

Online Supporting Information's for

Enhanced Catalytic and SERS Activities of CTAB stabilized Interconnected Osmium Nanoclusters

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Instruments.

The synthesized CTAB-Os NCs were characterized with several spectroscopic techniques like UV-Vis, TEM, EDS, XRD and FT-IR analyses 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 a 1 cm quartz cuvette holder for liquid samples. The transmission electron microscopy (TEM) analysis was done with JEOL-JEM 2010 and Tecnai model TEM instrument (Tecnai™ 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 $30\text{-}90^\circ$ using a PAN analytical Advanced Bragg-Brentano X-ray powder diffractometer (XRD) with Cu $K\alpha$ radiation ($\lambda = 0.154 \text{ nm}$). 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 $\sim 10 \text{ mW}$ 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 .

Sample preparation for various spectroscopic characterizations.

The CTAB-Os NCs solution in DI water was used for the measurement in UV-Vis spectrophotometer. The samples for TEM analysis was prepared by placing a drop of the corresponding CTAB-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 CTAB-Os NCs solution and dried in air. After the first layer was deposited, subsequent layers were deposited by repeatedly adding more CTAB-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 FE-SEM instrument containing a separate EDS detector. For the preparation of SERS sample, a stock solution of R Be of 10^{-3} (M) was made and other different concentration was prepared by proper dilution with DI water as necessary. A measured volume of dye solution at a specific concentration were mixed with the CTAB-Os NCs solution and finally deposited over the glass slides and dried in air. The dried samples were used for the SERS measurement.

Energy Dispersive X-ray Spectroscopy (EDS) Analysis.

Figure S-1 shows the energy dispersive X-ray spectroscopic (EDS) analysis of the synthesized Os NPs in CTAB surfactant media. The EDS spectrum consists the expected peaks for Ca, Si, Na, O, Os and Br. The Ca and Si peak came from the glass substrate used for the deposition of Os NPs for EDS analysis. The Na peak came from the NaOH and O peak came from the 2,7-DHN or from the Os salt. The Os peak came from the Os NPs solution and the small intense Br peak came from the CTAB as we used CTAB as stabilizing agent during the synthesis of Os NPs. So from the EDS analysis it is clear that the Os NPs are formed and they stabilized by CTAB molecule.

