Online Supporting Information for

Self-assembled Wire-like and Honey-comb like Osmium Nanoclusters (NCs) in DNA with Pronounced Catalytic and SERS Activities

U Nithiyanantham, Sivasankara Rao Ede and Subrata Kundu*

Electrochemical Materials Science (ECMS) Division, CSIR-Central Electrochemical Research Institute (CECRI), Karaikudi-630006, Tamil Nadu, India.

Instruments

The synthesized Os NCs solutions were characterized with several spectroscopic techniques as discussed below. The UV-visible (UV-Vis) absorption spectra were recorded in a double beam UV-Vis spectrophotometer purchased from Unico (model 4802) equipped with 1 cm quartz cuvette holder for liquid samples. The high resolution transmission electron microscopy (HR-TEM) analysis was done with JEOL-JEM 2010 and Tecnai model TEM instrument (Tecnai^{TM} G2 F20, FEI) with an accelerating voltage of 200 KV. The Energy Dispersive X-ray Spectroscopy (EDS) analysis was done with the SEM instrument (Tescan) with a separate EDS detector connected to that instrument. A thin film of the Os NCs solutions was made in a glass substrate and the fabricated thin films were characterized by X-ray diffraction (XRD), and Fourier Transform Infrared Spectroscopy (FT-IR) analyses. The XRD analysis was done with a scanning rate of 0.020 s^{-1} in the 2θ range 10-100° using a PAN analytical Advanced Bragg-Brentano X-ray powder diffractometer (XRD) with Cu Kα radiation (λ = 0.154178 nm). The FT-IR analysis was done with the model Nexus 670 (FT-IR), Centaurms 10X (Microscope) having spectral Range 4,000 to 400 cm^{-1} with a MCT-B detector. The surface enhanced Raman scattering (SERS) study was done with Renishaw inVia Raman Microscope using an excitation wavelength of 632.8 nm (He-Ne laser). The excitation light intensity in front of the objective was ~10 mW with a spectral collection time of 1 sec for both Raman and SERS experiment. The integration time for our measurement was set to 10 sec. A domestic microwave (MW) oven (Samsung Company, DE68-03714B)

was used for microwave heating for the entire synthesis. The output power was 100-900 W and the operating frequency was 2450 MHz.

Preparation of samples for various characterizations

The DNA-Os NCs solutions were characterized using UV-Vis, TEM, EDS, XRD and FT-IR measurements. The aqueous solution of DNA-Os NCs was used for the measurement in UV-Vis spectrophotometer. The samples for TEM analysis was prepared by placing a drop of the corresponding DNA-Os NCs solution onto a carbon coated Cu grid followed by slow evaporation of solvent at ambient conditions. For EDS, XRD and FT-IR analysis, glass slides were used as substrates for thin film preparation. The slides were cleaned thoroughly in acetone and sonicated for about 30 min. The cleaned substrates were covered with the DNA-Os NCs solution and dried in air. After the first layer was deposited, subsequent layers were deposited by repeatedly adding more DNA-Os NCs solution and drying. Final samples were obtained after 12-15 time depositions and then analyzed using the above techniques. The EDS analysis was done using the SEM instrument containing a separate EDS detector.

X-ray diffraction (XRD) analysis

The X-ray diffraction pattern of the self-assembled Os NCs on DNA are shown in supporting Figure S-1. The peaks are assigned to the diffraction from the (002), (101), (102), (110) and (103) planes of hexagonally close pack (hcp) Os NPs (JCPDS card No: 06-0662) matching with other reports as given in the main document. One comparatively sharp peak at lower angles are observed due to the crystallization of the DNA molecules from the Os NCs solution. At higher angle the observe peaks are mostly broaden without any sharp peak with low intensity this is probably due to the grain size is extremely small and the material is non-crystalline in nature. We have not observed any impurity peaks for oxide formation which shows the purity of our synthesized samples.

