

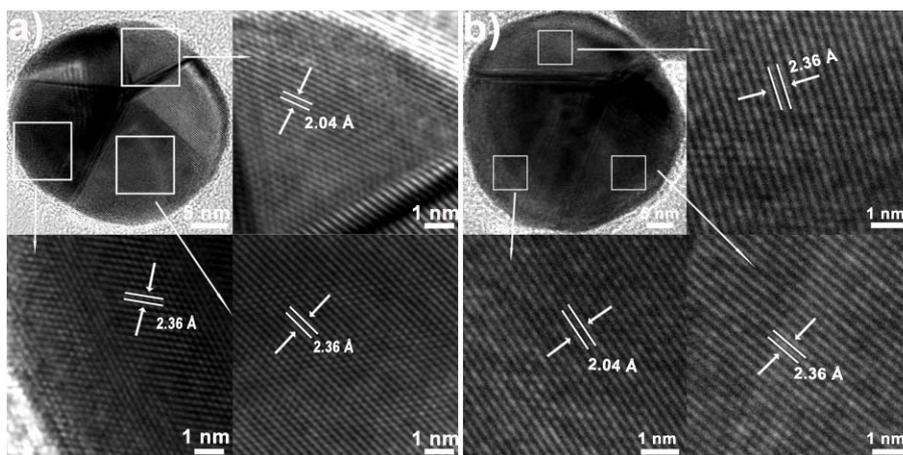
## Electronic Supplementary Information

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

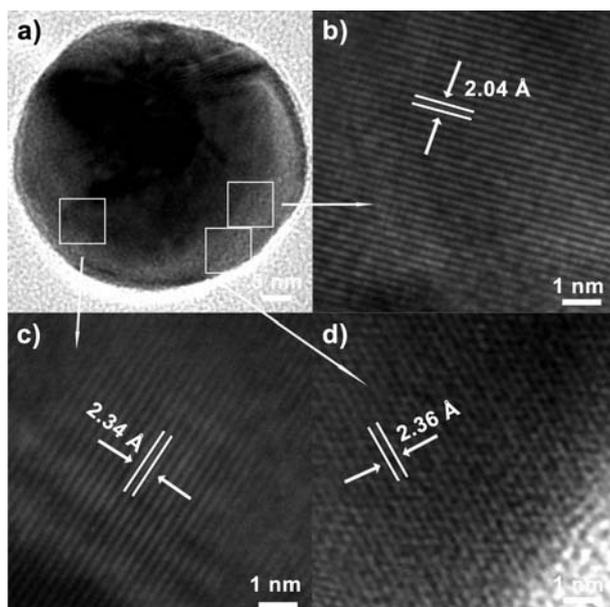
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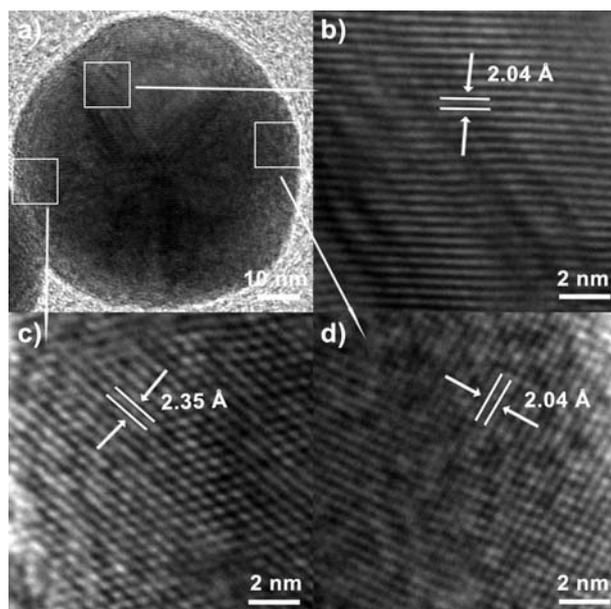
<sup>b</sup>Ian Wark Research Institute, University of South Australia, Adelaide, SA 5095, Australia



