

Electronic Supplementary Information

“Doping-induced Detection and Determination of Propellant Grade Hydrazines by Kinetic Spectrophotometric Method based on Nano and Conventional Polyaniline using Halide ion Releasing Additives”

by

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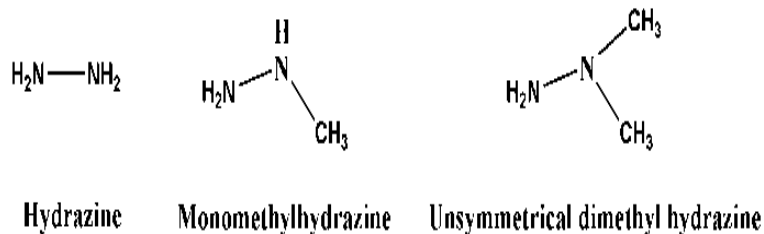
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1. Chemical Structures

Chemical Structures of Hydrazine, Monomethylhydrazine and Unsymmetrical dimethylhydrazine are given as follows. For Hydrazine hydrate, water molecule is present in the hydrated form of Hydrazine.



2. Characterization

Spectrophotometric measurements were performed on a UV–VIS spectrophotometer (Techcomp-8500) in the wavelength range of 200–900 nm with 1 cm quartz cells thermostated by a thermostatic water bath (Shimadzu-TB 85) at 50 °C and 60 °C. The morphology of conventional and nano Pani was characterized by using the field emission scanning electron microscopy (FESEM, SIRION-Netherland). Wide-angle X-ray diffraction (WAXD) for sample powders was carried out at room temperature by using a Rigaku D / max 2500 VPC X-ray diffractometer with Cu-K_α irradiation and scan speed of 5 °C. All the kinetic data were obtained from the plots using the program Microcal Origin 7.0. A stopwatch was applied to record the reaction time. *N*-methyl-2-pyrrolidone was used as a solvent to prepare sample solutions of Pani.

3. Characterization by FT-IR and UV- Vis Spectras :

FT-IR spectra of the conventional Pani-EB in NMP shows five peaks, at 1585 cm⁻¹ (C=N stretching of the quinoid ring), at 1494 cm⁻¹ (stretching of the benzenoid ring), at 1310 cm⁻¹ (C-N stretching of the benzenoid ring), at 1162 cm⁻¹ (in-plane C-H bending motion of the quinoid ring) and at 829 cm⁻¹ (out-of-plane bending of C-H bond in the aromatic ring). The peaks identified are consistent with previously published data¹. FT-IR spectra of the nano Pani-EB taken in KBr Pellet form also shows these main five peaks (1578, 1492, 1295, 1147 & 824 cm⁻¹). Slight variation in peak positions of samples taken in KBr pellet and NMP medium is due to solvent (NMP) effect.