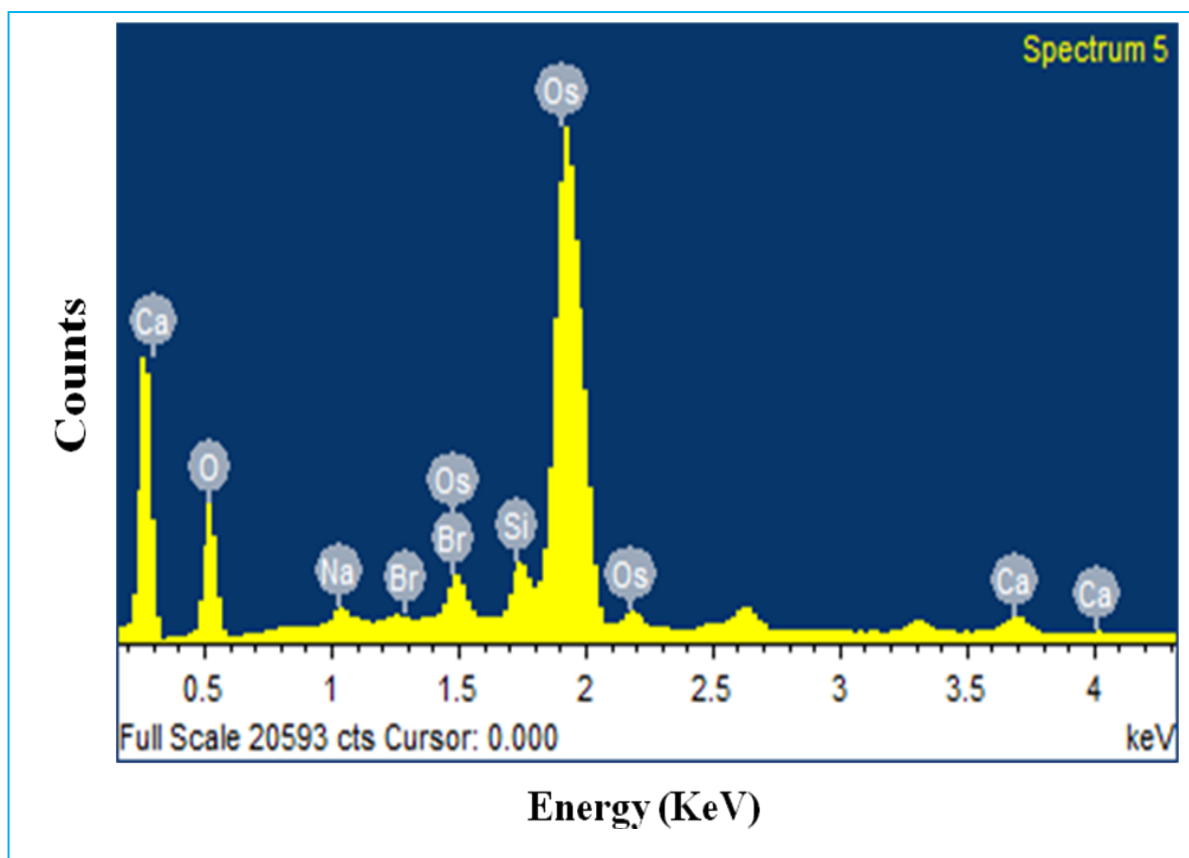


Figure S-1: The energy dispersive X-ray spectroscopic (EDS) analysis of the Os NPs having different peaks for Ca, Si, Na, O, Os and Br.

