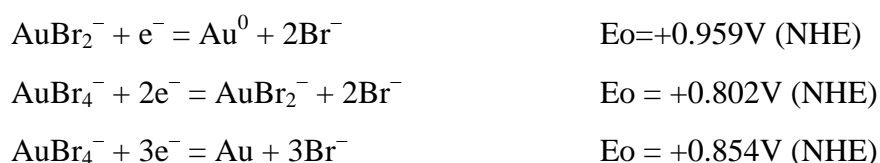


# Curvature-Dependent Oxidation of Gold Nanoparticles by Au(III)-CTAB Complexes

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## Discussion on the effect of bromide ions on the equilibrium constant of equation (1):

For the discussion of the redox reaction (1) between  $\text{AuCl}_4^-$  and  $\text{Au}^0$  in the presence of CTAB, the possibility of having  $\text{AuBr}_4^-$  and  $\text{AuBr}_2^-$  instead of  $\text{AuCl}_4^-$  and  $\text{AuCl}_2^-$  should be considered, since at least two of the chloride ions can be exchanged by bromide. The redox potentials are then:



The value of the equilibrium constant for the conproportionation of  $\text{AuBr}_2^-$  can then be calculated as:



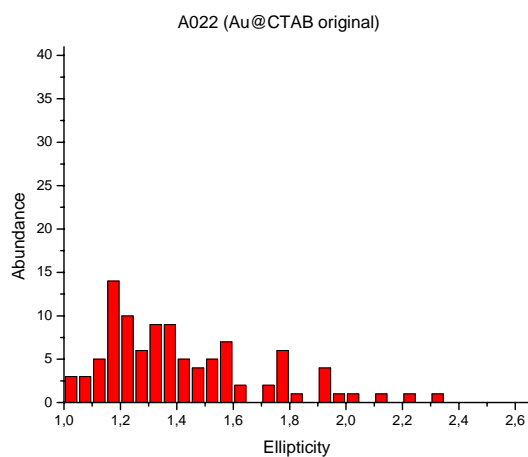
being almost 260 times higher than in the case of gold chloride ions.

Additionally, the presence of CTAB 0.05M leads to another change in the equilibrium constant since now the free bromide ions arising from surfactant dissociation must be considered. Assuming a value of  $\beta=0.8$  ( $\beta$  being the fraction of micellar charge neutralized by the counterions), at least 20% of the bromide from CTAB will be in solution. Hence, if  $[\text{CTAB}]=0.05\text{M}$ , then  $0.01\text{M Br}^-$  enters the equilibrium and,

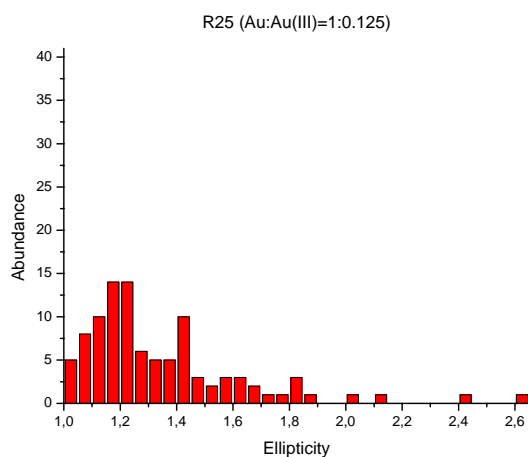
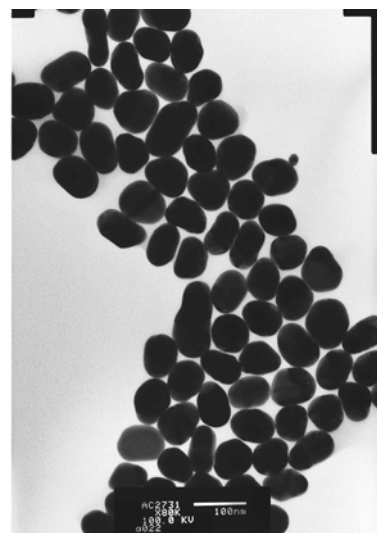
$$K > (3.75 \times 10^{-4})^3 / [1 \times 10^{-6} \times (0.01)^2] = 0.527$$

The value of the constant is thus lower, but still the equilibrium constant will increase at least by a factor of  $1.07 \times 10^5$  due to binding with CTAB. It should be taken into account that an amount of  $\text{AuBr}_2^-$ -CTAB left in solution of  $1\mu\text{M}$  has been used, while it can be considerably lower.