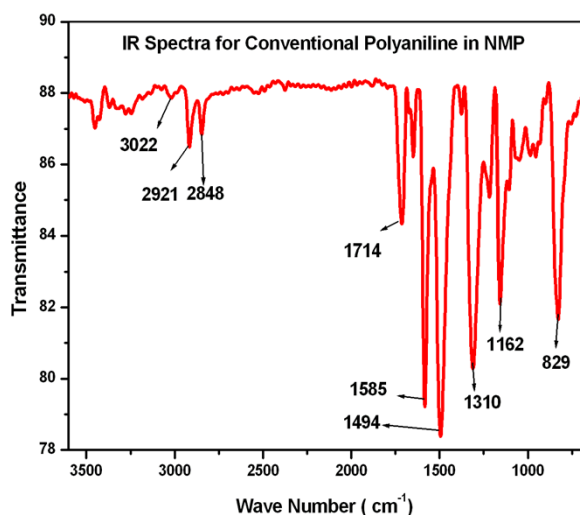


Fig.S1 FT-IR spectra of conventional Pani in NMP medium

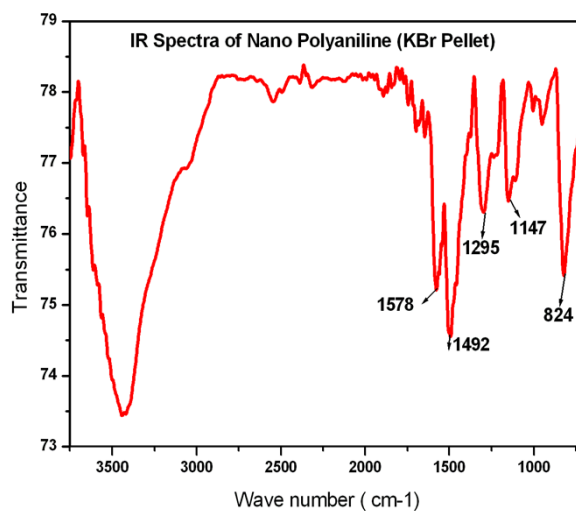


Fig.S2 FT-IR spectra of nano Pani in KBr Pellet form

UV-Vis spectroscopy analysis of these two forms shows two absorption peaks at 326 and 626 nm (Fig.6 of manuscript) which can be assigned to the $\pi-\pi^*$ transition of the benzenoid ring and the exciton absorption of the quinoid ring respectively. The peaks identified are consistent with previously published data¹.

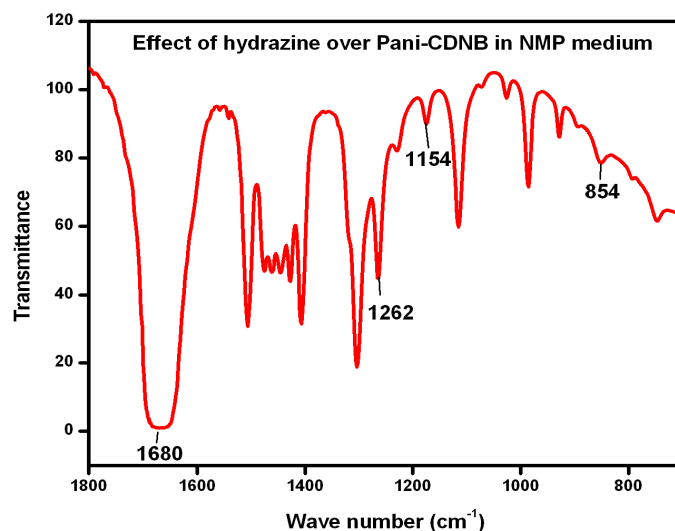


Fig.S3 FT-IR spectra-Hydrazine effect over Pani-CDNB in NMP medium

FT-IR spectra of Pani-ES (taken in NMP medium) formed by the release of HCl (Figure S3) shows new peaks at 1154 and 854 cm^{-1} . Peak at 1154 cm^{-1} indicates the broken symmetry mode of the quinoid ring. Peak at 854 cm^{-1} (out of plane bending of the aromatic ring) indicates the change from the quinonoid structure to the benzenoid structure upon doping¹.