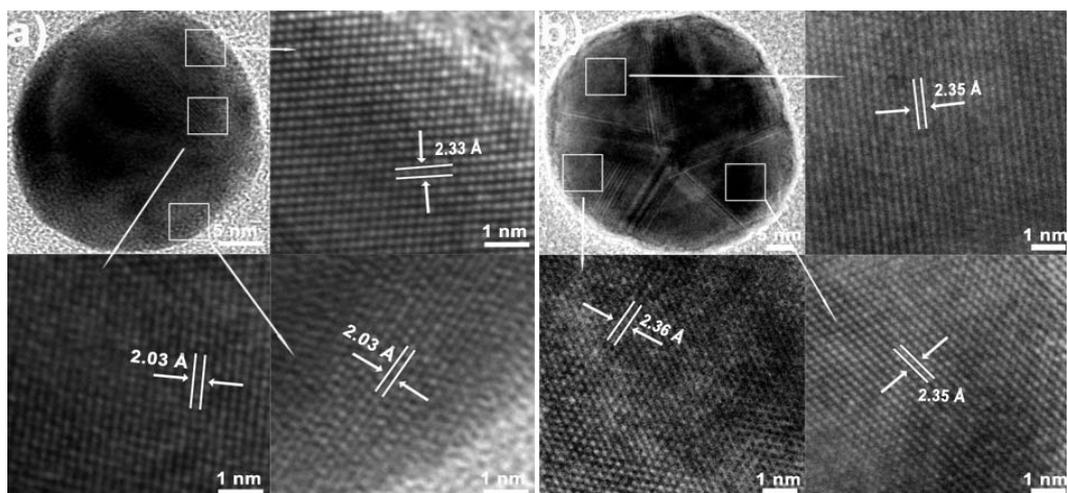
**Fig. S1** HRTEM images (a and b) of Au NCs shown in Fig. 1e and Fig. 1f, respectively.



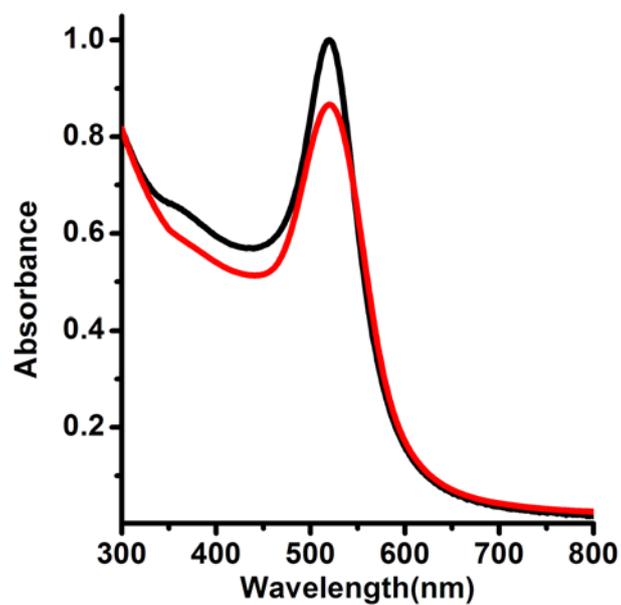
**Fig. S2** HRTEM images of Au NCs shown in Fig. 4c.



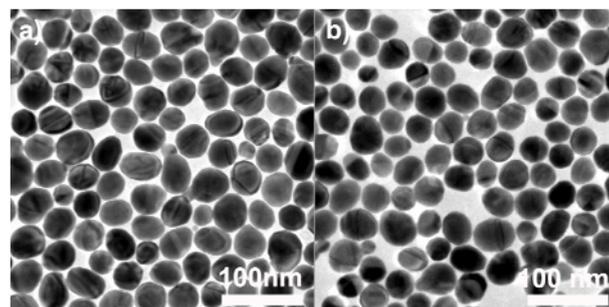
**Fig. S3** HRTEM images of Au NCs shown in Fig. 5a.



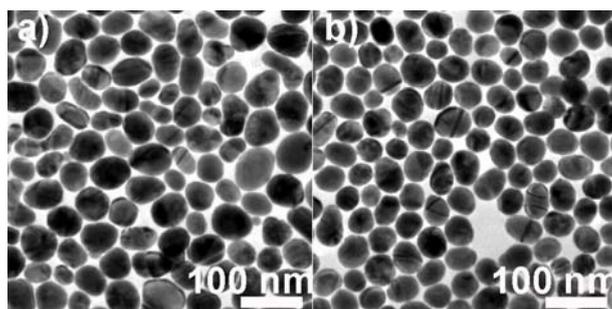
**Fig. S4** HRTEM images (a and b) of Au NCs shown in Fig. 7a and Fig. 7b, respectively.