Study with other reaction parameters

We have checked the various reaction parameters for the formation of self-assembled Os NCs on DNA. We have seen that the wire-like and honey-comb like structure are formed at a particular concentration that are given in the Table 1 (main document). While we used very high concentration of DNA (≥ 0.06 gm/ 50 mL), the Os NPs are formed but they aggregated together and formed big cluster like structure as seen in Figure 5A (main document). When we used DNA concentration very less, the particles are not attached properly in DNA and the particles are dispersed all over the sample. We also varied the concentration of Os salt solution and we observed that when Os salt concentration is less, the Os NPs are formed but number of particle are less as observed from the intensity of the colloidal solution and from the UV-Vis spectrum (not shown here). We also tested the volume of ethanol added and observed that if we add very less volume of ethanol (~ 10 μL), the Os particles are not formed in the experimental time scale while if we add more volume of ethanol (~ 1 mL), the Os particles are formed suddenly but they precipitated after sometime. We checked the microwave heating time and observed that Os particles started forming after 15-20 sec of microwave heating. Figure 5B (main document) shows the TEM image of Os particles in DNA after 20 sec of microwave heating where we can see particles are not fully attached with the DNA chains due to lesser number of particles available in the solution. Figure 5C (main document) shows the TEM image of Os particles after 30 sec of microwave heating where we can see more number of particles on DNA compared to Figure 5B which speaks that with increasing microwave heating, more number of particles are forming. We also checked our reaction with longer time microwave heating (~ 5 min) and we have not seen any remarkable change in particles morphology. We also tested our reaction in absence of DNA where we see that Os particles are formed but they aggregated without any specific shape (Figure 5D, main document) and gets precipitated after sometime due to absence of any specific stabilizer in the solution. So all these control experiments proves that Os NCs having wire-like and honey-comb like morphology are formed at a specific reaction condition that are given details in Table 1(main document).

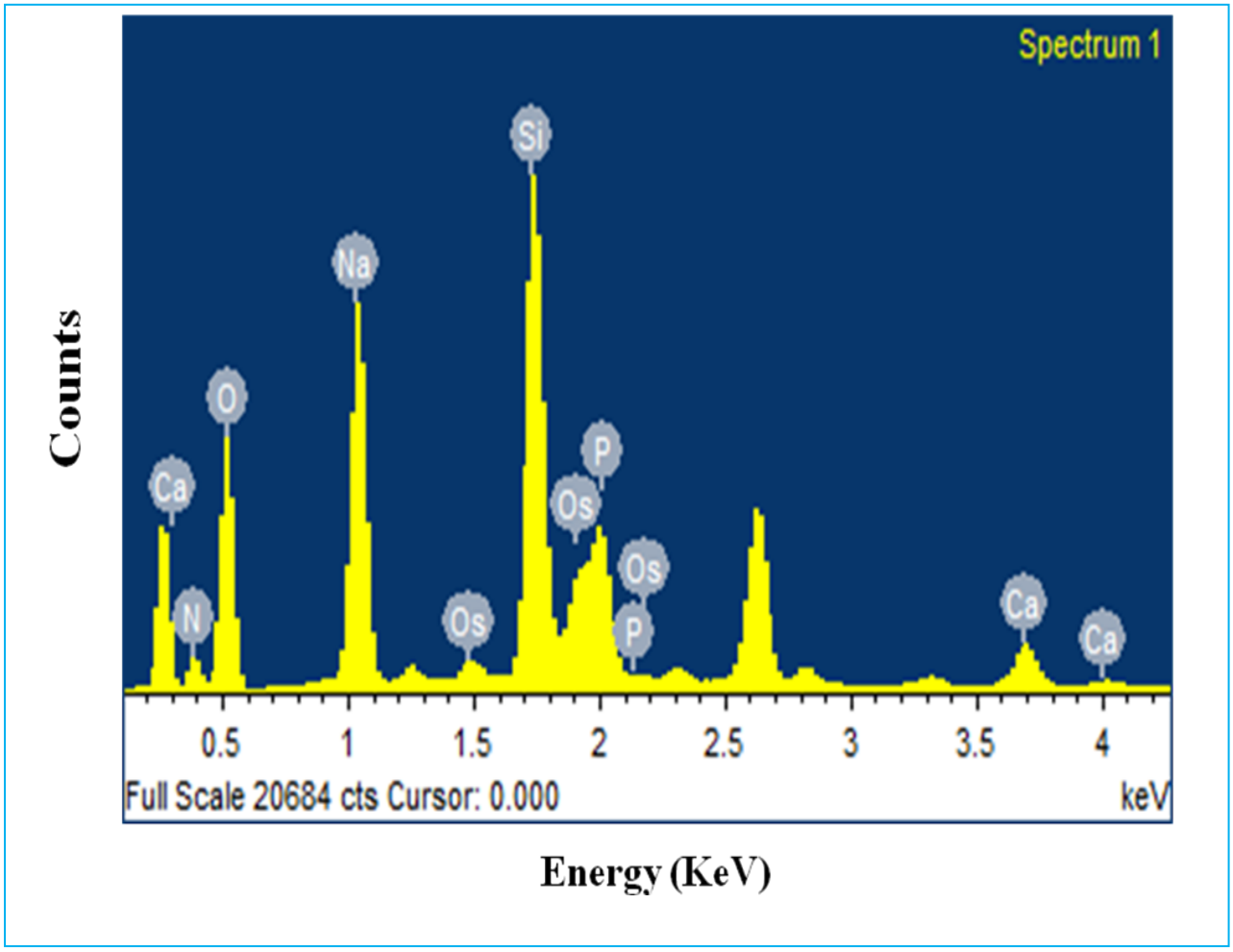

Figure S-1: The energy dispersive X-ray spectroscopic (EDS) analysis of the self-assembled Os NCs in DNA having different peaks of Os, O, N, P, Si and Ca.

