Online Supporting Information's for

Enhanced Catalytic and SERS Activities of Size-selective Rh NPs on DNA Scaffold

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Preparation of Samples for Catalytic Reduction of Aromatic Nitro Compounds and SERS Studies

The catalytic reduction of aromatic nitro compounds was tested with the synthesized Rh NPs@DNA of three different average particle sizes as catalyst for the first time. The catalytic reduction was done with 4-NA as a specific example. However, few other nitro compounds were also tested. All the three Rh NPs solutions as catalyst were tested for comparison purposes. For a typical catalysis reaction, 4 mL of DI water was mixed with 600 μL of (10^{-3} M) stock 4-NA solution and stirred for 2-3 min for homogeneous mixing. After that, 600 μL of 0.1 M ice-cold $NaBH_4$ solution was added and shaken thoroughly by hand. Then 100 μL of freshly prepared Rh NPs solution was added and then the reaction was monitored by an UV-Vis spectrophotometer at regular time intervals. The absorption spectra were recorded every 1–2 min until the completion of the reduction process. The total time required for the reduction was ~13 min for large-size Rh

NPs as catalyst and the light yellowish 4-NA solution became colorless due to the formation of reduced product *para*-phenylenediamine (*p*-PDA). The completion of the reaction was confirmed by the de-coloration and from the absorption bands in the UV-Vis spectrum. It is significant to remember here that in catalysis reaction, the number of particles and the approx. surface area of the particles were calculated based on the concentration of Rh(III) ions used and with three basic assumption. First, we assumed that almost all the particles in the synthesized solution are in the same size and shape and the same was confirmed from TEM micrographs. Secondly, the density of bulk Rh was assumed to be the same to that of Rh NPs and the same was confirmed by similar crystal structure and bond lengths. Finally, the yield of NPs was assumed to be 100%, i.e., that all the Rh(III) was converted to Rh NPs. Samples for SERS studies were prepared as follows. Several standard MB solutions with concentrations of 10^{-3} M, 10^{-4} M, 10^{-5} M, 10^{-6} M and 10^{-8} M were prepared in DI water. Then 200 μL of each of those MB stock solutions were separately mixed with 200 μL of the Rh NPs solution and shaken vigorously for homogeneous mixing. Then after 20-30 min, 20 μL of each of the mixed solutions was placed on a clean glass substrate and dried in air before SERS studies.

Preparation of Samples for Various other Characterizations

The synthesized Rh NPs on DNA having three different particle sizes were characterized using UV-Vis, TEM, EDS, XRD and XPS analyses. The aqueous solution of Rh NPs was directly used for the measurement in UV-Vis spectrophotometer. The samples for TEM analysis was prepared by placing a drop of the corresponding Rh NPs solution onto a carbon coated Cu grid followed by slow evaporation of solvent at ambient conditions. The EDS analysis was done in a FE-SEM instrument separately and the sample was deposited over the glass substrate repeatedly few times to make a thin film of the Rh NPs on it. For XRD and XPS analyses, clean glass slides were taken as substrates for thin film preparation. The cleaned substrates were covered with the Rh NPs solution and dried in air. After the first layer was deposited, subsequent layers were deposited by repeatedly adding more Rh NPs solution and drying. Final, samples were prepared after 8-10 time depositions and then analyzed using the above techniques.

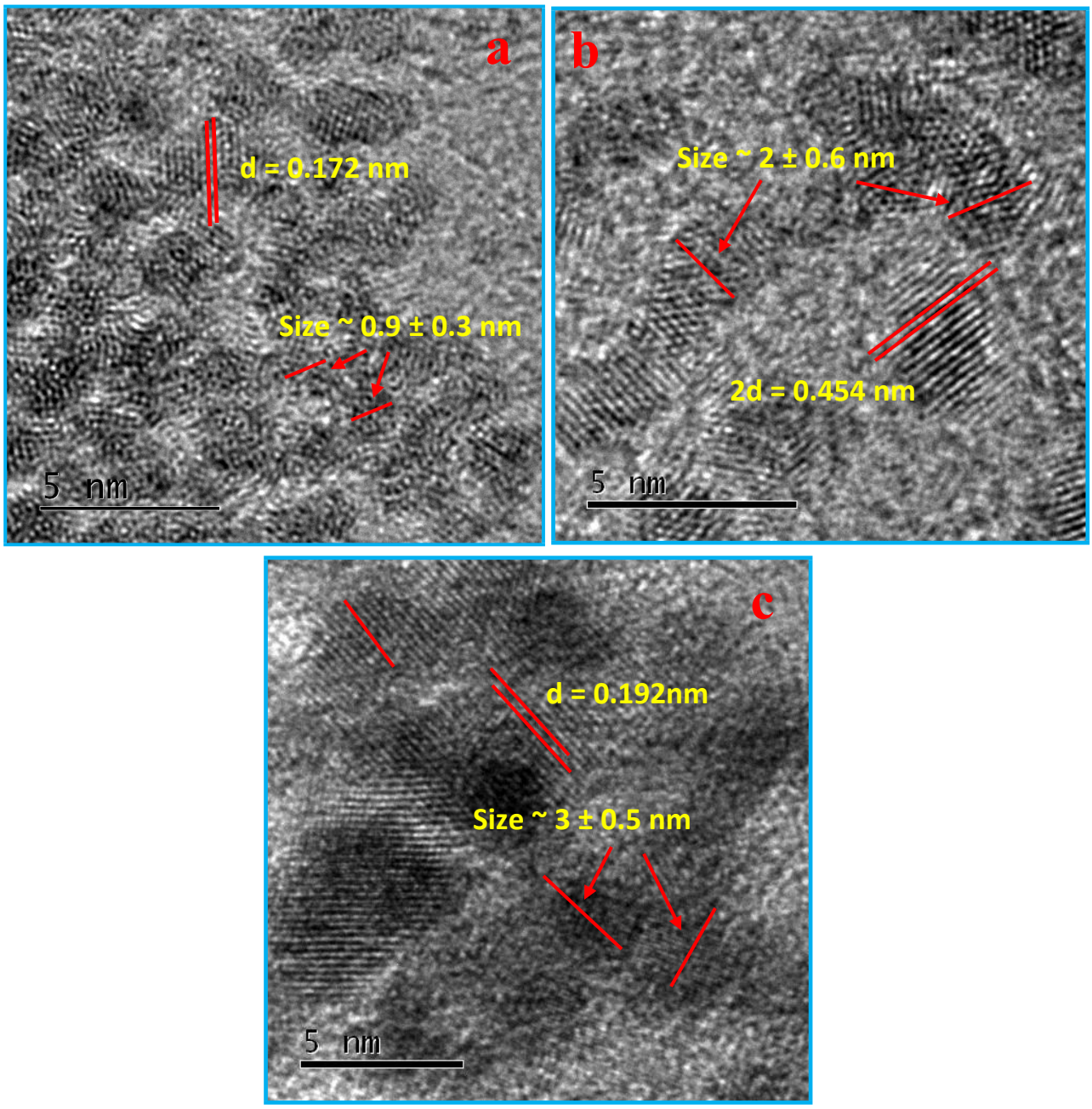


Figure S1: High resolution TEM micrographs of the size-selective, self-assembled Rh NPs on DNA scaffold where (a), (b) and (c) are the small size, medium size and large size Rh NPs respectively.