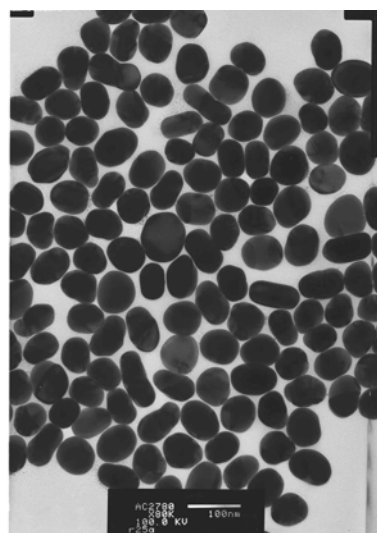
**Supporting Information Figure 1.** TEM micrographs and ellipticity distributions (histograms) of Au nanoparticles before (a) and after addition of  $\text{HAuCl}_4$  with different  $\text{Au}:\text{Au}^{\text{III}}$  molar ratios [1:0.125 (b), 1:0.25 (c), 1:0.30 (d), 1:0.34 (e), 1:0.4 (f)] in the presence of CTAB 0.05 M.

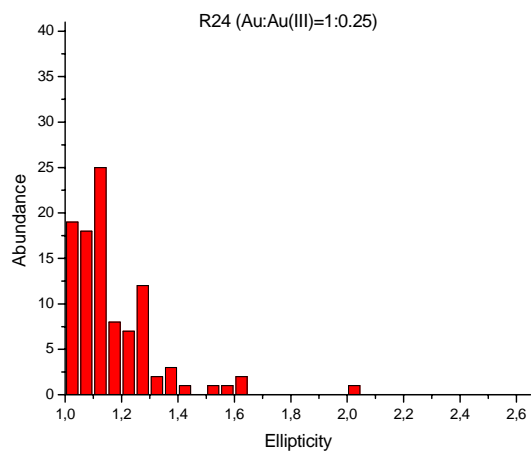


(a)

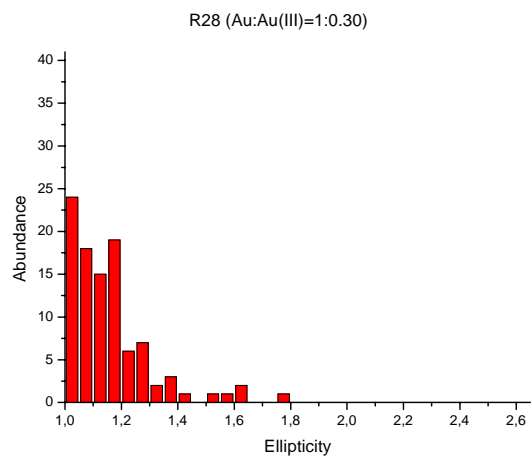
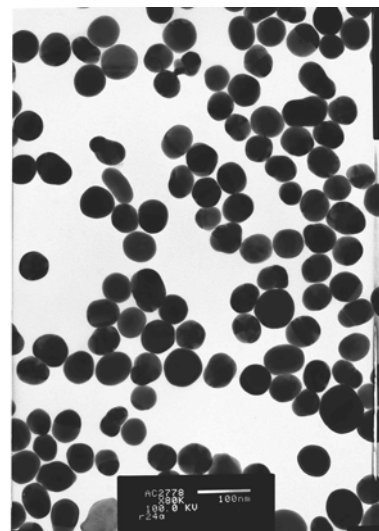


(b)

