SUPPLEMENTARY INFORMATION

Gold nanoshells with magnetic cores and an urea-based receptor for SERS sensing of fluoride anions: experimental and computational study

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1. Synthesis

1.1 Materials

Besides basic inorganic materials and common reagents, the following chemicals were used for the synthesis of gold nanoshells with silica-coated Mn-Zn ferricore: tetraethoxysilane (TEOS) (≥99.0 % (GC)), poly(vinylpyrrolidone) (PVP) (K90 with average $M_r$ ≈ 360,000, ≥99.0 %) tetrakis(hydroxymethyl)phosphonium chloride (80 wt% solution in H$_2$O), poly(diallyldimethylammonium chloride) (PDADMAC) ($M_r$ ≈ 100,000, 35 wt% in H$_2$O), and poly(sodium 4-styrenesulfonate) (PSS) ($M_r$ ≈ 70,000, 30 wt% in H$_2$O). Several organic chemicals were employed for the functionalization of gold nanoshells and for the synthesis of the model urea-based sensor: 4-nitrothiophenol (80 %), 4-aminothiophenol (97 %), 4-nitrophenylisocyanate (97 %), and 4-bromoaniline (97 %). All the mentioned chemicals were purchased from Sigma Aldrich and used as received.

Commercial dimethyl sulfoxide (DMSO) (Riedel-de Haén, 99.5 %) was used as a solvent in the Raman spectroscopic study of the model urea-based sensor, whereas the SERS study on sensing of fluoride ions was carried out in acetonitrile (Carl Roth, ROTISOLV®, ≥99.9 %, für die DNA-Synthese, H$_2$O ≤0.001 %).

1.2. Synthesis of Mn$_{0.6}$Zn$_{0.4}$Fe$_3$O$_4$ nanoparticles (MZF)

Aqueous solutions of Mn(II), Zn(II) and Fe(III) nitrates, slightly acidified with nitric acid (1.3 %) and with concentrations accurately determined by chelometric titrations, were combined in a molar ratio of Mn:Zn:Fe = 0.60:0.40:1.80, reaching a total metal content of 5.6 mmol in the mixture. The solution was concentrated in vacuo and transferred to the inert atmosphere. While magnetically stirring, ≈2 M NaOH solution was slowly added to the mixture to reach pH = 10.0, which led to the formation of brown precipitates. The final volume was adjusted to 25 mL. The mixture was transferred into a Berghof DAB-2 pressure vessel with a 50 mL Teflon insert and subjected to the hydrothermal treatment under autogenous pressure at 180 °C for 12 h while magnetically stirring. The product was separated by centrifugation, washed several times with water and ethanol and then dried in vacuo. The amount of material prepared in a single batch was 0.43 g.

1.3. Encapsulation of MZF into silica (MZF@sil)

The amount of 115 mg of MZF particles was added into 300 mL of 1.2 wt% PVP K90 solution in water and sonicated overnight. The particles were separated by centrifugation and washed with 20 mL of ethanol. The residue was redispersed in 190 mL of ethanol by ultrasound agitation for 2 h. Then a Teflon mechanical stirrer was introduced into the flask and while both sonicating and mechanical stirring, 0.6 mL of TEOS was added, followed by 32 mL of 29 wt% NH$_4$OH.
solution. After one minute, the ultrasound was terminated, and the mixture was further mechanically stirred overnight.

The raw product was separated by centrifugation and washed four times with ethanol, three times with water and then redispersed in 240 mL of water. The heavy fractions were removed by mass fractionation at 260 RCF for 15 min, the supernatant was collected and concentrated to the volume of 20 mL. The ferrite content was determined to 1.1 mg(MZF) mL\(^{-1}\) based on SQUID magnetometry, which corresponds to a yield of 19 % with respect to MZF particles.

1.4. Synthesis of the gold nanoshells (MZF@sil@Au)

At first, gold seeds (GNP) were prepared by the Duff’s method as follows. To the mixture of 45.5 mL of water, 1.5 mL of 0.2 M NaOH, and 1 mL of 33 μM THPC in a round-bottom flask, 2 mL of chloroauric acid with a concentration of 10 mg(HAuCl\(_4\)·3H\(_2\)O) mL\(^{-1}\) was added while magnetic stirring. A brownish suspension was immediately formed. After 2 h, the suspension was concentrated \textit{in vacuo} to ca. 15 mL and destabilized with 35 mL of acetone. The mixture was centrifuged at 7,450 RCF for 1 h, and the supernatant was carefully removed. The corresponding residue was dispersed in water, and the residual acetone was evaporated \textit{in vacuo}. The final volume of GNP suspension was adjusted to 50 mL.