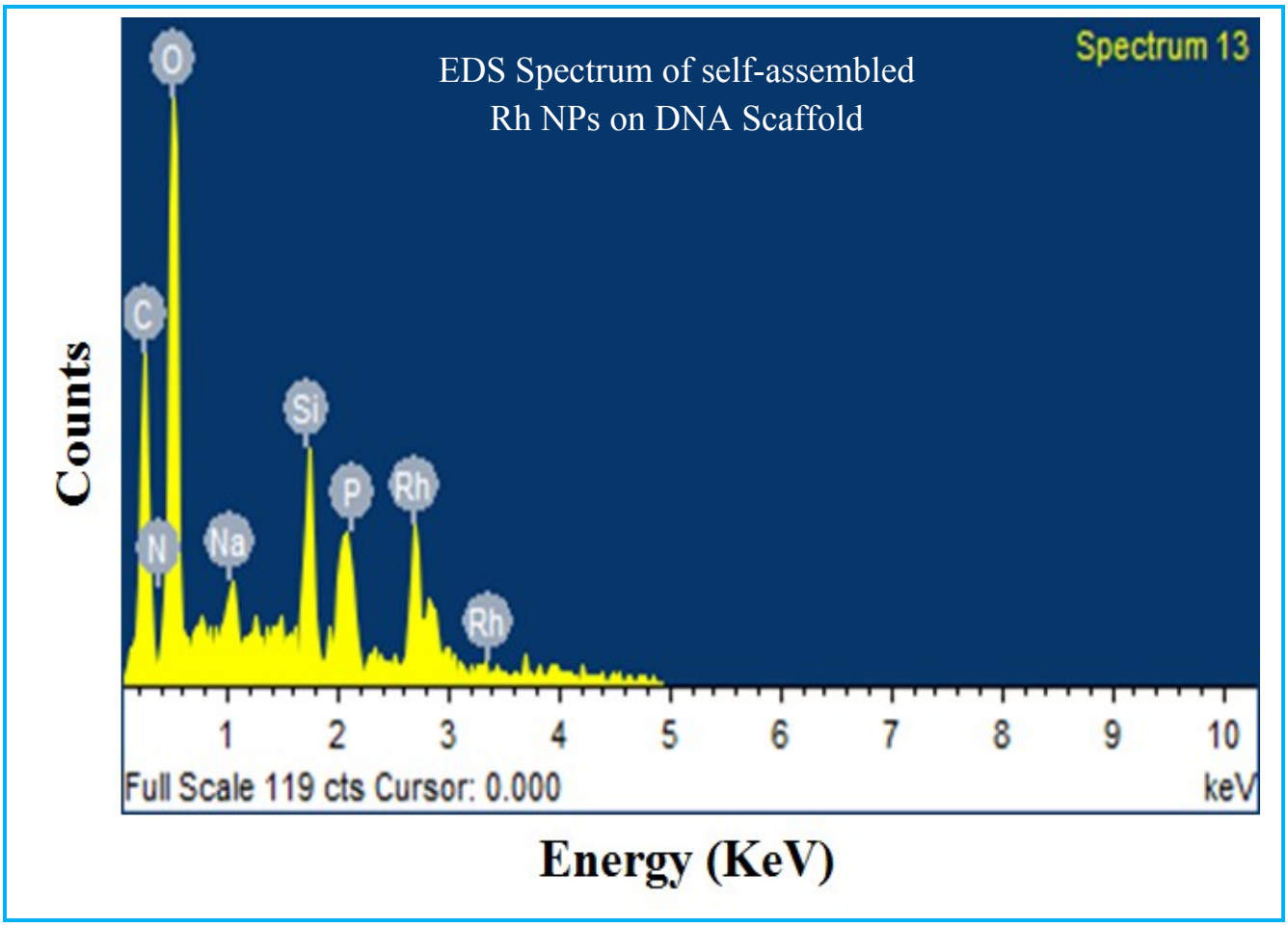


Figure S2. The Energy dispersive X-ray spectroscopic (EDS) analysis of the synthesized Rh NPs on DNA Scaffold.