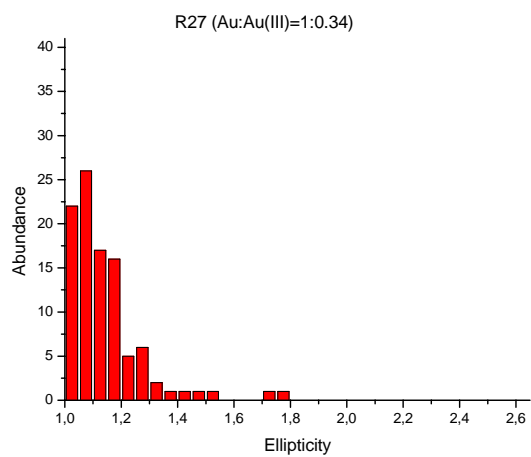
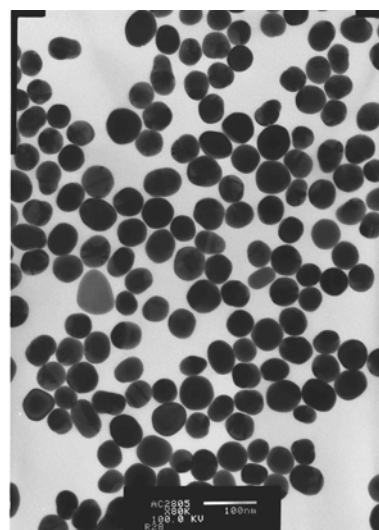




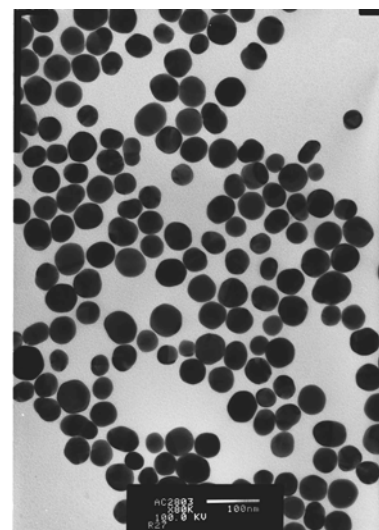
(c)

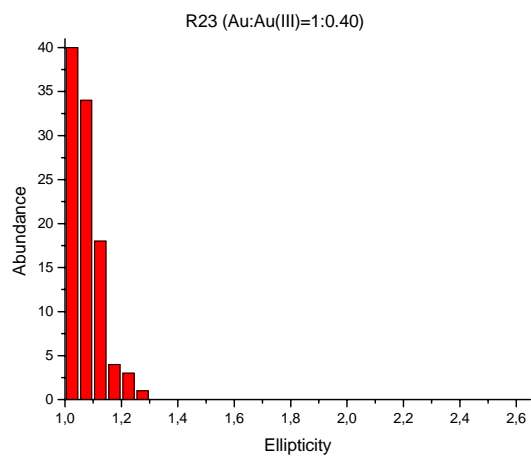


(d)

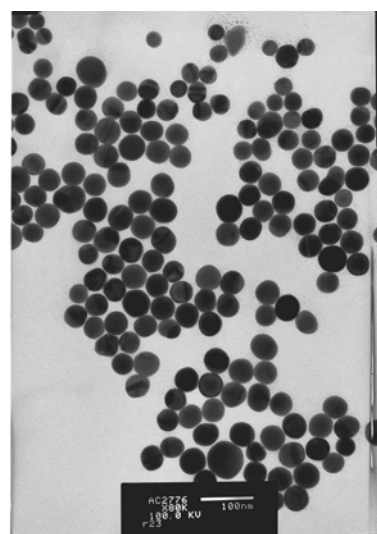


(e)

