ELECTRONIC SUPPLEMENTARY INFORMATION

PVP stabilized Pt nano particles catalyzed de-oxygenation of phenoxazine group by hydrazine in physiological buffer media: surfactant competes with reactants for the same surface sites

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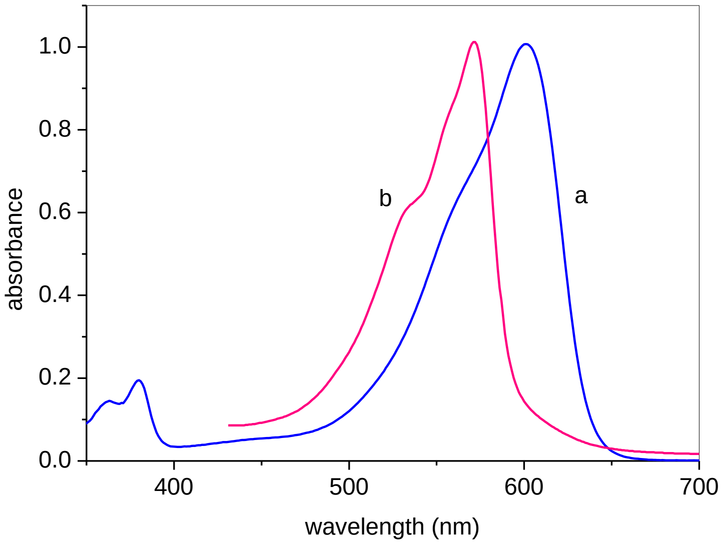

Fig. S1: UV-VIS spectra of resazurin (a) and resorufin (b) in phosphate buffer media (pH = 7.0).

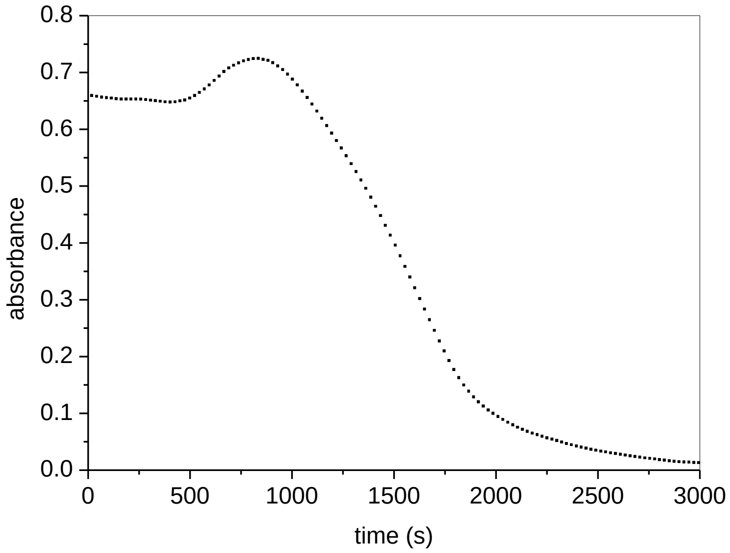

Fig. S2: Formation and then PNP catalyzed reduction of resorufin by hydrazine at 572 nm. Condition: [**1**] = 0.025 mM; [Hydrazine] = 5.0 mM; [PNP] = 5.46 × 10^{-11} M; μ = 0.25 M; pH = 7.0; T = 25.0 ± 0.1 ^{0}C.

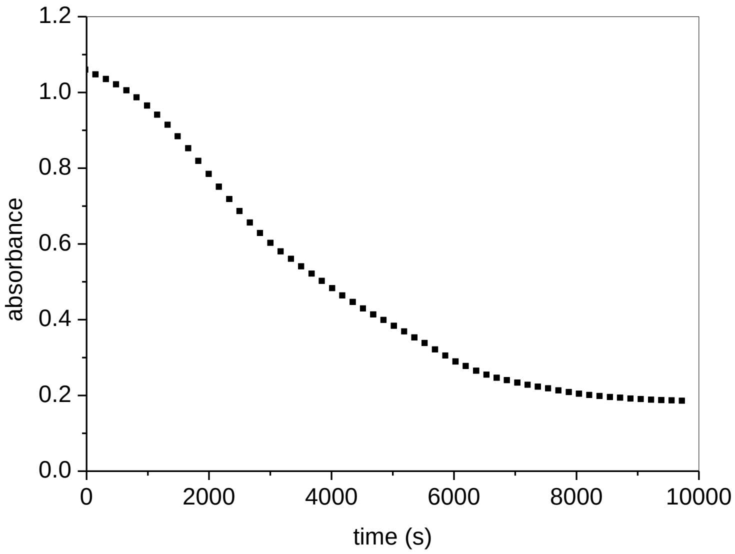

Fig. S3: Uncatalyzed reduction of **1** by hydrazine. Condition: [**1**] = 0.025 mM; [Hydrazine] = 5.0 mM; μ = 0.25 M; pH = 7.0; T = 25.0 ± 0.1 ^{0}C.