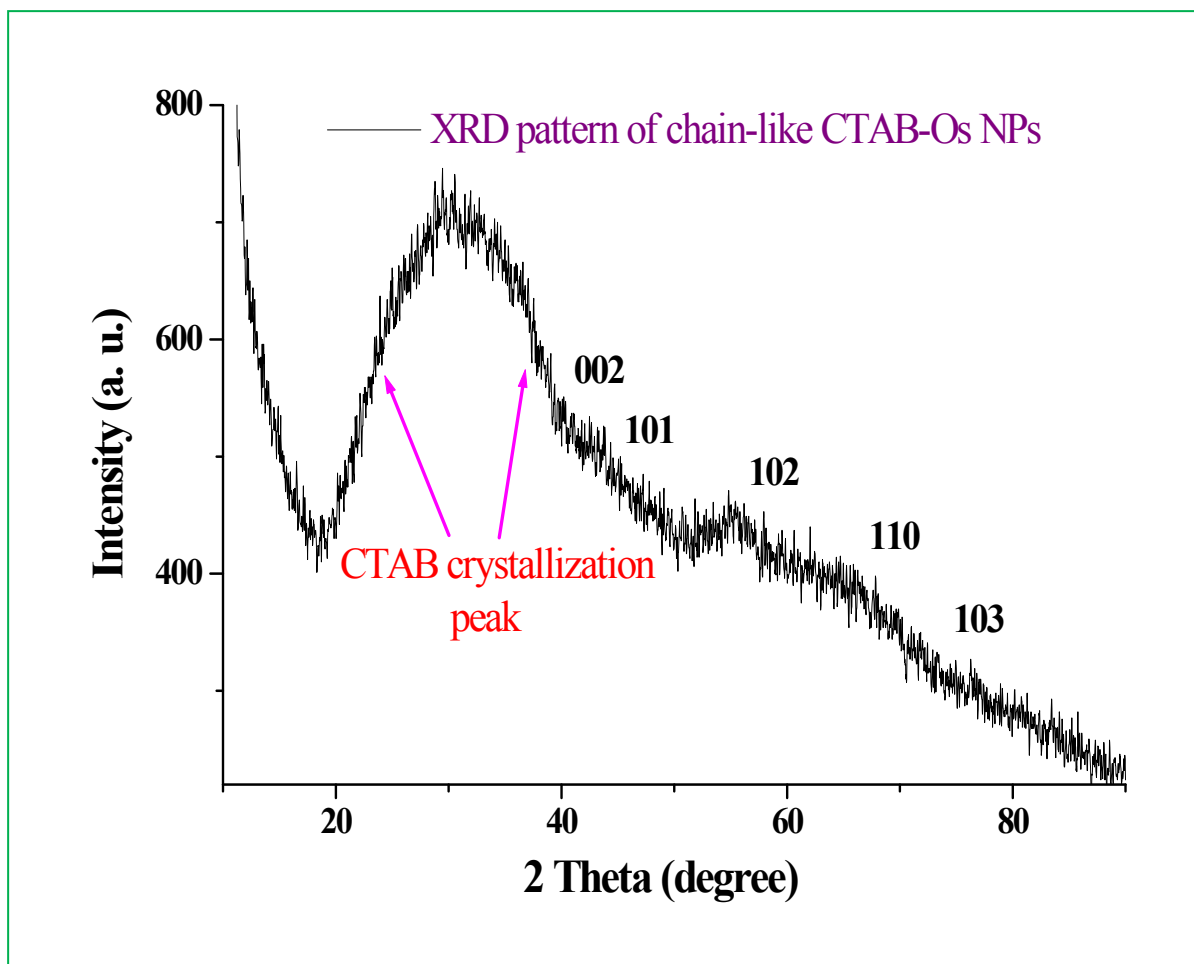


Figure S-2: The X-ray diffraction (XRD) spectrum of the CTAB stabilized chain-like Os NPs. The diffraction observed from the (002), (101), (102), (110) and (103) planes of hexagonal phases of osmium.