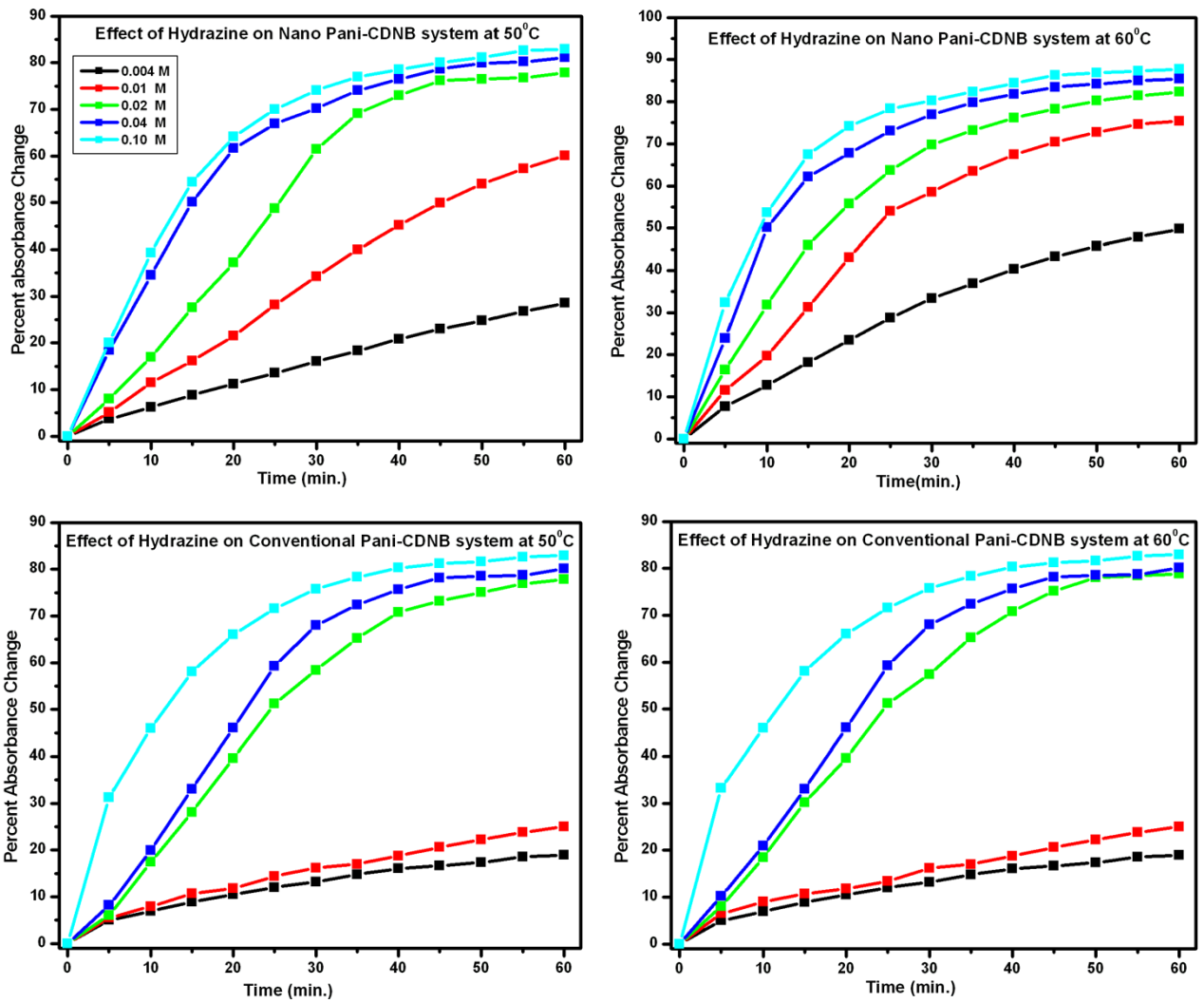


Fig. S4. Percent absorbance change-Time curves for nano and conventional Pani – CDNB systems for the addition of hydrazine at different concentrations (at 50 °C & 60 °C)

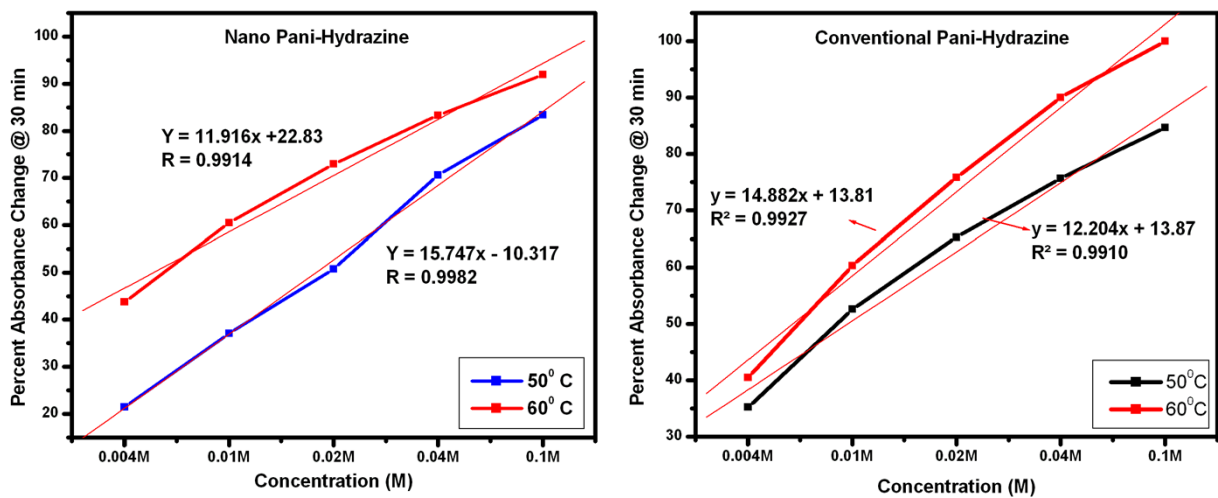


Fig.S5. Calibration graphs of percent absorbance change recorded at 30 min.Vs concentration of hydrazine at 50 °C & 60 °C