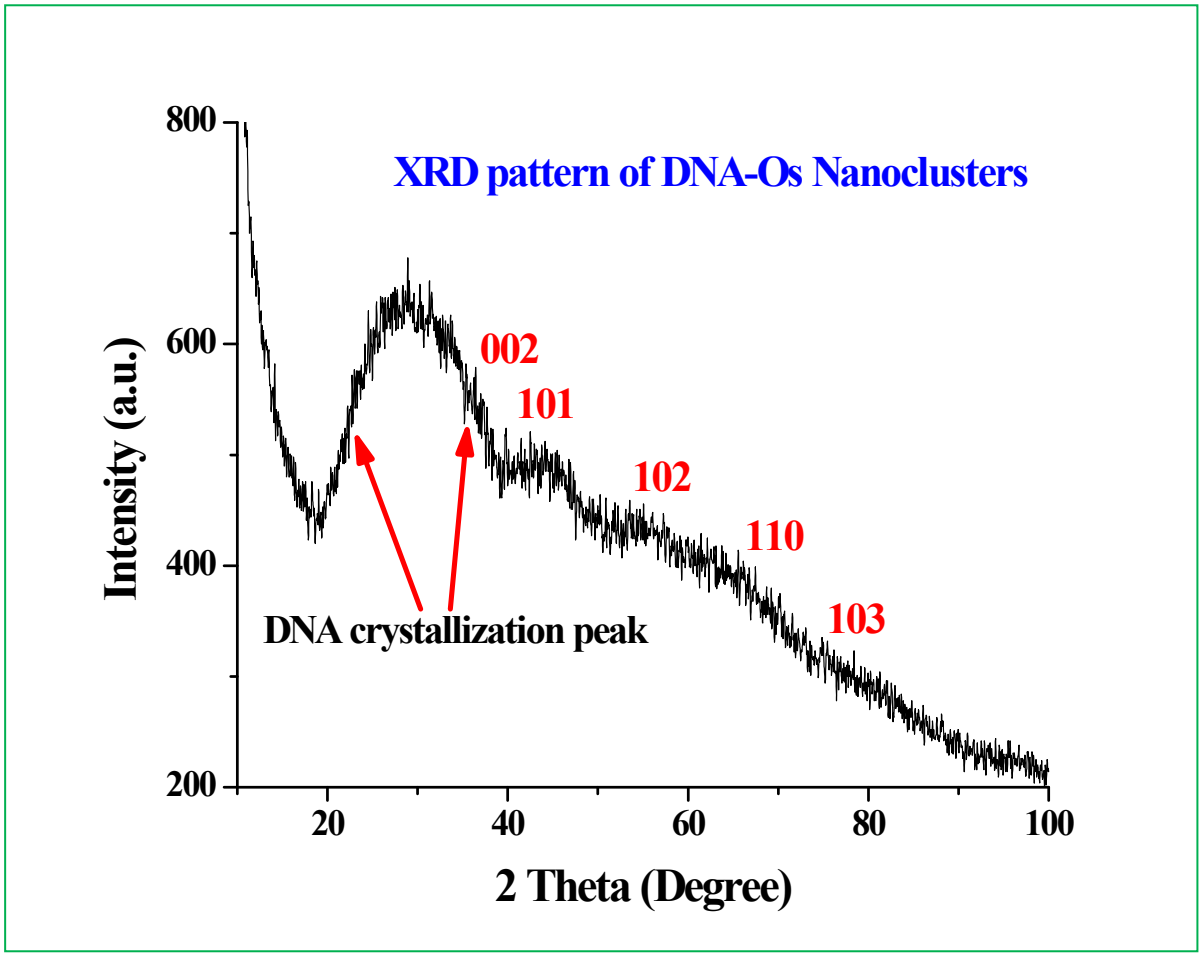

Figure S-2. The X-ray diffraction (XRD) pattern of the self-assembled Os NCs on DNA. The diffraction observed from the (002), (101), (102), (110) and (103) planes of hexagonally close pack (hcp) Os NCs.