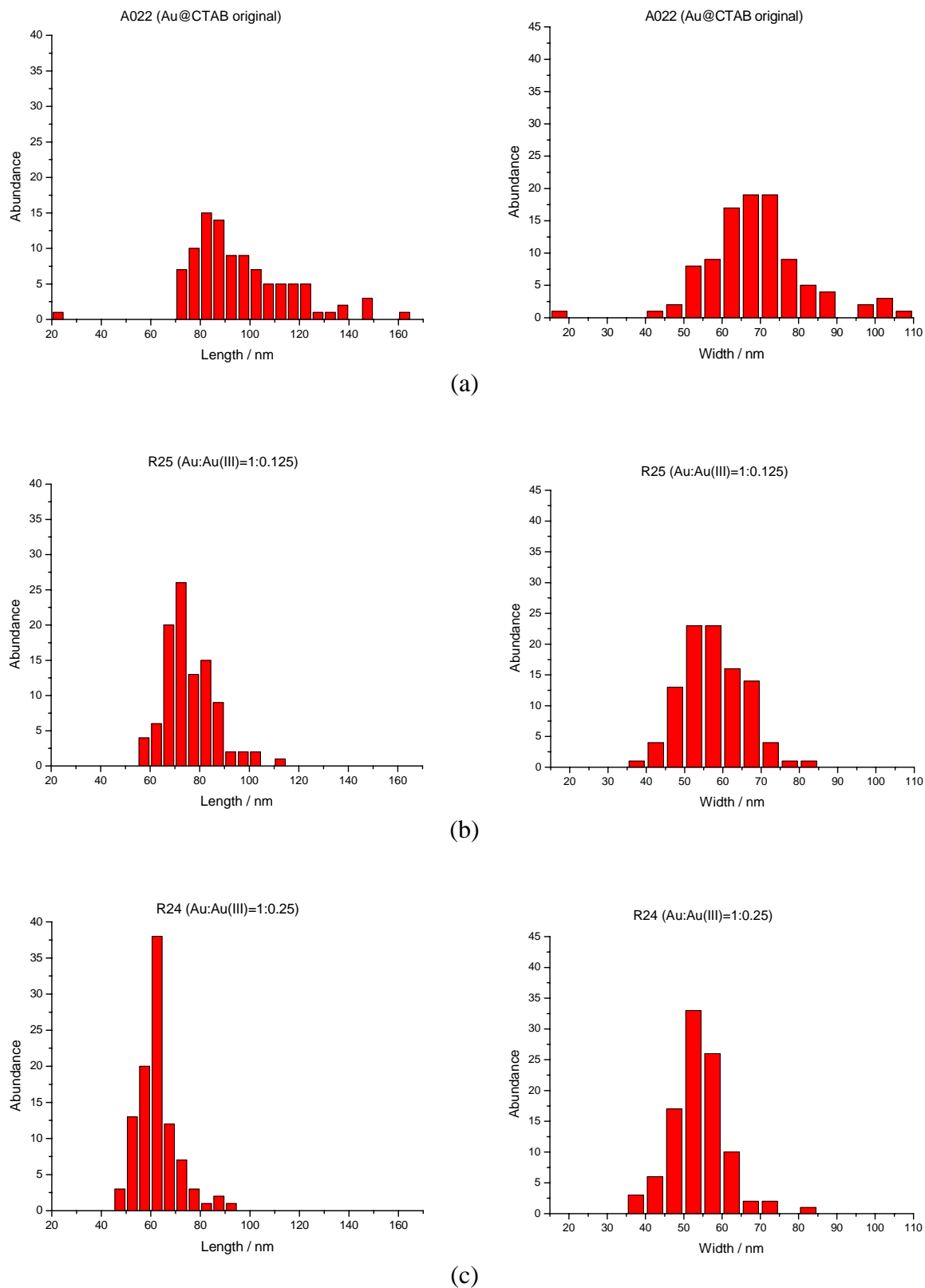


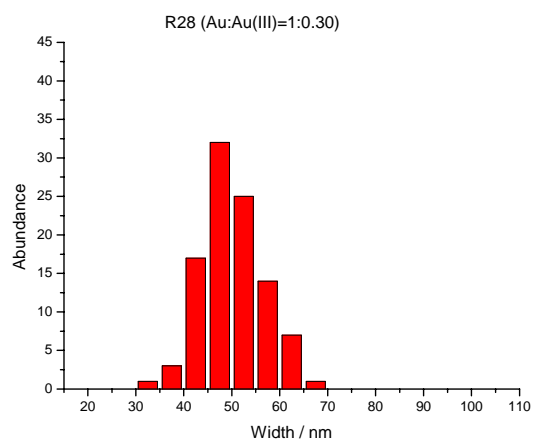
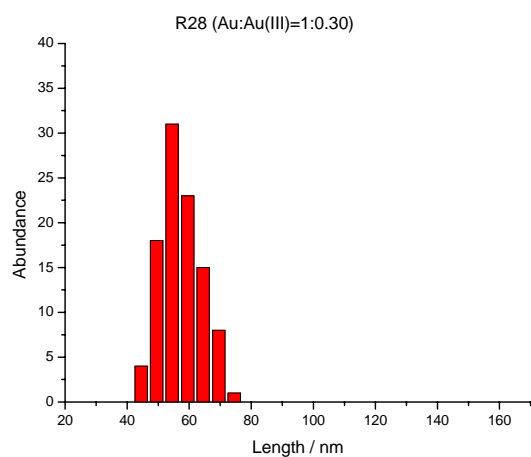