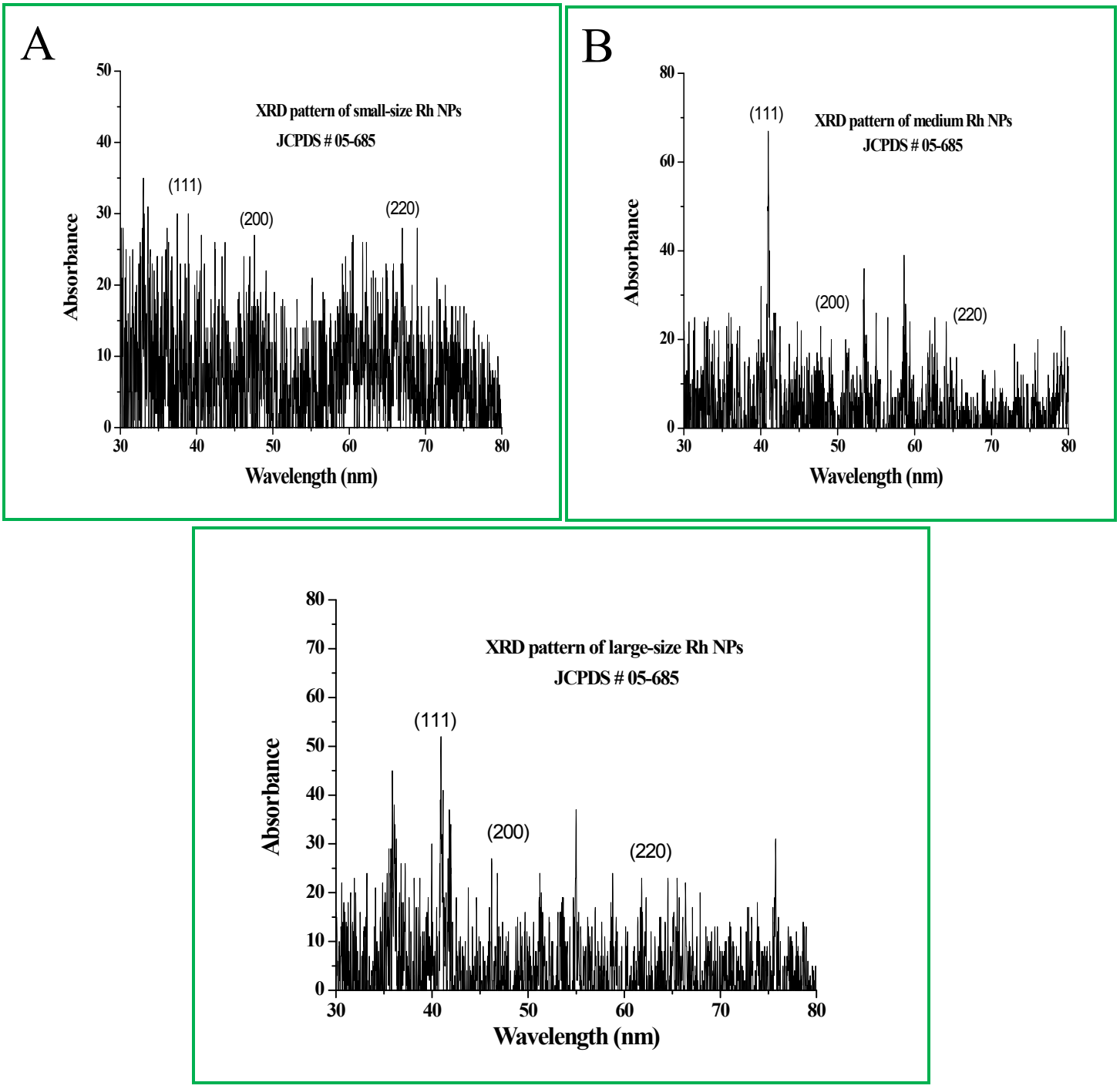


Figure S3: The X-ray diffraction (XRD) pattern of the size-selective, self-assembled Rh NPs on DNA scaffold where Figure 3A for small size, 3B for medium size and 3C for large size Rh NPs respectively.

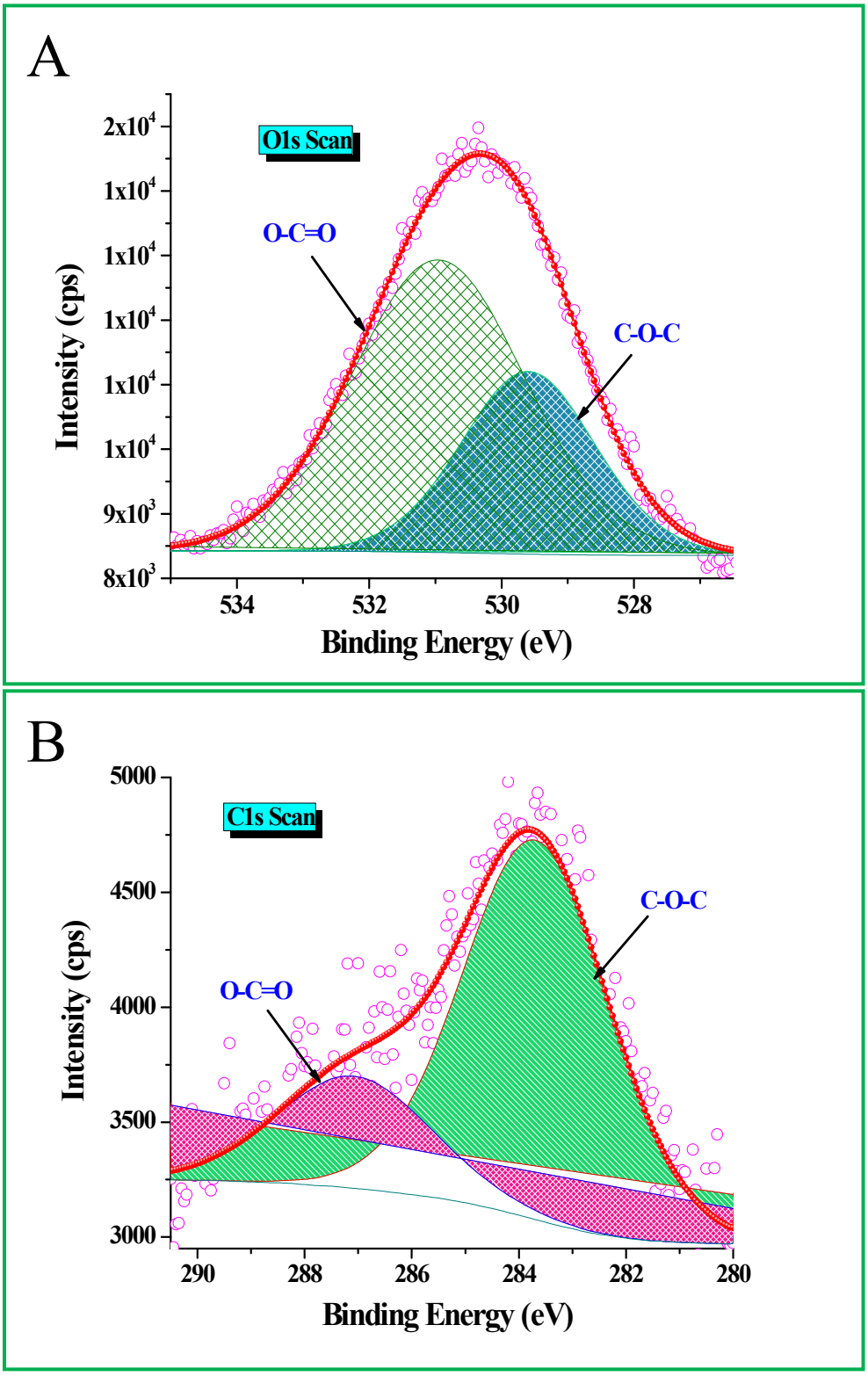


Figure S4: The high resolution X-ray photoelectron spectroscopic (XPS) images of O (1s) (A) and C (1s) (B).