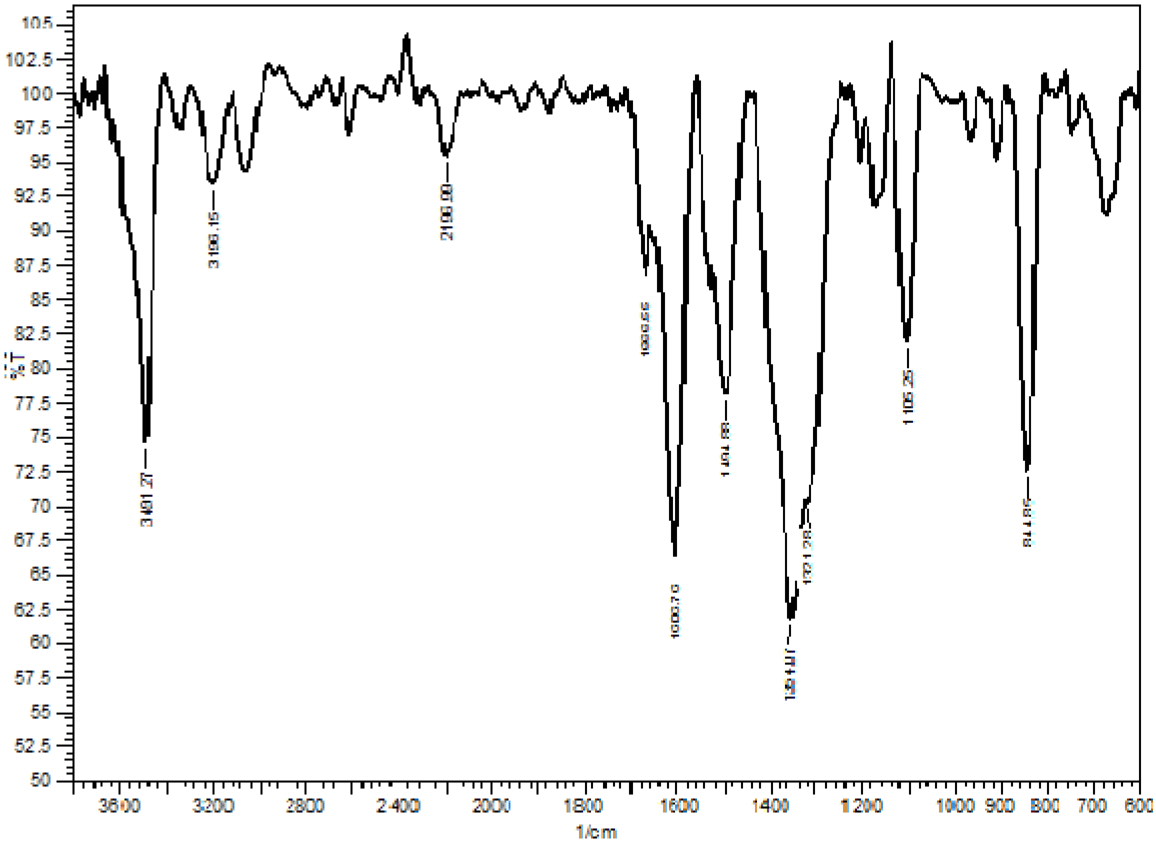

Fig. S4: FTIR spectrum of **1**.

