. After 3 ml 0.1 M NaBH$_4$ (0.3 mmol) aqueous solution was promptly added while stirring, the color of the solution could be observed to quickly turn to burgundy. The reaction proceeded at room temperature for 24 h with stirring. The mixture solution was centrifuged to collect the sediments at substratum, and the solid was dried at 80 °C, affording MWCNTs@Au nanocomposites (Yield: 72%; theoretical amount of Au NPs: 0.0353 g, 2.10 mmol g$^{-1}$). Likewise, MWCNTs@Au nanocomposites with MWCNTs:Au (w/w)=1:2 and 1:4 could be prepared in the same way.

3. Preparation and characterization of monomer MAEFc containing ferrocenes

2-Methacryloyloxyethyl ferrocenecarboxylate (MAEFc) was synthesized through the esterification reaction between FCA and HEMA, as shown in Figure S1(a). In detail, 9.2 g FCA (40.0 mmol), 4.88 g DMAP (40.0 mmol) and 5.86 ml HEMA (48.4 mmol) were added into a hermetic 500 ml three-neck flask in sequence, and then completely dissolved in 300 ml dried DCM at a stirring rate of 1500 rpm. The reaction system was charged with nitrogen and kept stirring for about 60 min. Meanwhile, 9.9 g DCC (48.0 mmol) was fully dissolved in 60 ml desiccative DCM in a 200 ml beaker. When the reaction temperature was cooled to 0 °C, the DCC-DCM solution was dropwise added to the reaction flask within about 60 min through constant pressure funnel. After that, the reaction proceeded at 30 °C for 24 h. The reaction mixture was filtered two or three times to completely remove the byproduct, 1,3-dicyclohexylurea (DCU). The filtrates were evaporated via rotary evaporator, and extracted with saturated NaHCO$_3$ solution several times to remove redundant and/or unreacted DMAP, HEMA and FCA, and extracted with deionized water three times to remove the residual saturated NaHCO$_3$ solution. Anhydrous magnesium sulfate was added into the extractant, and then the crude product was let stand for overnight. The suction filtration was performed to
remove anhydrous magnesium sulfate, and the rotary evaporation operation was conducted to get rid of partial solvents. The purified product was obtained through silica gel column chromatography using petroleum ether and ethyl acetate (v/v=9:1) as developing solvent. The collected orange solution from the first dot was rotarily evaporated and dried in a vacuum oven at 30 °C for 24 h, giving a pure MAEFc (Mean yield: 76%).

Figure S1 Synthesis scheme (a), 1H NMR in CDCl₃ (b) and FTIR spectra (c) of monomer MAEFc containing ferrocenes.

1H NMR spectrum of monomer MAEFc containing ferrocenes is shown in Figure S1(b). The chemical shift signals reflecting ferrocene structural features are located at δ=4.21, 4.48 and 4.82 ppm, which are assigned to the hydrogen proton signals in unsubstituted dicyclopentadienyl rings (5H, s, -Cp/-C₅H₅), the proton signals in the meta-position (2H, m, m-C₅H₄) and the ortho-position (2H, m, o-C₅H₄) of monosubstituted dicyclopentadienyl rings, respectively. The methylene proton shift signals near terminal double bonds and close to Cp appear at δ=4.48 (2H, t, Cp-OCOCH₂=CH₂OCO-) and 4.42 ppm (2H, t, Cp-OCOCH₂=CH₂OCO-), respectively,
where the two signals at $\delta=4.48$ ppm are overlapped corresponding to the above ferrocene and methylene signals. The hydrogen proton resonance signals assigned to the splitting of terminal vinyl groups emerge at $\delta=5.64$ and 6.21 ppm (2H, $d$, -OOC(CH$_3$)=CH$_2$), and the shift signal at $\delta=2.00$ ppm is attributed to the methyl proton shift (3H, s, -OOC(CH$_3$)=CH$_2$) [1,2]. FTIR spectrum of MAEFe is presented in Figure S1(c). It is noticed that MAEFe produces characteristic vibration bands at 3100 and 772-824 cm$^{-1}$ assigned to the $=C$-H stretch in Cp rings including terminal double bonds and $=C$-H bending vibration modes in ferrocene rings; peaks at 2880-2980, 1715, 1600, 1133-1277, 1022-1056 and 457-540 (or 496) cm$^{-1}$ are attributed to the C-H stretch, C=O stretch, C=C stretch, C-O stretch, skeleton characteristic peak of Cp rings and Fe-C or Cp-Fe stretch modes [3], respectively. These findings suggest the successful synthesis of the monomer MAEFe containing ferrocenes.

4. EDX results

EDX results are demonstrated in Figures S2 and S3.

![EDX spectrum](image)

Figure S2 EDX spectrum attached to TEM of MWCNTs@Au nanocomposites.