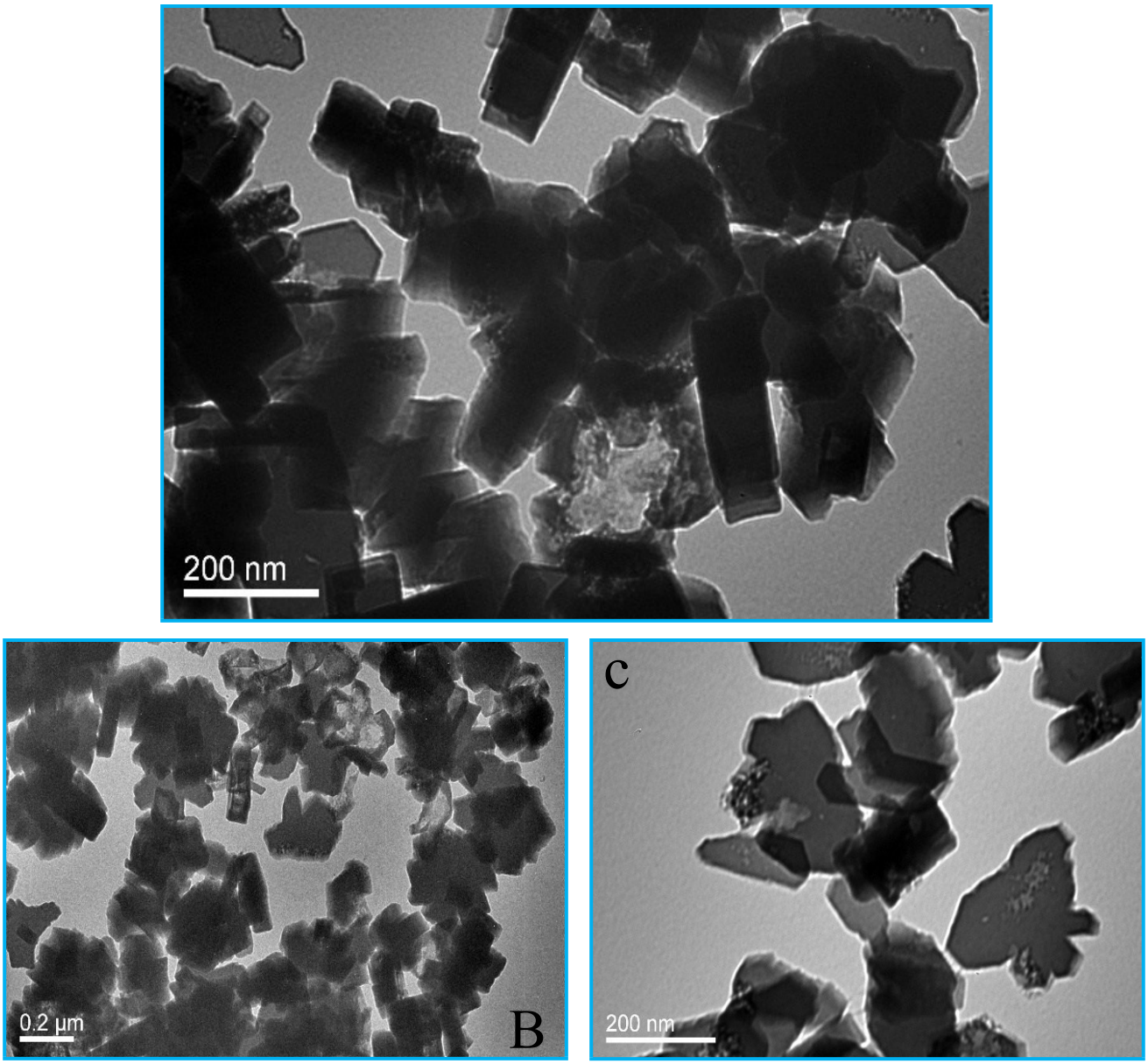


Figure S5: Transmission electron microscopic (TEM) images for control experiments. (A) image of Rh NPs while synthesized without DNA; (B) while synthesis is done with conventional heating instead of UV-irradiation; (C) synthesis is done for a longer period of UV-irradiaion (~ 15 hour).