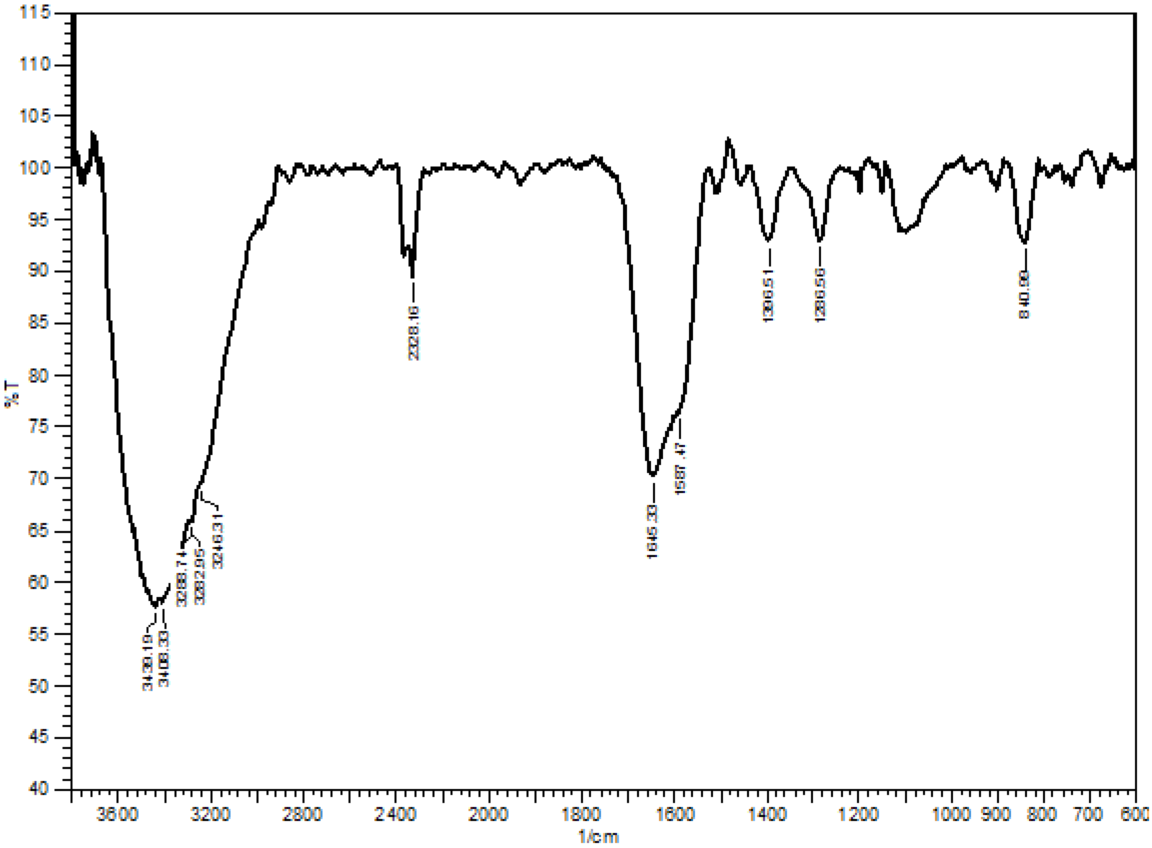

Fig. S5: FTIR spectrum of PNP-**1**.

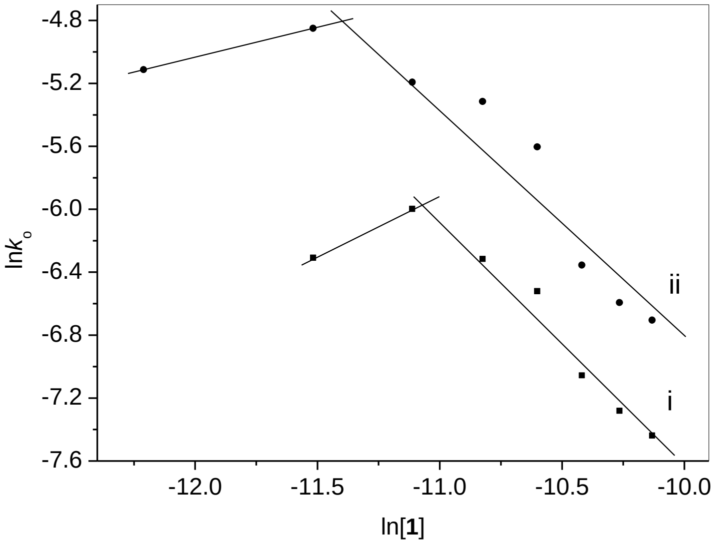

Fig. S6: The slopes of lnk_o *vs*. ln[**1**] plots at different constant [Hydrazine] values gives the exponent α values. Condition:

(i). [Hydrazine] = 5.0 mM; [PNP] = 5.46 × 10^{-11} M; μ = 0.25 M; pH = 7.0; T = 25.0 ± 0.1 ^{0}C.