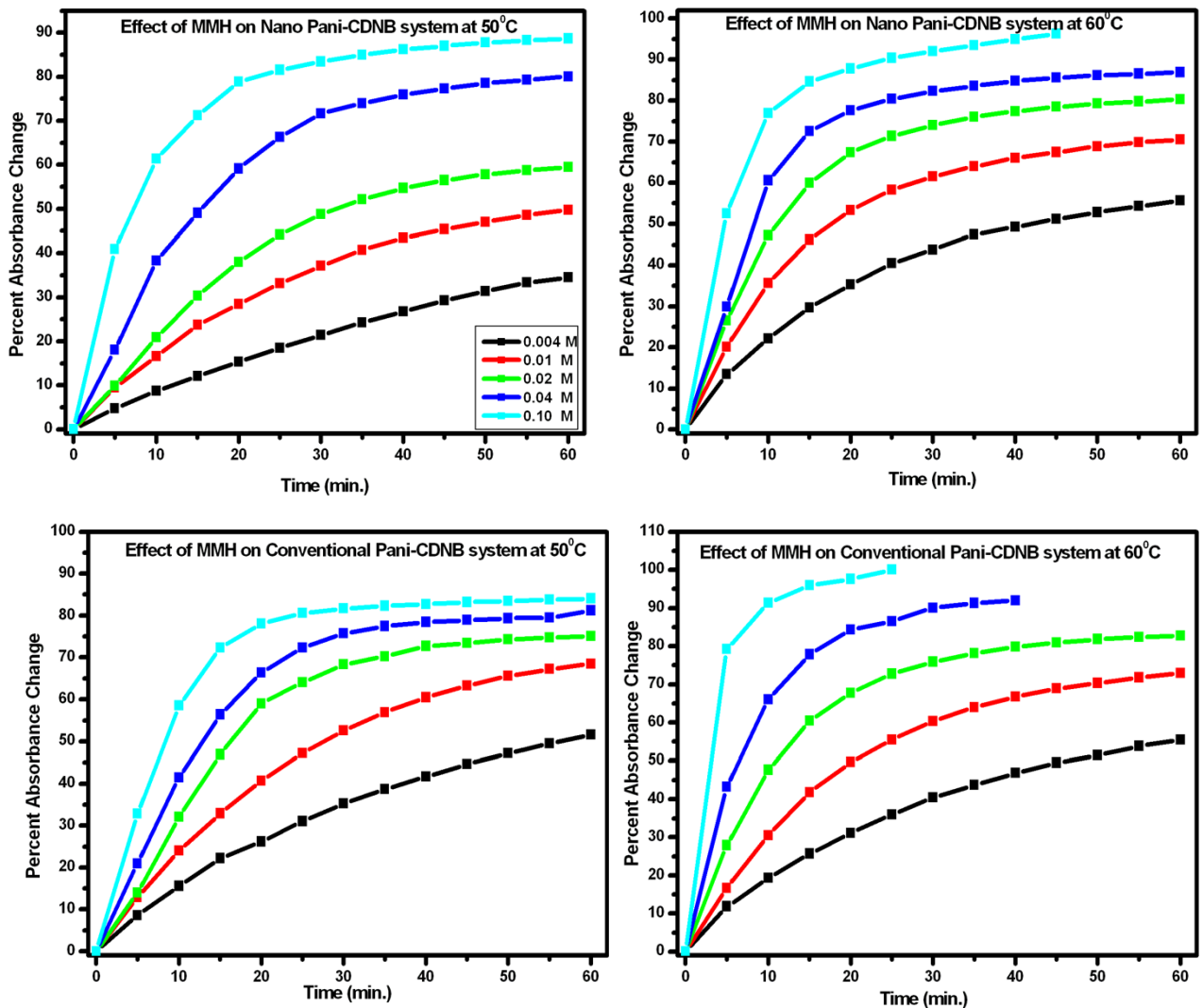


Fig. S6. Percent absorbance change-Time curves for nano and conventional Pani – CDNB systems for the addition of MMH at different concentrations (at 50 °C and 60 °C)