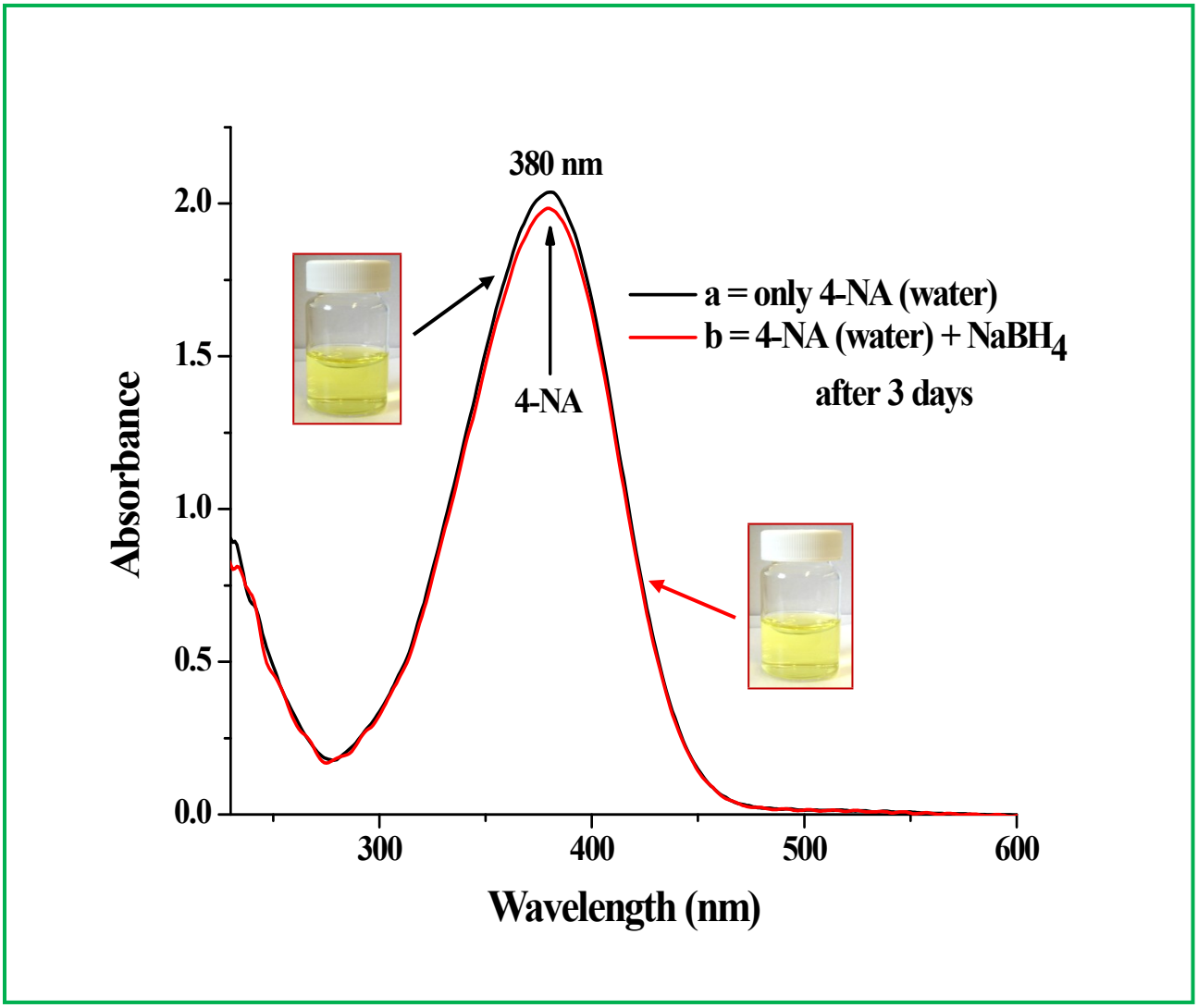


Figure S6: UV-Vis absorption spectrum of 4-NA reduction with only $NaBH_4$. Curve a shows the absorption spectra of only 4-NA in water; absorption spectra of a mixture of 4-NA + $NaBH_4$ after keeping the solution mixture for 3 days. Inset shows the color of two different 4-NA solution one is before adding the $BaBH_4$ and other is after adding the $NaBH_4$ and keeping the solution mixture for 3

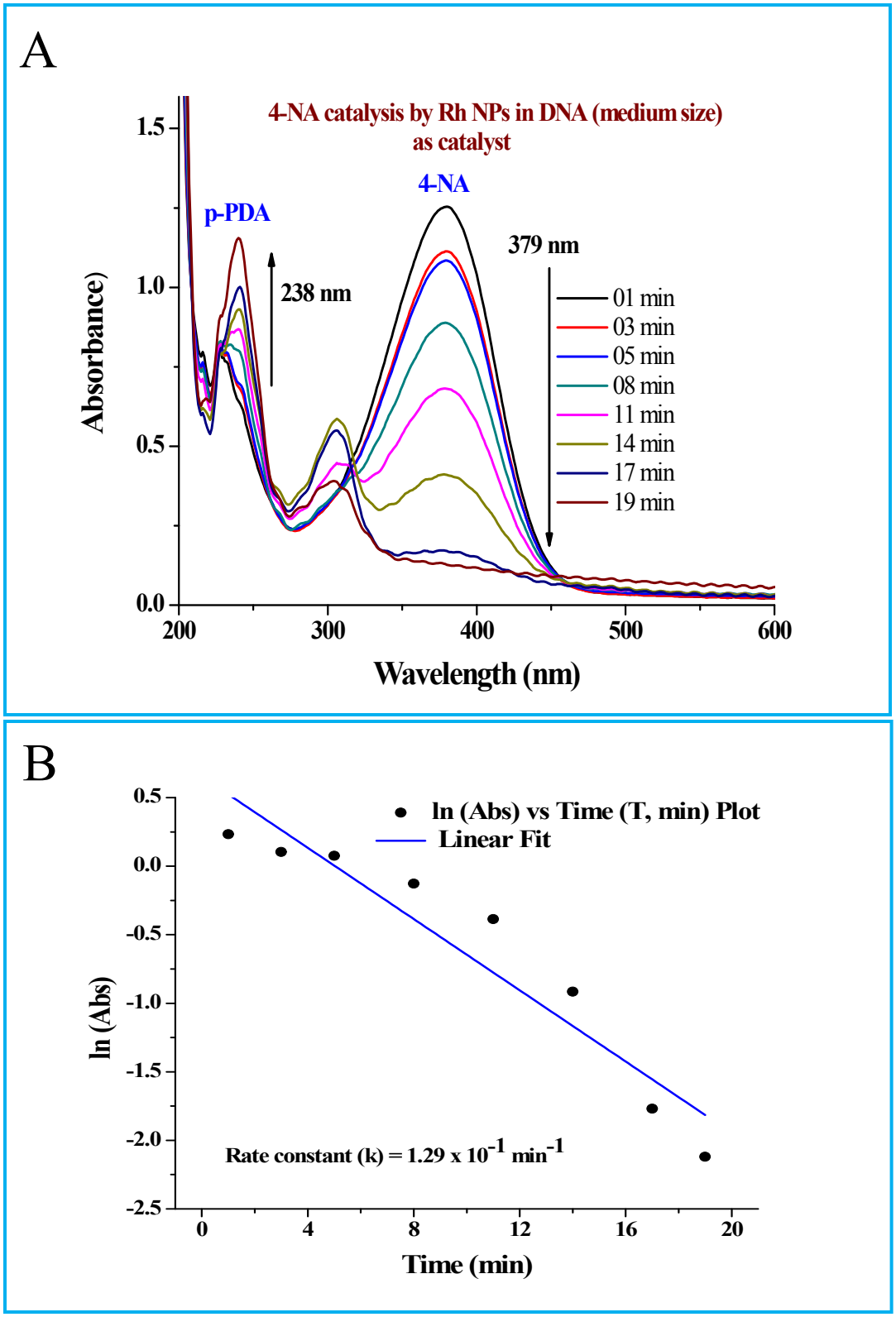


Figure S7: (A) Time-dependent UV-Vis absorption spectra for the reduction of 4-NA using medium size Rh NPs on DNA scaffold s as catalyst. (B) The first order plot for the determination of rate constant with respect to the 4-NA concentration.

