ELECTRONIC SUPPLEMENTARY INFORMATION

Gold nano particles catalyzed oxidation of hydrazine by a metallo-superoxide complex: Experimental evidences for surface activity of gold nanoparticles

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Derivation of the proposed rate law:

$$\text{GNPs} + \mathbf{1} \underset{}{\overset{K_1}{\rightleftharpoons}} \text{GNPs}.\mathbf{1}$$

$$\text{GNPs}.\mathbf{1} + N_2H_5^+ \overset{K_2}{\rightleftharpoons} \text{GNPs}.\mathbf{1}.N_2H_4 + H^+$$

$$\text{GNPs}.\mathbf{1}.N_2H_4 \xrightarrow{k} \mathbf{2} + \text{GNPs}$$

$K_1 = [\text{GNPs}.\mathbf{1}] / [\text{GNPs}] [\mathbf{1}]$

$K_2 = [\text{GNPs}.\mathbf{1}.N_2H_4] [H^+] / [\text{GNPs}.\mathbf{1}] [N_2H_5^+]$

$[\text{GNPs}.\mathbf{1}.N_2H_4] = [A]$ (say)

$= (K_2 [\text{GNPs}.\mathbf{1}] [N_2H_5^+] / [H^+]) = (K_1K_2 [\text{GNPs}] [\mathbf{1}] [N_2H_5^+] / [H^+])$

Total concentration of $\mathbf{1} = T_{\mathbf{1}}$ (say)

$= [\mathbf{1}] + [\text{GNPs}.\mathbf{1}] + [\text{GNPs}.\mathbf{1}.N_2H_4]$

$= [\mathbf{1}] + K_1 [\text{GNPs}] [\mathbf{1}] + (K_1K_2 [\text{GNPs}] [\mathbf{1}] [N_2H_5^+] / [H^+])$

$= [\mathbf{1}] (1 + K_1 [\text{GNPs}] + (K_1K_2 [\text{GNPs}] [N_2H_5^+] / [H^+]))$

$[\mathbf{1}] = T_{\mathbf{1}} [H^+] / ([H^+] + K_1 [\text{GNPs}] [H^+] + K_1K_2 [\text{GNPs}] [N_2H_5^+])$

$k_o T_{\mathbf{1}} = k [A]$

$= (kK_1K_2 [\text{GNPs}] [N_2H_5^+]) / ([H^+] + K_1 [\text{GNPs}] [H^+] + K_1K_2 [\text{GNPs}] [N_2H_5^+])$

$\approx (kK_1K_2 [\text{GNPs}] [T_{\text{Hydrazine}}]) / ([H^+] + K_1 [\text{GNPs}] [H^+] + K_1K_2 [\text{GNPs}] [T_{\text{Hydrazine}}])$

$1 / k_o = ([H^+] / kK_1K_2 [\text{GNPs}] [T_{\text{Hydrazine}}]) + ([H^+] / kK_2 [T_{\text{Hydrazine}}]) + (1 / k)$

This equation is the Eqn. (7) of the main text ($T_{\mathbf{1}}$ and $[T_{\text{Hydrazine}}]$ are the stoichiometric concentration of complex **1** and hydrazine).

Table S1: The variation of k_o values with different concentration of 23 nm GNPs.

10^{13} [GNPs] (M)	6.7	13.3	20.0	26.7	33.3	50.0	66.7	83.3
10^3 k_o (s^{-1})	0.4	0.8	1.7	2.6	3.1	4.6	5.7	7.3

Table S2: Variation of k_o values with pH of the medium.

pH	10^{-4} / [H+] (M^{-1})	10^3 k_o (s^{-1})
3.5	0.32	1.0
4.0	1.00	3.1
4.7	5.00	5.6
5.0	10.00	4.0
5.2	16.70	14.3
5.7	50.00	37.8

[**1**] = 0.30 mM; $T_{Hydrazine}$ = 30.0 mM; [GNPs] = 33.3×10^{-13} M (23 nm); [dpa] = 2.0 mM; T = 25.0 (± 0.1) ^{0}C

Table S3: The slope, intercept and the regression values for Fig. 10.

Temperature (K)	288	293	298	303	308
Slope	23 ± 3	17.2	10.2 ± 0.4	7.6 ± 0.6	5.9 ± 0.1
Intercept	412 ± 62	184.7	56 ± 8	68 ± 12	65 ± 2
r	0.982	0.999	0.998	0.994	0.999

Table S4: Total surface area of GNP of size 23 nm and the corresponding k_o values.

10^{13} [GNPs] (M)	6.7	13.3	20.0	26.7	33.3	50.0	66.7	83.3
10^4 SA $(C.4\pi r^2.N_A)^b$ (m^2L^{-1})	6.7	13.3	20.0	26.7	33.3	50.0	66.7	83.3

^{b} Surface area of single particle ($4\pi r^2$) = 16.6 x 10^{-16} m^2; N_A is Avogadro number.

[**1**] = 0.30 mM; $T_{Hydrazine}$ = 30.0 mM; [dpa] = 2.0 mM; pH = 4.0; T = 25.0 (± 0.1) ^{0}C.

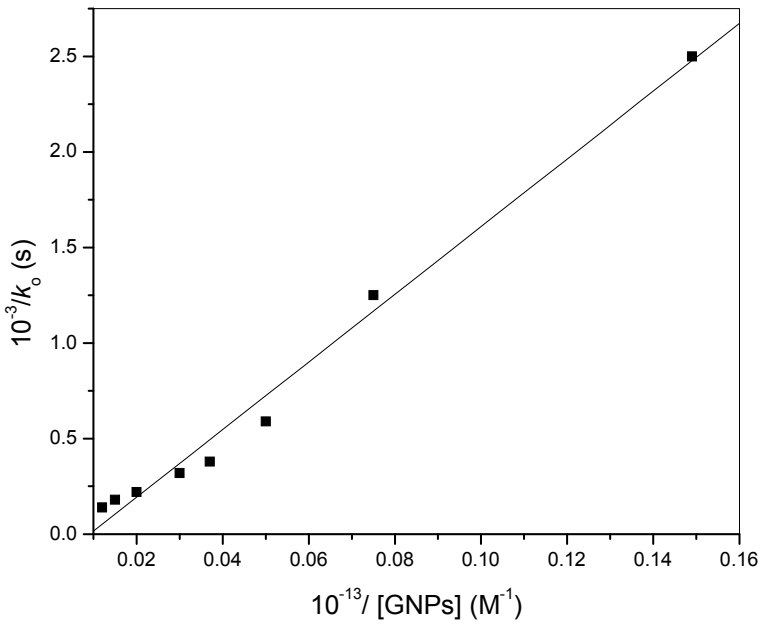

Fig. S1: A plot of variation of 1/ k_o with 1/ [GNPs] (see Table S1).