In the second step, MZF@sil nanoparticles were decorated by GNP seeds as follows. To the mixture of 1 mL of 3 M NaCl and 5 μL of PDADMAC in a small round-bottom flask, 2 mL of the stock suspension of MZF@sil particles (1.1 mg(MZF) mL\(^{-1}\)) was added. The mixture was sonicated for 30 min and then centrifuged at 15,800 RCF for 10 min. Supernatant was discarded, and nanoparticles were redispersed in 2 mL of water. This treatment was repeated in the same way with PSS and again with PDADMAC. After the last treatment, the nanoparticles were washed three times with water and redispersed in 2 mL of water. The suspension was added dropwise to 45 mL of the GNP suspension prepared in the first step, and the resulting mixture was sonicated overnight in a bath tempered to \(\approx 25 ^\circ\text{C}\). The mixture was subjected to centrifugation at 4,200 RCF for 30 min, whereby the decorated MZF@sil@GNP particles were sedimented while unattached GNP seeds remained in the supernatant. The residue was dispersed in water and additional five cycles of the centrifugation under the same conditions and removal of the supernatant were carried out to completely remove any free GNP seeds. The purified MZF@sil@GNP particles were dispersed in the final volume of 20 mL of water.

In the last step, gold nanoshells were achieved by the growth of gold seeds attached on the silica surface by reduction of a soluble Au(III) precursor with L-ascorbic acid as follows. As the precursor, so-called K-gold solution was prepared by adding 1 mL of chloroauric acid with a concentration of 10 mg(HAuCl\(_4\)·3H\(_2\)O) mL\(^{-1}\) was added to 9 mL of 15 mM K\(_2\)CO\(_3\). The mixture was stored in a dark overnight at 5 \(^{\circ}\text{C}\), accompanied by a transition from pale yellow to colourless. The so-obtained K-gold solution was diluted 10 times and added dropwise at a rate of 1 mL min\(^{-1}\) to the mixture of 2.5 mL of the MZF@sil@GNP suspension, 37.5 mL of water and 10 mL of 3 mM L-ascorbic acid in a round-bottom flask while both mechanically stirring and sonication were applied. The flask was placed in an ultrasound bath tempered to \(\approx 25 ^\circ\text{C}\). Throughout the addition of the K-gold solution, a colour transition was observed from pale red through purple to deep blue-green, indicating gradual growth and fusion of GNP attached to the silica surface. The resulting product (MZF@sil@Au) was separated by centrifugation and washed with water.

1.5. Synthesis of the gold nanoshells with varying thickness (MZF@sil@Au-x)

For the preparation of the MZF@sil@Au-x series, where \(x = I, II, III, IV\), the same procedure was applied but the last step, when the growth of gold seeds occurs, was modified as follows. The diluted K-gold (100 mL in total) was added dropwise at a lower rate of 0.42 mL min\(^{-1}\) to the same initial mixture (2.5 mL of the MZF@sil@GNP suspension with a concentration of 0.11 mg(MZF) mL\(^{-1}\), 37.5 mL of water and 10 mL of 3 mM L-ascorbic acid) with a starting volume of 50 mL. During the gradual addition of the K-gold that lasted for 4 hours, a series of samples was obtained. The \(x\)-th sample with a volume of \(V_{sa}(x)\) was collected from the flask once a required volume of the K-gold, \(V_{kg}(x)\), was added to the reaction mixture with an initial volume (the final volume from the previous step) of \(V_{0}(x)\). Each separated sample was subjected to exhaustive centrifugation, and the particles were washed with water and acetonitrile, and were redispersed in acetonitrile. The final suspensions were accurately adjusted, by weighing and adding acetonitrile, to final weights of \(m(x)\) to achieve the same concentration of MZF cores of 0.14 mg(MZF) g\(^{-1}\) (110 mg(MZF) L\(^{-1}\)) in each sample. In total, five samples were obtained according to Table S1.
Table S1. Preparation of MZF@sil@Au-\(x\), where \(x = I, II, III, IV\), by successive sampling of particles during the growth stage of gold nanoshells (for the meaning of symbols, see the text above).

<table>
<thead>
<tr>
<th>MZF@sil@Au-(x)</th>
<th>(V_0(x)) [mL]</th>
<th>(V_{Kg}(x)) [mL]</th>
<th>(V_{sa}(x)) [mL]</th>
<th>(m(x)) [mg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>50</td>
<td>10</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>MZF@sil@Au-I</td>
<td>50</td>
<td>10</td>
<td>10</td>
<td>275</td>
</tr>
<tr>
<td>MZF@sil@Au-II</td>
<td>50</td>
<td>10</td>
<td>10</td>
<td>229</td>
</tr>
<tr>
<td>MZF@sil@Au-III</td>
<td>50</td>
<td>20</td>
<td>12</td>
<td>197</td>
</tr>
<tr>
<td>MZF@sil@Au-IV**</td>
<td>58</td>
<td>50</td>
<td>108</td>
<td>950</td>
</tr>
</tbody>
</table>

* The first sample with just slightly enlarged gold seeds was omitted from this study.
** The last sample corresponded to the remaining reaction mixture after the addition of K-gold had been completed.

2. Characterizations of nanoparticles and identification of molecular compounds

![Figure S1](image1)

Fig. S1. \(^1\)H NMR spectrum of the BrPNPU.