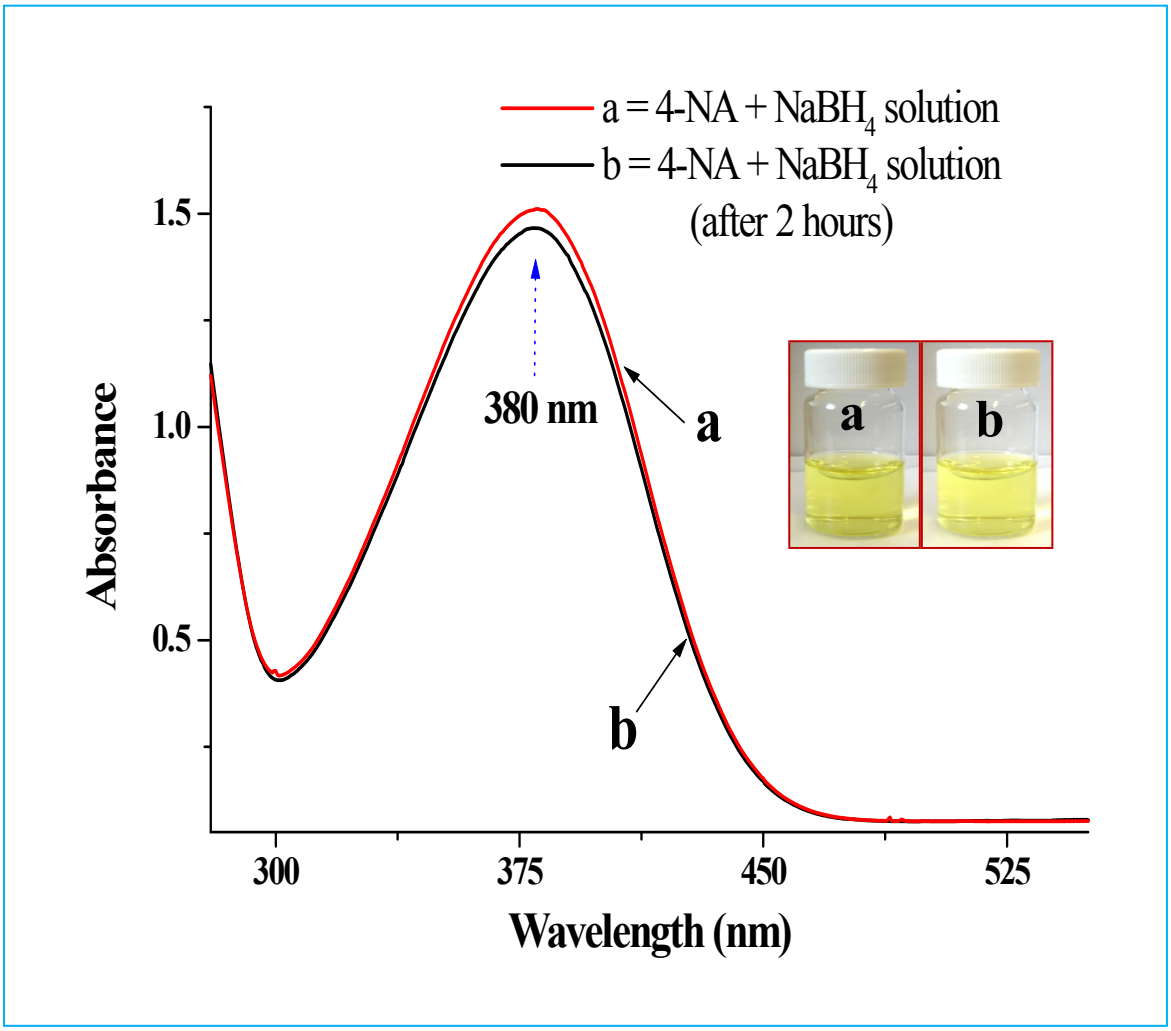

Figure S-3. The UV-Vis absorption spectrum of a mixture of 4-NA with $NaBH_4$ just after mixing (curve a) and after aging the mixture for 2 hour (curve b). Inset shows the camera image of the two solutions.

Raman bands for MB (reported)[56]	Raman bands for MB in water (observed)	MB – Os NCs (SERS) (observed)	Assignment of various peaks[56]
449	451	452	δ (C-N-C)
502	502	504	δ (C-N-C)
612	598	-	δ (C-S-C)
670	673	-	γ(C−H)
-	776	774	-
-	808	-	-
-	896	-	-
-	951	954	
1030	1043	1043	β(C−H)
1184	1190	1188	ν(C−N)
-	1217	-	-
1301	1301	1301	-
1396	1396	1400	α(C−H)
1442	1440	1439	ν_{asym}(C−N) ring
-	1468	1472	ν_{asym}(C-C) ring
1513	1503	1503	ν(C−C) ring
1617	1622	1628	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 56 is given in the main document.

Table T-1: The position of the original MB Raman bands and the bands observed in our experiment with the assignments various peaks are summarized.