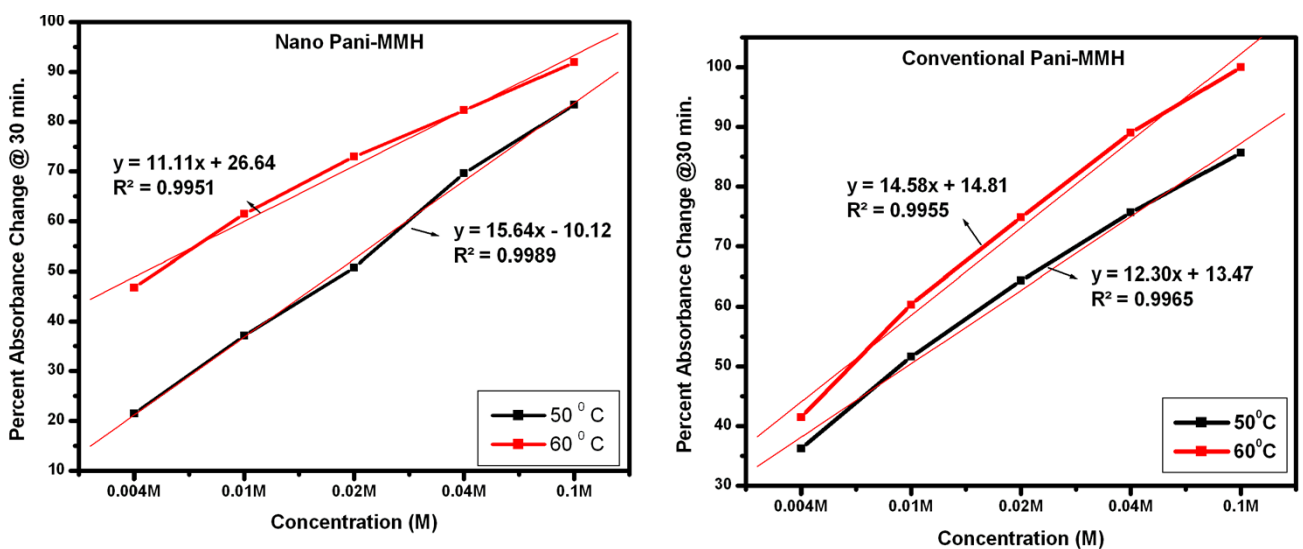


Fig.S7. Calibration graphs of percent absorbance change recorded at 30 min. Vs concentration of MMH at 50 °C & 60 °C