![Figure S2](image2)

Fig. S2. Powder XRD pattern of the bare MZF nanoparticles. The red line shows the fit by the Rietveld method, the green bars mark the diffraction lines of the spinel structure (space group \(Fd\bar{3}m\)).
Fig. S3. Magnetic properties of bare MZF nanoparticles. (a) Hysteresis loops at 5 K and 300 K, a detail at low fields is shown in the inset (the apparent coercivity of the room-temperature loop is of the order of remanent fields in the superconducting winding of the magnetometer). (b) Mass susceptibilities measured in the zero-field-cooled (ZFC) and field-cooled (FC) regimes, $\chi_{ZFC}$ and $\chi_{FC}$, in the magnetic field of $\mu_0 H = 2$ mT (left axis) and the temperature derivative of the $\chi_{FC} - \chi_{ZFC}$ susceptibility difference (right axis), reflecting the distribution of blocking temperatures. (c) Temperature-dependent measurement of remanent magnetization, which was recorded during heating in zero magnetic field after magnetizing the sample at 5 K and in magnetic field of 1 T.
Fig. S4. Transmission electron micrographs, at two different magnifications, of supplemental samples MZF@sil@Au-x (x = I, II, III, IV) with gradually growing relative content of gold in the given series: (a,b) MZF@sil@Au-I, (c,d) MZF@sil@Au-II, (e,f) MZF@sil@Au-III, (g,h) MZF@sil@Au-IV.
Fig. S5. APCI-MS of the acetonitrile extract of the residue obtained by subjecting the MPNPU-functionalized gold nanoparticles to cyanide leaching. The inset shows the most intense peak, which is assigned to the [M–H]$^-$ ion of the MPNPU sensor.

3. Raman spectroscopy and DFT calculations

Fig. S6. Experimental Raman spectra of BrPNPU (0.1 mol L$^{-1}$) and Bu$_4$NF (2 mol L$^{-1}$) in DMSO. The intensities of all spectra were normalized to unity at the maximum of the DMSO band at 669 cm$^{-1}$. 
Fig. S7. Comparison of the calculated Raman spectra of BrPNPU in DMSO approximated solely by the PCM (red) and with a DMSO molecule included explicitly, forming hydrogen bonds with the urea moiety, also in the PCM approximation of the solvent (black). The inset shows a selected vibrational mode of the BrPNPU at 1300 cm$^{-1}$, which is impacted by the hydrogen-bonded DMSO molecule, and the optimized geometry of the given supramolecular complex (C – black, H – grey, O – red, N – blue, S – yellow, Br – claret, the arrows indicate the movement of the atoms).

Fig. S8. Comparison of SERS spectra of MZF@sil@Au nanoshells functionalized solely with the urea-based sensor (MPNPU) or with $p$-nitrothiophenol (NTP) or with the combination of both compounds (MPNPU and NTP in a molar ratio of 10:1), measured in acetonitrile. Note that the concentration of the acetonitrile suspension of the NTP-functionalized nanoshells was 2.3 times higher, and the given functionalization was performed at a higher concentration of 10 mmol L$^{-1}$ of NTP, which results in the lower relative intensity of acetonitrile bands in the respective Raman spectrum.
Fig. S9. (a) Selected region of the SERS spectra of MZF@sil@Au nanoshells functionalized with MPNPU or/and NTP (a detail of Fig. S8) and (b) their second derivatives. The marked bands correspond to the bands of the respective molecules according to the colour legend, and arbitrary scaling was applied.

Fig. S10. Detail of second derivatives of the SERS spectra in Fig. S9, shown for illustration in the same range of Raman shifts as in Fig. 7b in the main text. Dashed lines mark the examined peaks, and arbitrary scaling was applied.
Fig. S11. (a) SERS spectra measured on the functionalized (with both MPNPU and NTP) gold nanoshells in acetonitrile with varying concentrations of Bu₄NF. (b) Their second derivatives normalized by dividing them by the absolute value of the 2nd derivative at 854 cm⁻¹ (the NTP band).
Fig. S12. SERS spectra of the series of MZF@sil@Au-x (x = I, II, III, IV) samples functionalized with NTP: (a) raw spectra measured at a constant concentration of 110 mg(MZF) L⁻¹, (b) the spectra rescaled to match the intensity of the acetonitrile band at 2943 cm⁻¹.

Fig. S13. Comparison of the calculated Raman spectra of the MPNPU molecule bonded to a cluster of seven gold atoms in acetonitrile and of the free BrPNPU molecule in DMSO, the solvents were approximated by PCM. The comparison of calculated spectra in the gas phase follows in the lower part of the figure.
Fig. S14. Comparison of the calculated Raman spectra of the neutral MPNPU molecules bonded to gold clusters of three different sizes in acetonitrile, supplemented by the calculated spectrum of the free BrPNPU molecule in DMSO. For the combination MPNPU-Au₃, the calculated intensities highly exceeded the other spectra.

Fig. S15. Comparison of calculated spectra of the MPNPU⁻ anions bonded to gold clusters of three different sizes in acetonitrile and of the free BrPNPU⁻ anion in DMSO. The band of the nitro group vibrations with the intensity independent of the cluster size, as mentioned in the main text, is marked with the black arrow.