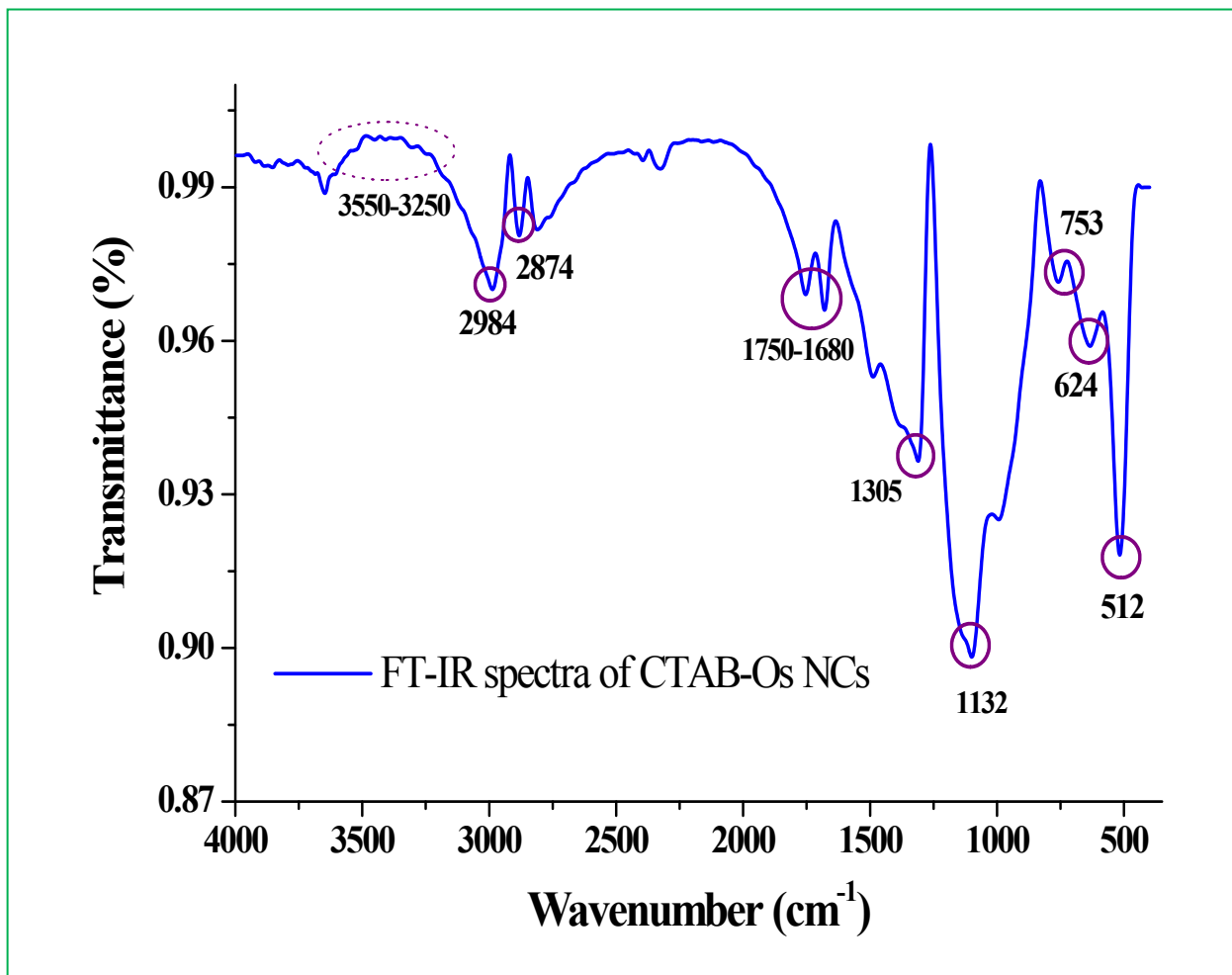


Figure S-3: An enlarge view of the FT-IR spectra of CTAB-Os NCs as given in Figure 4 in main document.

Study with other reaction parameters.

In our synthesis we have examined details about the different reaction parameters. We have seen that Os nanostructures with aggregated clusters, nano-chain like networks and small spheres are formed at particular concentrations that are given in Table 1. When we used CTAB concentration very high ($\geq 10^{-1}$ M), the Os particles are formed but it is difficult to remove the excess surfactant from the NCs samples even after 5-6 times centrifugation. While we used CTAB concentration very low ($\leq 10^{-6}$ M), mostly spherical particles formed but the synthesized particles are not stable and gets precipitated within couple of hour of synthesis. Once we used Os salt concentration high ($\geq 10^{-1}$ M), reaction results Os NCs formation in less time but they generates aggregated particles without any specific morphology. If we used Os salt concentration very low ($\leq 10^{-4}$ M), the reaction takes longer time (> 1 hour) to generate the Os particles due to less number of Os ions available in solution. Similarly, while 2,7-DHN concentration is low ($\leq 10^{-5}$ M), reaction takes longer time to generate the particles while concentration is high ($\geq 10^{-1}$ M), the reaction generates Os particles very fast (within 10 min of reaction). Similarly, when NaOH concentration is high ($\geq 5 \times 10^{-2}$ M), the solution formed the particles in shorter time and formation takes place instantaneously just after addition of NaOH. When NaOH concentration is low ($\leq 10^{-5}$ M), the reaction generates particles but take long time and solution results mixture of small spherical particles and large nanocubes. Figure S-4 in the SI shows the TEM images at different NaOH concentrations. So all the above control experiment speaks that the reagents concentration is extremely important for the generation the Os nano structures with specific morphologies.