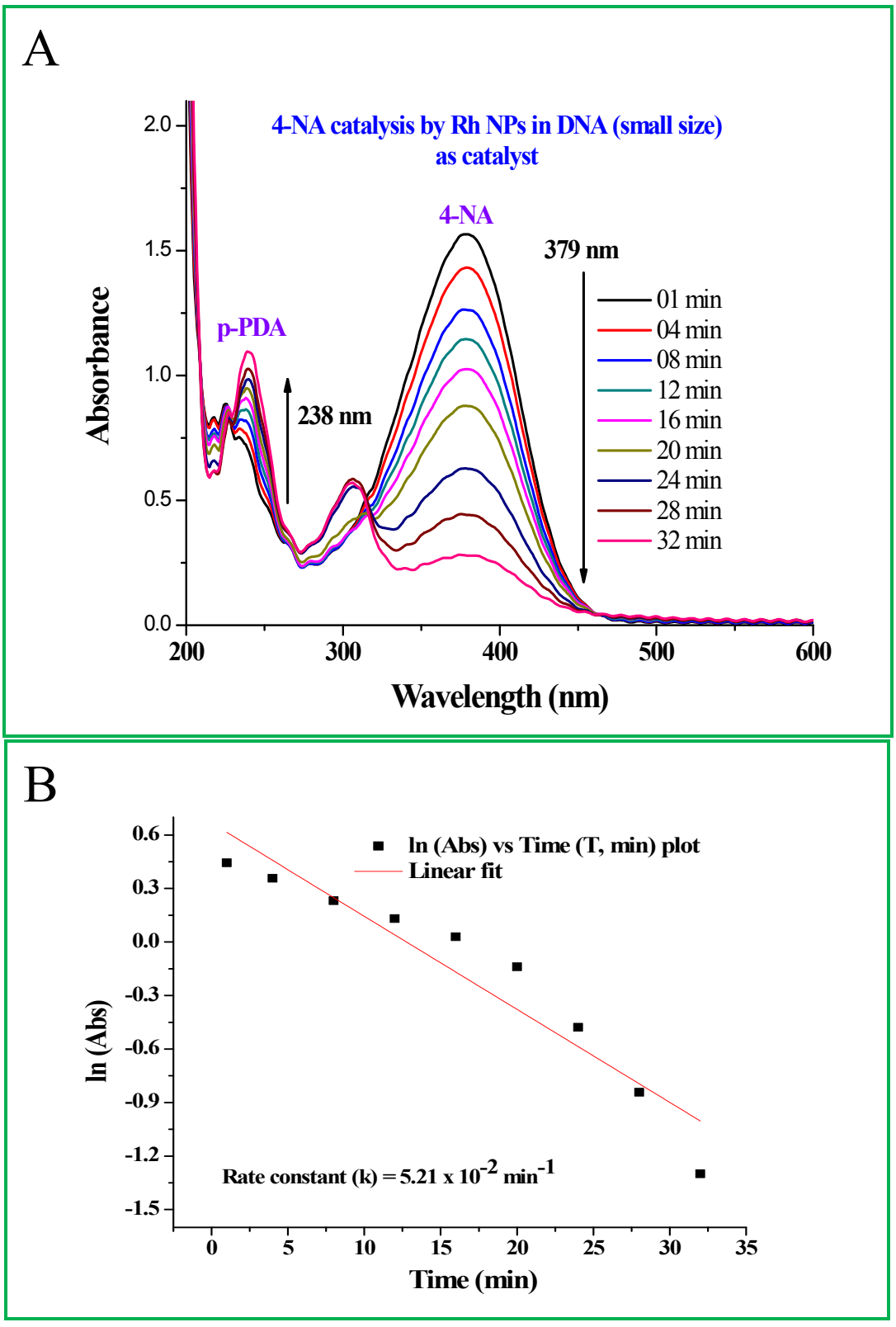


Figure S8: (A) Time-dependent UV-Vis absorption spectra for the reduction of 4-NA using small size Rh NPs on DNA scaffold s as catalyst. (B) The first order plot for the determination of rate constant with respect to the 4-NA concentration.

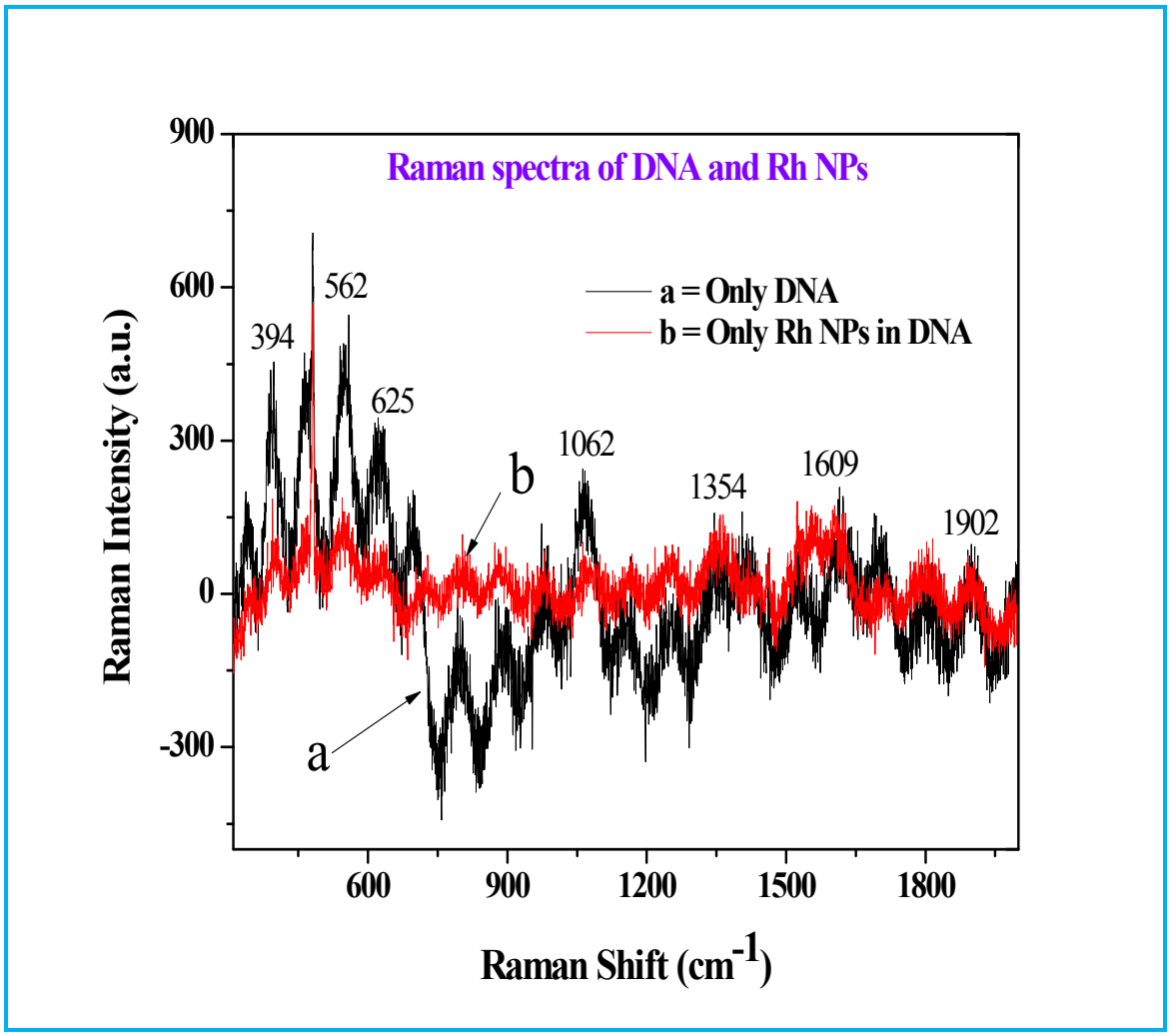


Figure S9: Raman spectra of only DNA (curve a) and Raman spectra of Rh NPs solution on DNA scaffold (curve b).

