Electronic Supplementary Information

Transition Metal Ions–Assisted Synthesis of Monodisperse, Quasi-Spherical Gold Nanocrystals via Citrate Reduction

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Fig. S1 HRTEM images (a and b) of Au NCs shown in Fig. 1e and Fig. 1f, respectively.
Fig. S2 HRTEM images of Au NCs shown in Fig. 4c.
Fig. S3 HRTEM images of Au NCs shown in Fig. 5a.
Fig. S4 HRTEM images (a and b) of Au NCs shown in Fig. 7a and Fig. 7b, respectively.
Fig. S5 UV-vis spectra of Au NCs obtained via Frens method (black curves) and the solution of as-prepared Au NCs after centrifugation treatment (red curves). The concentrations of HAuCl₄ and sodium citrate used are 0.01 wt % and $3 \times 10^{-2}$ wt %, respectively.
Fig. S6 TEM images of Au NCs obtained via Ag⁺-assisted Frens method under different concentrations of silver ions: $6 \times 10^{-4}$ wt% (a) and $1.0 \times 10^{-3}$ wt% (b). The concentrations of HAuCl₄ and citrate used were 0.01 wt% and $6 \times 10^{-3}$ wt%, respectively.
Fig. S7 TEM images of Au NCs obtained via Ag⁺-assisted Frens method under different AgNO₃ concentrations: $5 \times 10^{-4}$ wt% (a) and $6 \times 10^{-4}$ wt% (b). The concentrations of HAuCl₄ and citrate used were 0.01 wt% and $4.2 \times 10^{-3}$ wt%, respectively.
**Fig. S8** TEM images of the corresponding Au NCs obtained via Ag⁺/Fe²⁺-assisted Frens method under different FeCl₂ concentrations: $1.0 \times 10^{-5}$ wt % (a) and $2 \times 10^{-5}$ wt % (b). The concentrations of HAuCl₄, AgNO₃ and citrate used were always 0.01 wt %, $8.5 \times 10^{-4}$ wt %, and $6 \times 10^{-3}$ wt %, respectively.
Fig. S9 TEM images of Au NCs obtained via Ag⁺/Fe²⁺-assisted Frens method under different FeCl₂ concentrations: $4 \times 10^{-6}$ wt % (a) and $6 \times 10^{-6}$ wt % (b). The concentrations of HAuCl₄, citrate and AgNO₃ used were 0.01 wt%, $4.2 \times 10^{-3}$ wt % and $5.5 \times 10^{-4}$ wt %, respectively.
Table S1 Summary of the redox potential values of half-reaction of Au$^{3+}$/Au$^0$, Fe$^{3+}$/Fe$^{2+}$, and Cu$^{2+}$/Cu$^+$.  

<table>
<thead>
<tr>
<th>Half-reaction</th>
<th>Potential values (V)</th>
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<tbody>
<tr>
<td>Au$^{3+}$ + 3e ↔ Au$^0$</td>
<td>1.498</td>
</tr>
<tr>
<td>Fe$^{3+}$ + e ↔ Fe$^{2+}$</td>
<td>0.771</td>
</tr>
<tr>
<td>Cu$^{2+}$ + e ↔ Cu$^+$</td>
<td>0.153</td>
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