(f)

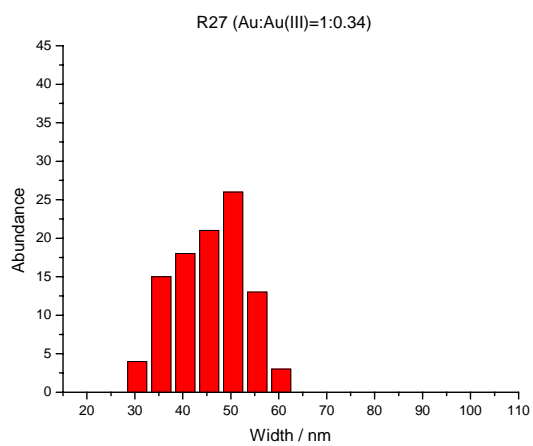
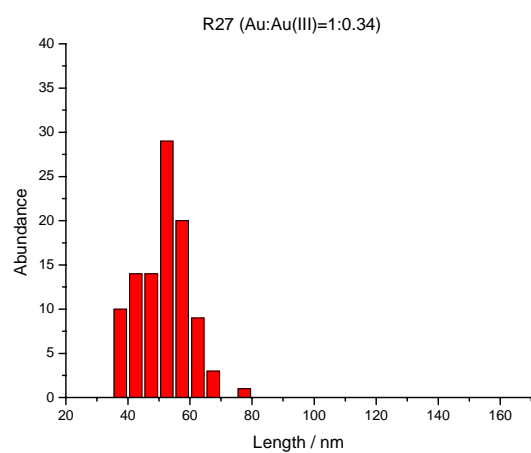


**Supporting Information Figure 2.** Length and width distributions (histograms) of Au nanoparticles before (a) and after addition of  $\text{HAuCl}_4$  with different  $\text{Au}:\text{Au}^{\text{III}}$  molar ratios [1:0.125 (b), 1:0.25 (c), 1:0.30 (d), 1:0.34 (e), 1:0.4 (f)] in the presence of CTAB 0.05 M.

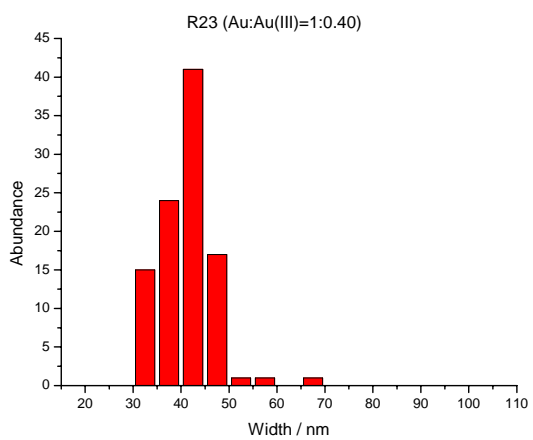
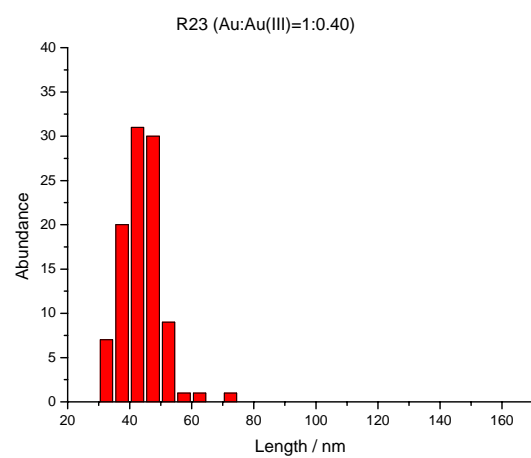




(d)



(e)



(f)