(ii). [Hydrazine] = 10.0 mM; [PNP] = 5.46 × 10^{-11} M; μ = 0.25 M; pH = 7.0; T = 25.0 ± 0.1 ^{0}C.

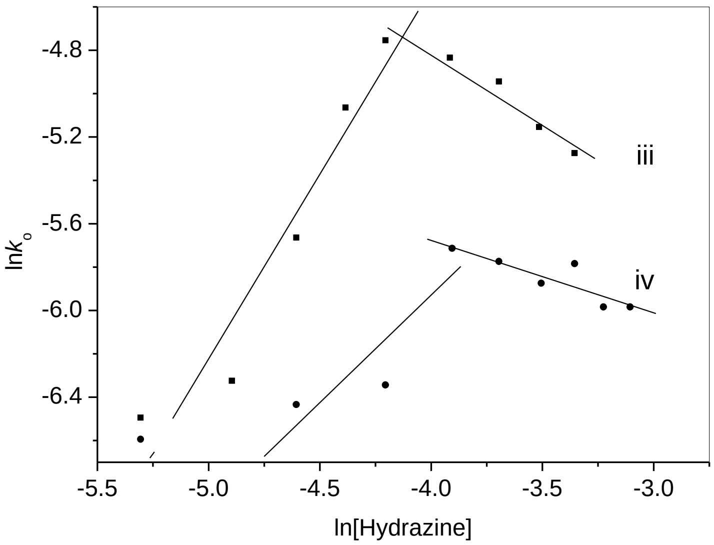

Fig. S7: From the slopes of lnk_o *vs*. ln[Hydrazine] plots at different constant [**1**], the exponent β values are obtained. Condition:

(iii). [**1**] = 0.025 mM; [PNP] = 5.46 × 10^{-11} M; μ = 0.25 M; pH = 7.0; T = 25.0 ± 0.1 ^{0}C.

(iv). [**1**] = 0.04 mM; [PNP] = 5.46 × 10^{-11} M; μ = 0.25 M; pH = 7.0; T = 25.0 ± 0.1 ^{0}C.

Table S1: Variation of k_o with [**1**] at fixed [Hydrazine] and [PNP].[a]

[**1**] (mM)	$10^3 k_o$ (s^{-1})^A	$10^3 k_o$ (s^{-1})^B
0.005	-	5.97
0.010	1.81	7.76
0.015	2.46	5.51
0.020	1.79	4.87
0.025	1.50	3.65
0.030	0.86	1.72
0.035	0.68	1.36
0.040	0.58	1.21

[a] In A and B, [Hydrazine] was 5.0 mM (A) and 10.0 mM (B) respectively. Condition: [PNP] = 5.46×10^{-11} M; μ = 0.25 M; pH = 7.0; T = 25.0 ± 0.1 ^{0}C.

Table S2: Variation of k_o with [Hydrazine] at fixed [**1**] and [PNP].[b]

[Hydrazine] (mM)	10^3k_o (s^{-1})^A	10^3k_o (s^{-1})^B
5.0	1.50	1.35
7.5	1.78	-
10.0	3.42	1.59
12.5	6.23	-
15.0	8.56	1.74
20.0	7.91	3.27
25.0	7.10	3.09
30.0	5.70	2.78
35.0	5.07	3.05
40.0	-	2.50
45.0	-	2.48

[b] In A and B, [**1**] was 0.025 mM and 0.040 mM respectively keeping the other conditions same. Condition: [PNP] = 5.46×10^{-11} M; $\mu = 0.25$ M; pH = 7.0; T = 25.0 ± 0.1 ^{0}C.

Table S3: Variation k_o with [PNP].

10^{11}[PNP] (ML^{-1})	[PVP] (%)	$10^3 k_o$ (s^{-1})	$10^3 k_o$ (s^{-1})[c]
5.46	0.0006	1.50	0.83
8.19	0.0009	1.67	1.14
10.92	0.0012	1.86	1.72
13.65	0.0015	2.04	2.01
16.38	0.0018	2.39	2.56

[c] At large excess of [PVP] = 0.01%, compensated by extra addition of [PVP].