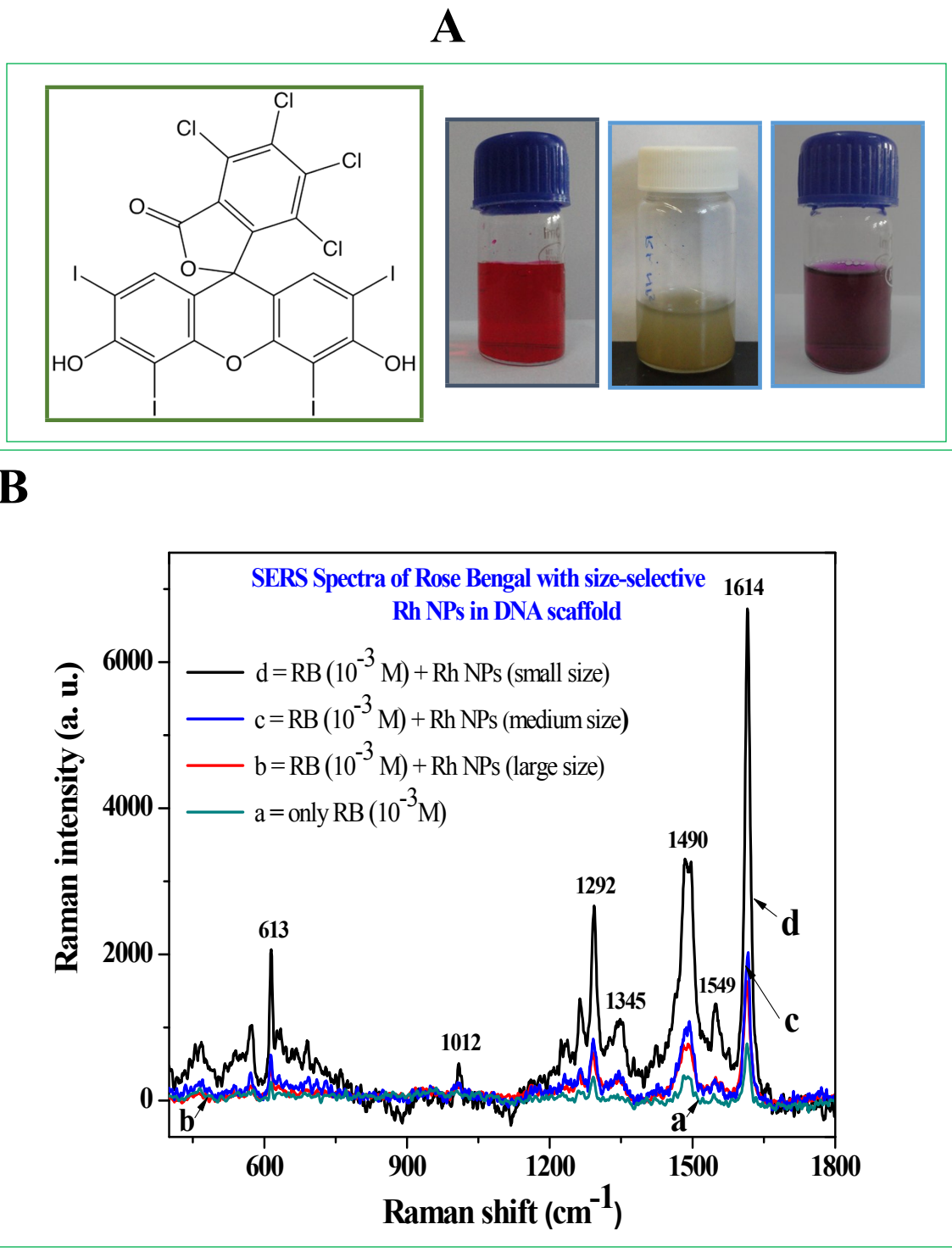
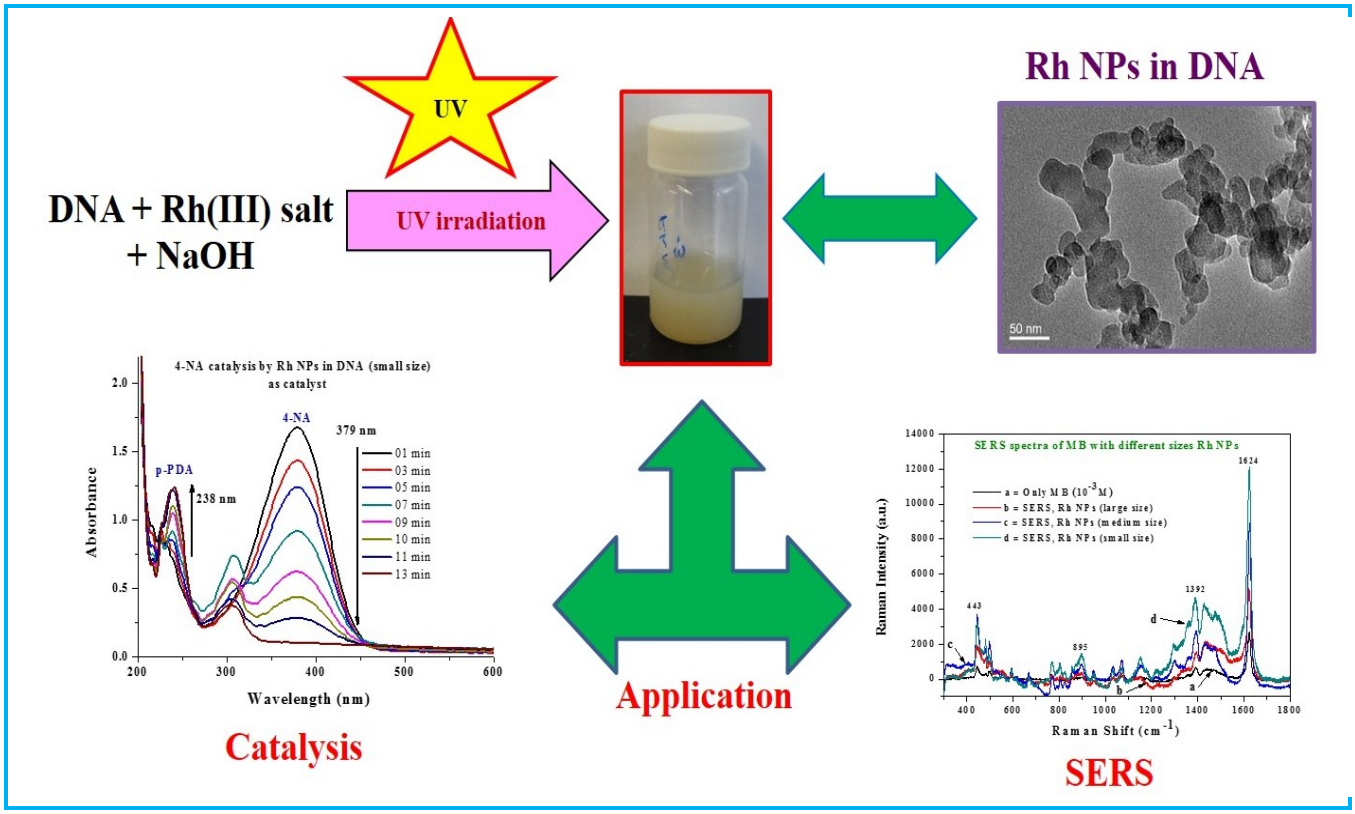