5. O 1s and C 1s core-level XPS spectra

Figure S4 shows high-resolution XPS spectra of elements C and O in the original pristine MWCNTs, MWCNTs@Au, monomer MAEFe, and MWCNTs@Au-g-PMAEFe nanohybrids. The C 1s high-resolution XPS spectrum of
MWCNTs in Figure S4(a) shows the existence of two main signal peaks at BEs of 284.8 and 285.5 eV, which correspond to the \( \text{sp}^2 \) hybridized carbon atoms in \( \pi^* \) conjugated systems (C=C) and \( \text{sp}^3 \) hybridized C-C bonds at defects and tube structural asymmetry. This indicates that MWCNTs mainly contains element C, reflecting the characteristics of the original MWCNTs [4]. The C 1s high-resolution XPS spectrum in MWCNTs@Au in Figure S4(b) offers four signal peaks at BEs of 284.7, 285.8, 287.0 and 289.2 eV, which separately correspond to the graphene carbon (C=C), C-C single bonds, C-O and -C=O/O=C-O bonds formed by the carbon atoms in MWCNTs and Au NPs sols. Compared with MWCNTs, the emergence of new signals at 287.0 and 289.2 eV and the slight change of BEs at 285.8 eV signify that there exist certain interactions between MWCNTs and Au NPs. The core-level XPS spectrum fitting peak of C 1s orbits in MAEFc is depicted in Figure S4(c). Six kinds of different C elements exist, which have BEs of about 284.2, 284.8, 285.4, 286.2, 287.0 and 288.9 eV corresponding to C=C, C-Fc, C-C, C-O, (R-) C=O and O-C=O, respectively [5-7]. The O 1s core-level spectrum in Figure S4(d) reveals the existence of three kinds of chemically different O species at BEs of about 529.8, 530.9 and 531.8 eV, which is assigned to the photoelectronic signals of the O=C, O-C and -O-C=O bonds in
Figure S4 High-resolution XPS spectra of elements C and O: (a) C 1s in the original pristine MWCNTs, (b) C 1s in MWCNTs@Au nanocomposites, (c) C 1s and (d) O 1s in MAEFc, and (e) C 1s and (f) O 1s in MWCNTs@Au-g-PMAEFc nanohybrids.
MWCNTs@Au-g-PMAEFc [8]. The C 1s core-level spectrum in MWCNTs@Au-g-PMAEFc is illustrated in Figure S4(e) (SI). It is noticed that there exist several signal peaks at BEs of 284.3, 284.7, 285.4, 285.8, 286.3, 286.7, 287.3 and 289.2 eV, which correspond to the C=C, ferrocenyl carbons (C-Fe), C-C, C-S, C-O, C-Br, (R-)C=O and O-C=O electronic transition, respectively [9,10]. The O 1s core-level XPS spectra in Figure S4(f) (SI) suggest the presence of three kinds of chemically different O species at BEs of about 529.8, 530.9 and 531.7 eV, which is associated with the photoelectronic signals of the O=C, O-C and -O-C=O bonds in MWCNTs@Au-g-PMAEFc [8]. These results are in consistent with the C 1s and O 1s XPS spectra in MAEFc in Figures S4(c) and S4(d) (SI), signifying that PMAEFc moieties are grafted onto the surface of MWCNTs or MWCNTs@Au, affording MWCNTs@Au-g-PMAEFc organic-inorganic nanohybrids.

6. CV determination

The CV determination results are listed in Table S1.

Table S1 Electrochemical data of the nanohybrids with various composition ratios.

<table>
<thead>
<tr>
<th>Response type</th>
<th>Curve type</th>
<th>E_{p,a}, V</th>
<th>E_{p,c}, V</th>
<th>ΔE_{p}, mV</th>
<th>I_{p,a}/I_{p,c}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au NPs</td>
<td>Curve a</td>
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<td>-0.30</td>
<td>340</td>
<td>1.31</td>
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<tr>
<td></td>
<td>Curve b</td>
<td>-0.045</td>
<td>-0.27</td>
<td>225</td>
<td>1.15</td>
</tr>
<tr>
<td></td>
<td>Curve c</td>
<td>-0.05</td>
<td>-0.25</td>
<td>200</td>
<td>0.91</td>
</tr>
<tr>
<td>PMAEFc</td>
<td>Curve a</td>
<td>0.20</td>
<td>-0.015</td>
<td>215</td>
<td>1.20</td>
</tr>
<tr>
<td></td>
<td>Curve b</td>
<td>0.19</td>
<td>0.018</td>
<td>172</td>
<td>1.60</td>
</tr>
<tr>
<td></td>
<td>Curve c</td>
<td>0.18</td>
<td>0.03</td>
<td>150</td>
<td>1.07</td>
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7. Reproducibility and stability of the modified electrodes

Figure S5 DPV current response in PBS of pH 7.0: (a) with time at trichlorfon concentration of $2.5 \times 10^{-8}$ mol L$^{-1}$, (b) determined by five modified electrodes fabricated individually at trichlorfon concentration of $2.5 \times 10^{-8}$ mol L$^{-1}$, and by six measurements using the same modified electrode at trichlorfon concentration of (c) $5 \times 10^{-7}$ and (d) $5 \times 10^{-8}$ mol L$^{-1}$.

8. Detection of trace poisonous and harmful substances

Experimental data of trace trichlorfon residues in real samples are summarized in Table S2 in the next page.
Table S2 Experimental data of trace trichlorfon residues in real samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Added (10⁻⁸ mol L⁻¹)</th>
<th>Found a (10⁻⁸ mol L⁻¹)</th>
<th>RSD (%)</th>
<th>Recovery (%)</th>
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</thead>
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<tr>
<td>Apple</td>
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<td>0.92</td>
<td>0.9</td>
<td>92.0</td>
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<td></td>
<td>2.0</td>
<td>1.88</td>
<td>4.3</td>
<td>94.0</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>4.06</td>
<td>2.8</td>
<td>101.5</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>0.89</td>
<td>0.6</td>
<td>89.0</td>
</tr>
<tr>
<td>Tomato</td>
<td>2.0</td>
<td>1.96</td>
<td>3.1</td>
<td>98.0</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>3.96</td>
<td>6.4</td>
<td>99.0</td>
</tr>
<tr>
<td>Cucumber</td>
<td>2.0</td>
<td>1.95</td>
<td>5.1</td>
<td>97.5</td>
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<tr>
<td></td>
<td>4.0</td>
<td>4.10</td>
<td>3.7</td>
<td>102.5</td>
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* represents the average value of five measurements.

References