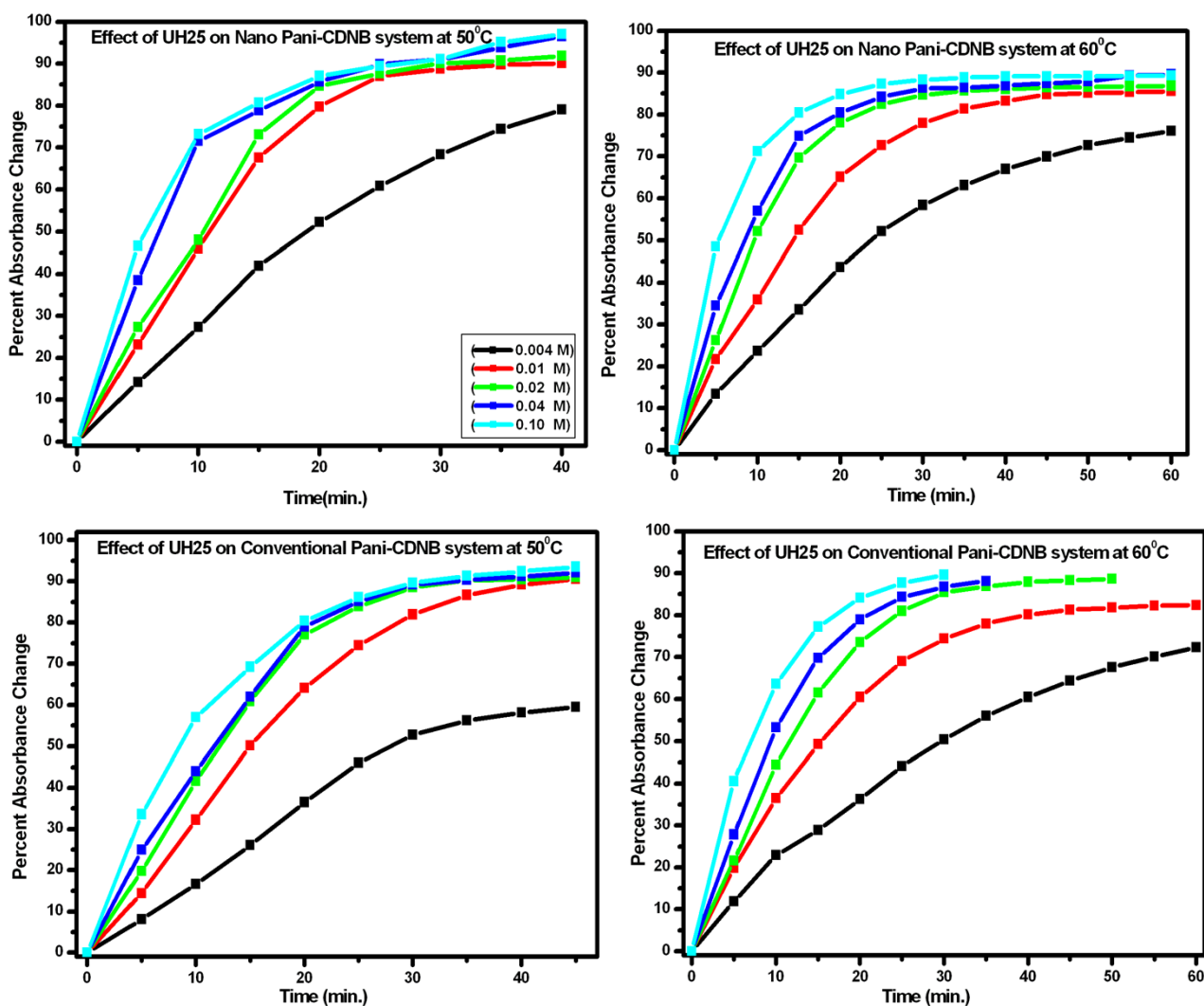


Fig.S8. Percent absorbance change-Time curves for nano and conventional Pani – CDNB systems for the addition of UH25 at different concentrations (at 50 °C and 60 °C)

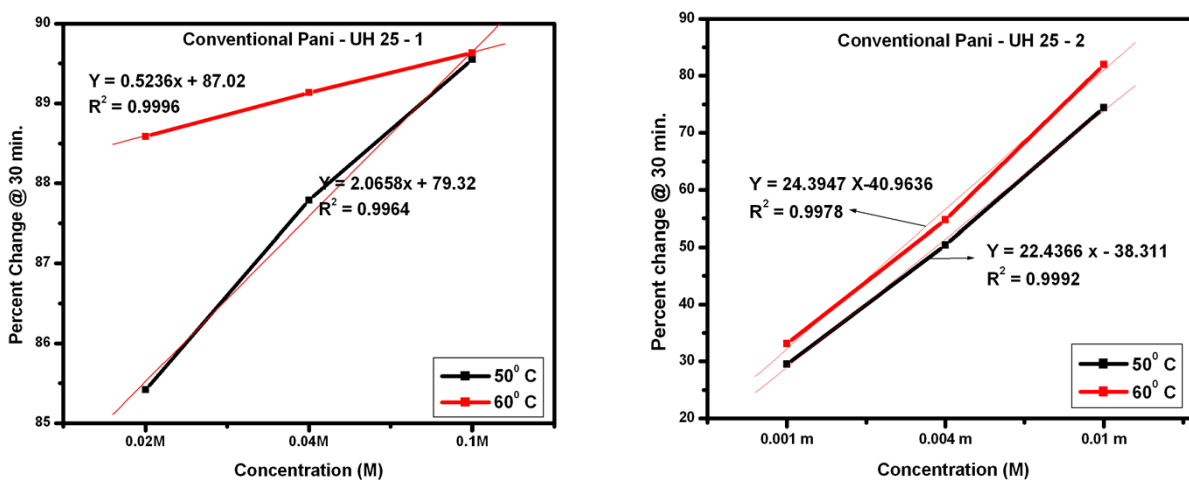


Fig.S9. Calibration graphs of percent absorbance change recorded at 30 min. Vs concentration of UH25 at 50 °C and 60 °C