Figure S10: (A) shows the chemical structure of rose Bengal (RB) dye, camera picture of only RB dye, only Rh NPs solution and mixture of RB and Rh NPs solution. (B) shows the normal Raman spectra of only RB (curve a) and SERS spectra taking size-selective Rh NPs on DNA scaffold for large, medium and small size Rh NPs (curve b-d) respectively.

Scheme S1: The application of Rh NPs in catalysis and in SERS studies are shown schematically in Scheme S1.



Scheme S2: Schematic presentation of the electron transfer process during catalysis reaction for the reduction of 4-NA with BH_4^- and Rh NPs as catalyst.

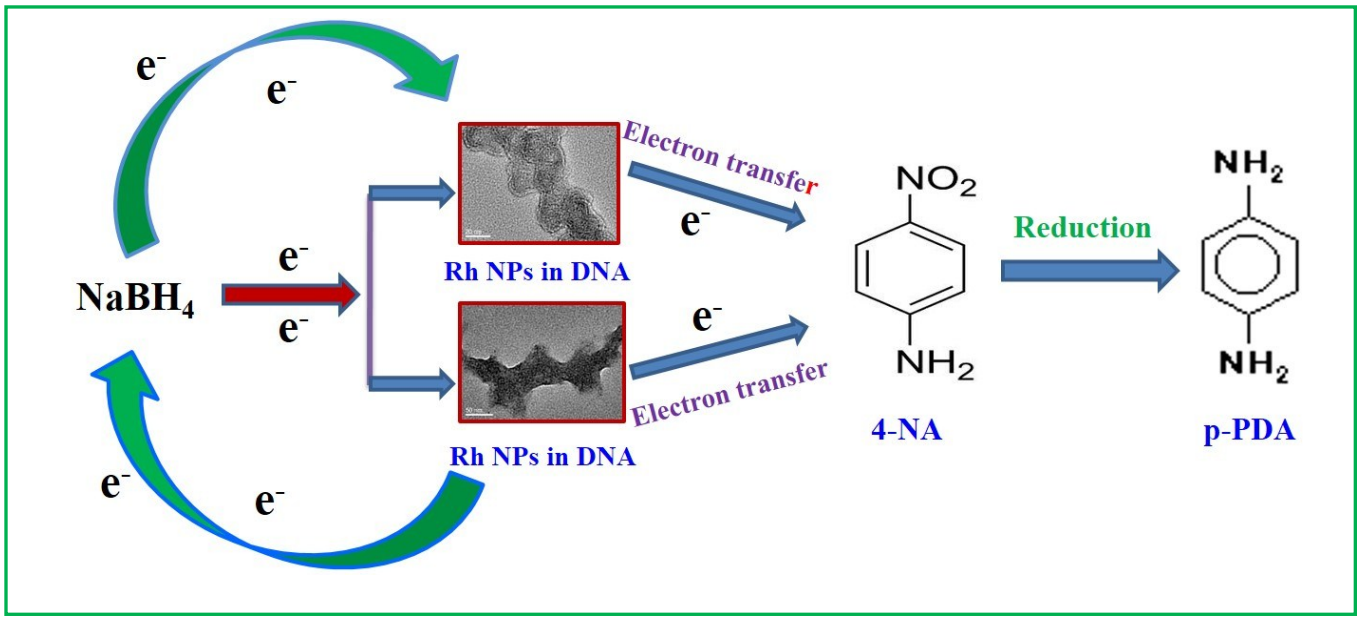


Table S1: Different reported Raman bands observed for MB and experimentally observed bands in our study with corresponding peak assignments.

The observed bands of MB in our experiment and the literature reported original MB bands with the corresponding band assignments.			
Raman bands for MB (reported)[70]	**Raman bands for aqueous MB (observed)**	**MB–Rh NPs in DNA (SERS) (observed)**	**Various peaks assignments**
449	443	443	δ(C–N–C)
502	478, 495	484	δ(C–N–C)
612	590	590	δ(C–S–C)
670	666	663	γ(C–H)
—	766	769	—
—	805, 821	806, 821	—
—	895	896	—
—	949	945	
1030	1031, 1071	1028, 1069	β(C–H)
1184	1149, 1178	1154	ν(C–N)
—	1218	1221	—
1301	1301	1300	—
1396	1363, 1392	1391	α(C–H)
1442	1439	1426	ν_{asym}(C–N) ring
—	-	1476	ν_{asym}(C–C) ring
1513	-	-	ν(C–C) ring
1617	1624	1624	ν(C–C) ring
Abbreviations: ν, stretching; α, in-plane ring deformation; β, in-plane bending; γ, out-of-plane bending; and δ, skeletal deformation. Reference 70 is given in main text.			