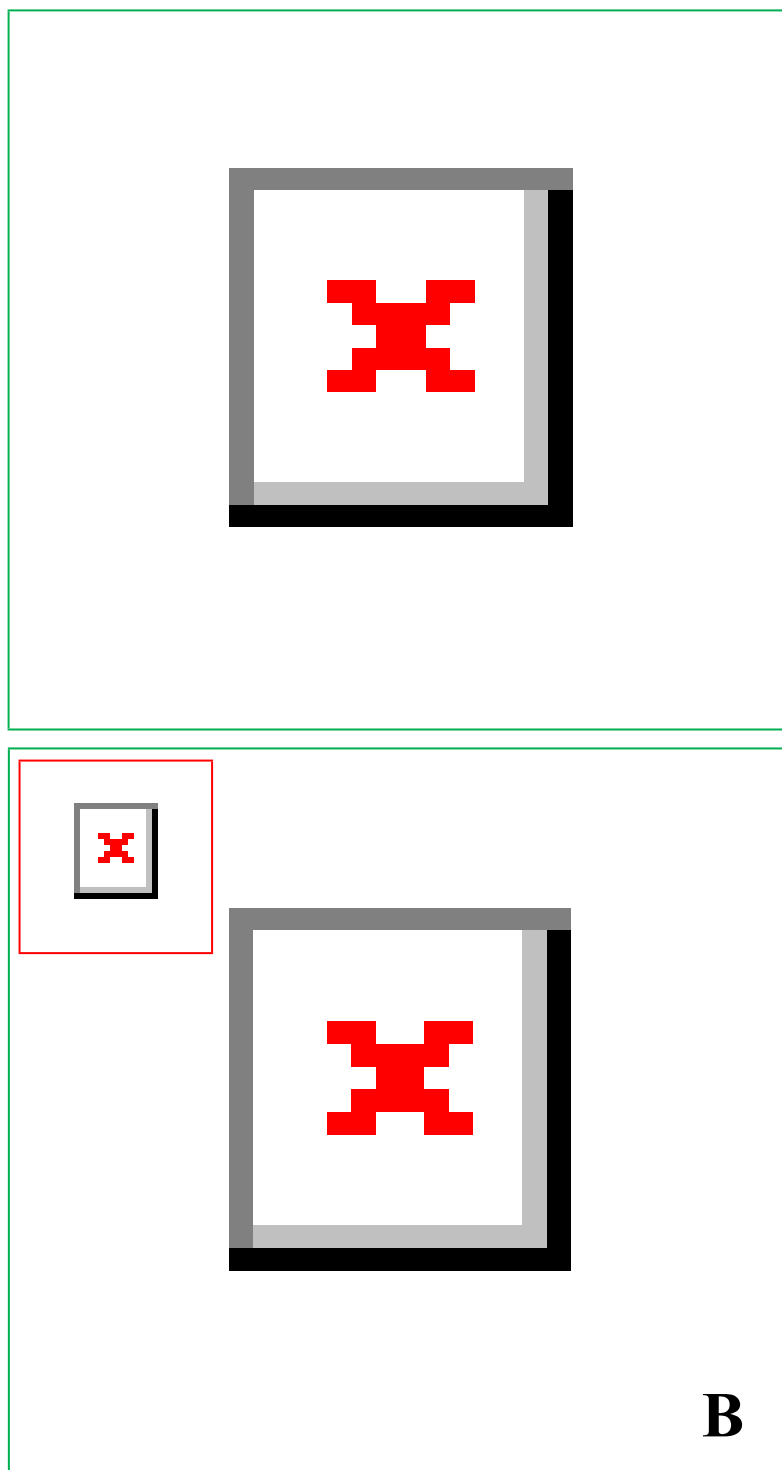


Figure S-4: The transmission electron microscopy (TEM) images of the Os particles at different NaOH concentrations. (A) shows the TEM image of aggregated Os NPs while NaOH concentration is very high and (B) shows the image of a nanocubes with mixture of small spheres when NaOH concentration is low. The inset of (B) shows the SAED pattern taken from the Os nanocube showing perfectly single crystalline nature.

Catalysis Study:

Figure S-5, curve a shows the UV-Vis absorption spectrum of a mixture of 4-NA solution with NaBH_4 . The absorption maxima came at a peak of 381 nm. The absorption value reduced to 7 % after keeping the same solution about ~ 6 hours which indicates that only NaBH_4 cannot reduce 4-NA significantly and the reaction rate is very slow. So it is assumed that there might be existence of some kinetic barrier which prevents the electron transfer from NaBH_4 to the nitro compound. Moreover, we check few control experiments, where we used 4-NA with CTAB alone, 4-NA with 2,7-DHN alone or 4-NA with alkaline 2,7-DHN alone. We have not observed any type of reduction of 4-NA using any of these reagents in presence of NaBH_4 . Although, in presence of Os NCs solution in the reaction mixture contains 4-NA and NaBH_4 , the absorbance value of 4-NA greatly reduced and reaction completed within a short time. So the presence of Os NCs as catalyst is extremely important to take place the catalysis reaction. We have measure the pH values of different solution mixtures and the pH value of 4-NA solution is 7.34, NaBH_4 solution is 9.92, 4-NA and NaBH_4 solution mixture is 9.48 and a mixture of 4-NA, NaBH_4 and Os NPs solution (aggregated clusters) is 9.33. Table T-1 shows the different nitro compounds tested for the catalysis reaction and corresponding time required for the full reduction.