Table S4: Representative values of k_o at different [PVP].

10^3[PVP] (%)*	$10^3 k_o$ (s^{-1})
7.0	0.82
13.4	0.64
19.8	0.56
26.2	0.46
32.6	0.38
39.0	0.33

*****[PVP] contributed by [PNP] (0.0006%) has been considered also. Condition: [**1**] = 0.025 mM; [Hydrazine] = 5.0 mM; [PNP] = 5.46×10^{-11} M; $\mu = 0.25$ M; pH = 7.0; T = 25.0 ± 0.1 ^{0}C.

Table S5: Variation of k_o values with [H$^+$].

pH	10^{-6}/[H$^+$] (LM^{-1})	$10^3 k_o$ (s^{-1})
6.0	1.00	0.76
6.5	3.16	1.28
7.0	10.00	1.50
7.5	31.62	4.09
8.0	100.00	8.78

Table S6: Exponent values are independent of temperature variation.

Temperature (K)	298	303	308	313
β (molar ratio = 200-600)	1.13 ± 0.5	1.11 ± 0.14	1.05 ± 0.02	1.3 ± 0.08

Table S7: Representative data of lnk_o at different temperature.

10^3/T (K^{-1})	3.47	3.41	3.35	3.3	3.24	3.19
lnk_o	-7.90	-6.80	-6.50	-5.75	-5.49	-5.24

Explanation of effects of surface restructuring on k_o:

Surface restructuring of platinum surface is an unavoidable process and it includes both the spontaneous as well as adsorbate induced restructuring. The induction period t_0 of the catalyzed reaction appears due to this very phenomenon and 1/t_0 can be treated as the rate of restructuring.[1,2] It includes both of the spontaneous and reactants induced restructuring effect. We can have an idea of the extent of spontaneous restructuring ($t_{0,sp}$) from plotting 1/t_0 against [Hydrazine] (Figure 16 in revised manuscript). The intercept of the plot gives a measure of spontaneous restructuring.[1] If we subtract the 1/ $t_{0,sp}$ value from 1/t_0 and plot (1/t_0 - $t_{0,sp}$) *vs*. [Hydrazine], the resulting graph is linear and it passes through the origin (Fig. 17 in revised manuscript). Figure 17 demonstrates the only effect of adsorbate induced restructuring which increase linearly with [Hydrazine] and passes through the origin as expected.

From figure 16, it can be noted that the rate of spontaneous surface restructuring is really small. Also recent reports show that the overall restructuring process is slow compared to the rate of the catalyzed reaction.[3] Moreover, in the absence of any reaction (since derived from the induction period) the change in rate of restructuring varies linearly.

Now, it can be seen that the change of rate constants (k_o) with **1** or [Hydrazine] follows linearity (Fig. 7 and 8, both increasing or decreasing part). Supposedly, the rate constants (k_o) include the effect of surface restructuring (however small it is). Now, if we subtract the effect of restructuring from the rate constants, the nature of the plots is supposed to be same because both the effects vary linearly. It can be realized mathematically more easily. If we represent two straight line equation, $y_1 = m_1x + c_1$ and $y_2 = m_2x + c_2$ representing each the nature of variation of k_o and surface restructuring, it is evident that the difference between the two will always be another equation of straight line. The sign of the slope will depend on the sign of the larger 'm' value. From the plots of k_o *vs*. [Hydrazine] (increasing part) and ($1/t_0$ - $t_{0,sp}$) *vs*. [Hydrazine] it can be seen that the corresponding slopes are 0.7 and 0.1 respectively. Thus on subtraction of restructuring effect, the trends of different plots will still remain same. Since in this work we have given more emphasis on the trends of different variations, all the arguments still holds inspite of the presence of surface restructuring effects.

References:

1. S. Wunder, F. Polzer, Y. Lu, Y. Mei and M. Ballauff, *J. Phys. Chem. C*, 2010, **114**, 8814-8820.
2. J. Kaiser, L. Leppert, H. Welz, F. Polzer, S. Wunder, N. Wanderka, M. Albrecht, T. Lunkenbein, J. Breu, S. Kummel, Y. Lu and M. Ballauff, *Phys. Chem. Chem. Phys.*, 2012, **14**, 6487-6495.
3. K. S. Han, G. Liu, X. Zhou, R. E. Medina and P. Chen, *Nano Lett.*, 2012, **12**, 1253-1259.