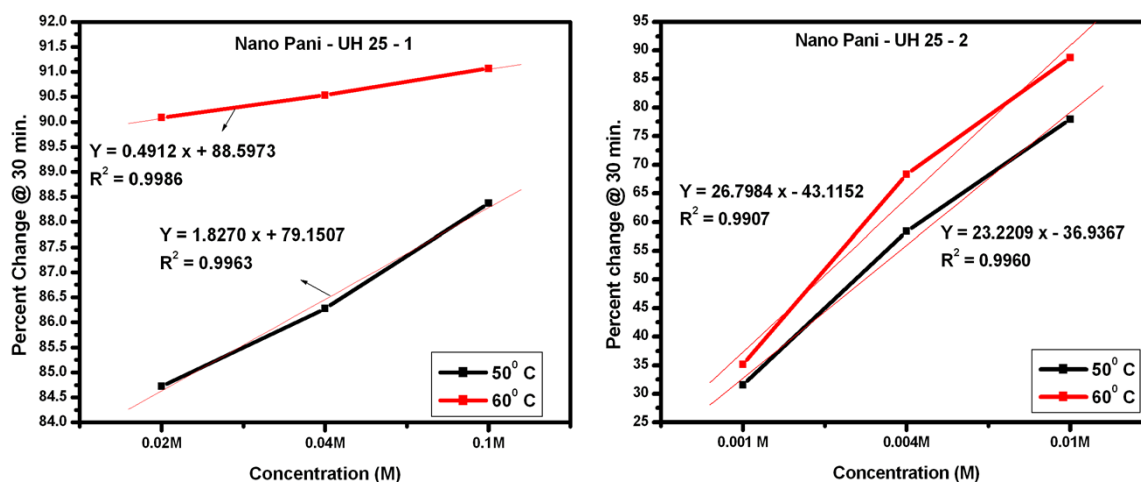


Fig.S10. Calibration graphs of percent absorbance change recorded at 30 min. Vs concentration of UH25 at 50 °C and 60 °C

Table S1 Statistical data obtained from fixed time method (15 min.) for the addition of hydrazine, MMH and UH25 @ 50°C & 60°C

Concentration (M)	Hydrazine		MMH		UH25	
Nano Pani @ 50°C						
	Slope	Correlation Coefficient	Slope	Correlation Coefficient	Slope	Correlation Coefficient
0.004	2.89	0.9901	4.02	0.9947	11.09	0.9943
0.01	5.49	0.9973	7.82	0.9948	17.16	0.9922
0.02	9.17	0.9958	10.19	0.9993	23.5	0.9919
0.04	16.64	0.9984	16.73	0.9858	24.69	0.977
0.1	18.26	0.9959	23.39	0.9173	26.41	0.8988
Nano Pani @ 60°C						
0.004	5.95	0.99	9.77	0.9807	13.88	0.9996
0.01	10	0.9816	15.41	0.9812	18.57	0.9997
0.02	15.31	0.9988	20.05	0.9767	24.01	0.9974
0.04	21.77	0.9733	24.85	0.9691	26.97	0.9321
0.1	22.37	0.9663	27.83	0.8841	26.88	0.9043
Conventional Pani @ 50°C						
0.004	2.87	0.9949	3.34	0.9961	8.66	0.9987
0.01	3.05	0.9984	6.99	0.9936	16.84	0.9973
0.02	9.08	0.9952	12.89	0.9976	20.42	0.9994
0.04	13.59	0.9708	15.96	0.9943	20.49	0.9938
0.1	16.68	0.8883	22.26	0.9697	23.1	0.9591
Conventional Pani @ 60°C						
0.004	5.75	0.9377	8.45	0.9778	9.76	0.9802
0.01	6.54	0.9325	13.92	0.9825	16.43	0.9907
0.02	14.19	0.9934	20.11	0.9726	20.73	0.9966
0.04	19.2	0.9897	25.64	0.929	23.48	0.9877
0.1	21.13	0.9295	30.19	0.7385	25.47	0.946

Table S2 Determination of hydrazine, MMH and UH25 in tap water by nano & conventional Pani systems @ 50°C (n=4)

Pani	Hydrazine		MMH		UH25	
	Added* (mg/ml)	RSD %	Added* (mg/ml)	RSD %	Added* (mg/ml)	RSD %
Nano – Trial 1	3.3	1.1	24.2	0.7	60.3	1.5
Nano – Trial 2	1.8	1.2	47.6	1.2	30.5	1.2
Conventional – Trial 1	3.4	0.8	23.8	0.9	30.1	1.1
Conventional – Trial 2	1.9	0.9	46.6	0.8	59.5	0.9

* mg/ml of respective hydrazine added to the respective Pani – CDNB system
n = No. of determinations for particular concentrations tried.

References:

1. L. Trachiwin, P.Kiattibutr, L.Ruangchuay, A.Sirivat and J. Schwank, *Synthetic Met.*, 2002, **129**, 303.