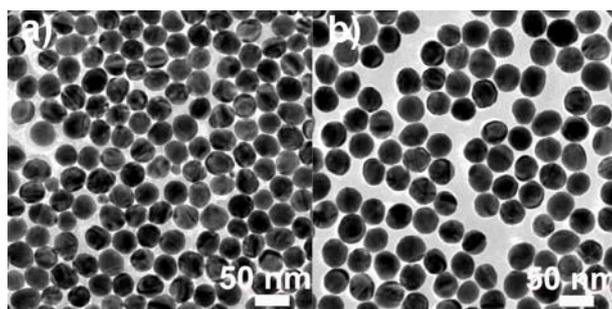
**Fig. S5** UV-vis spectra of Au NCs obtained via Frens method (black curves) and the solution of as-prepared Au NCs after centrifugation treatment (red curves). The concentrations of  $\text{HAuCl}_4$  and sodium citrate used are 0.01 wt % and  $3 \times 10^{-2}$  wt %, respectively.



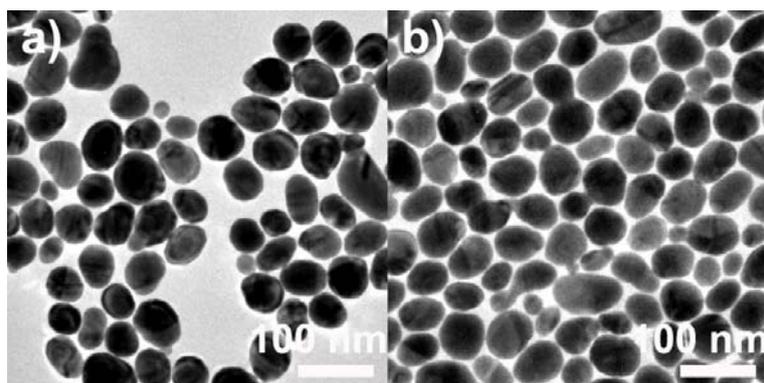
**Fig. S6** TEM images of Au NCs obtained via  $\text{Ag}^+$ -assisted Frens method under different concentrations of silver ions:  $6 \times 10^{-4}$  wt% (a) and  $1.0 \times 10^{-3}$  wt% (b). The concentrations of  $\text{HAuCl}_4$  and citrate used were 0.01 wt% and  $6 \times 10^{-3}$  wt%, respectively.



**Fig. S7** TEM images of Au NCs obtained via  $\text{Ag}^+$ -assisted Frens method under different  $\text{AgNO}_3$  concentrations:  $5 \times 10^{-4}$  wt% (a) and  $6 \times 10^{-4}$  wt% (b). The concentrations of  $\text{HAuCl}_4$  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  $\text{Ag}^+/\text{Fe}^{2+}$ -assisted Frens method under different  $\text{FeCl}_2$  concentrations:  $1.0 \times 10^{-5}$  wt % (a) and  $2 \times 10^{-5}$  wt % (b). The concentrations of  $\text{HAuCl}_4$ ,  $\text{AgNO}_3$  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  $\text{Ag}^+/\text{Fe}^{2+}$ -assisted Frens method under different  $\text{FeCl}_2$  concentrations:  $4 \times 10^{-6}$  wt % (a) and  $6 \times 10^{-6}$  wt % (b). The concentrations of  $\text{HAuCl}_4$ , citrate and  $\text{AgNO}_3$  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  $\text{Au}^{3+}/\text{Au}^0$ ,  $\text{Fe}^{3+}/\text{Fe}^{2+}$ , and  $\text{Cu}^{2+}/\text{Cu}^+$ .

Half-reaction	Potential values (V)
$\text{Au}^{3+} + 3\text{e} \leftrightarrow \text{Au}^0$	1.498
$\text{Fe}^{3+} + \text{e} \leftrightarrow \text{Fe}^{2+}$	0.771
$\text{Cu}^{2+} + \text{e} \leftrightarrow \text{Cu}^+$	0.153