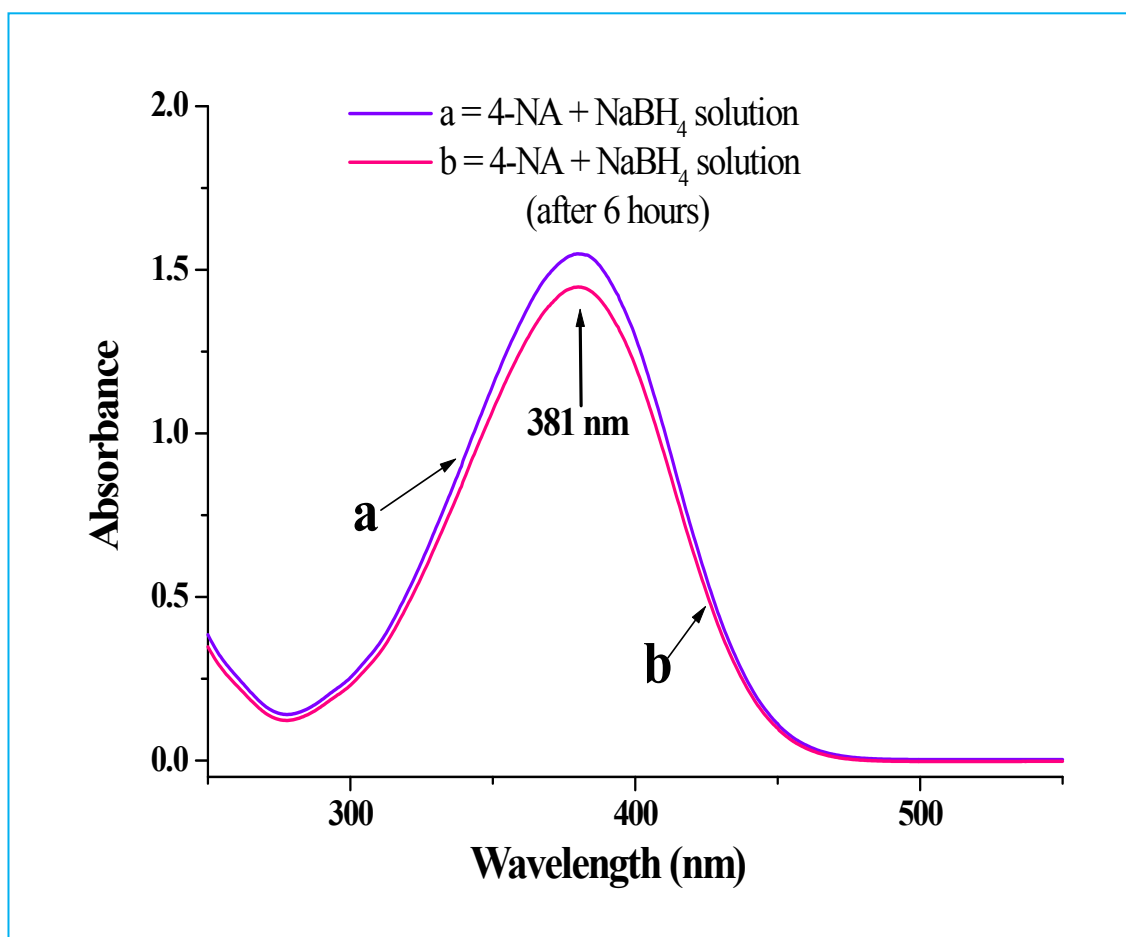
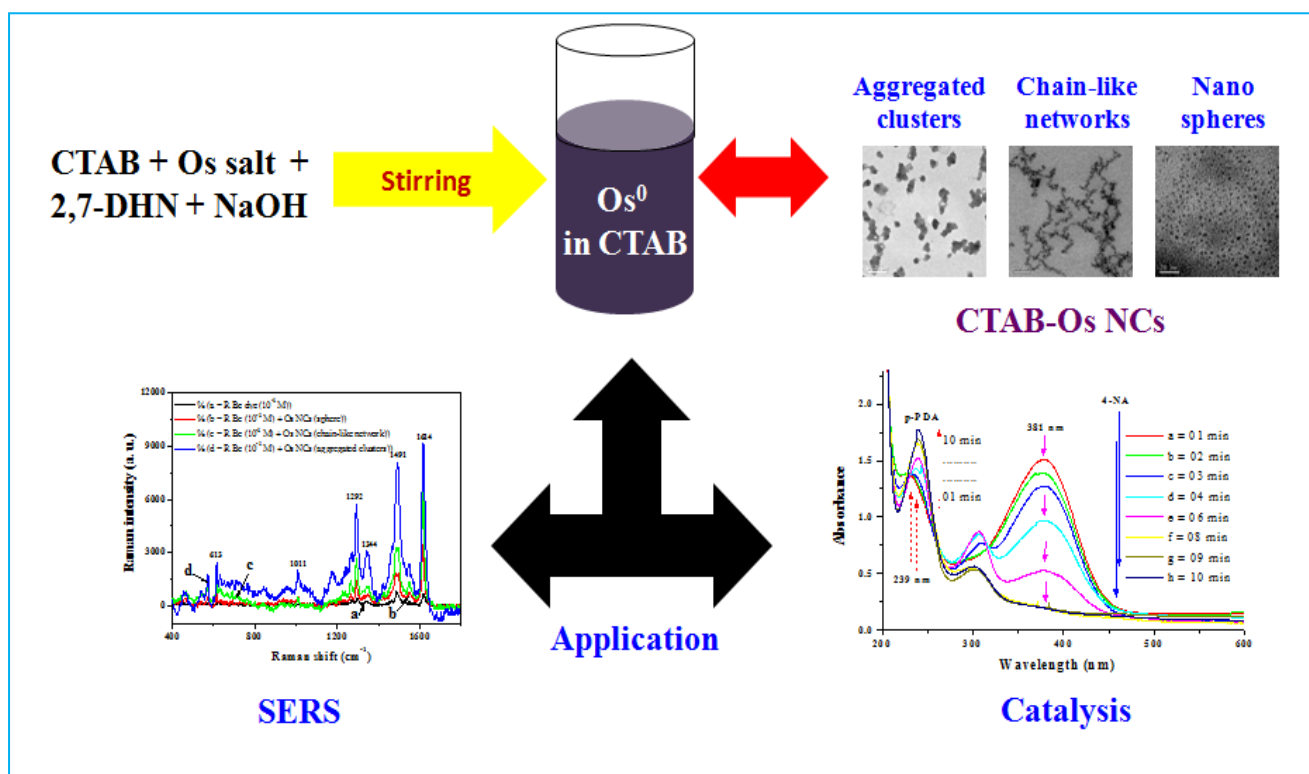
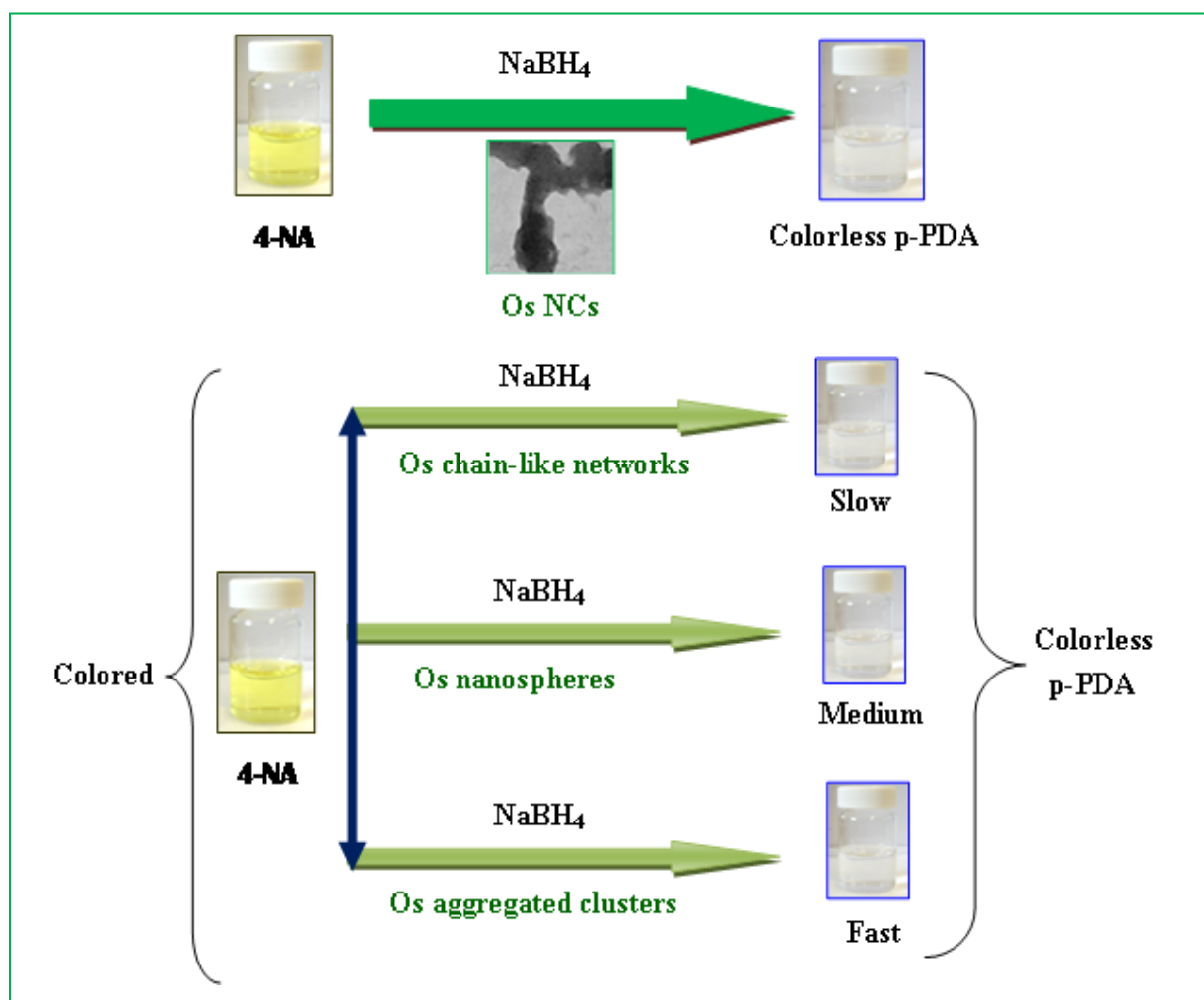


Figure S-5: The UV-Vis absorption spectrum of a mixture of 4-NA solution with NaBH₄ just after mixing (curve a) and after keeping the solution for about ~ 6 hours (curve b).



Scheme S-1: The generation of three different morphologies of Os nanostructures, their catalytic and SERS activity are shown schematically in Scheme S-1.



Scheme S-2: Different catalytic rate observed for three different morphologies of Os nanostructures.

Nitro compound	Shape and size of nano component (nm)	Approx. time for full reduction (min)	Final Product
4-nitro aniline	Aggregated clusters ($\sim 2 \pm 0.2$)	10	Para-phenylenediamine
4-nitrophenol		>240	4-aminophenol
2-nitrophenol		~ 120	2-aminophenol
2-nitro aniline		~ 70	Ortho-phenylenediamine

Table T-1: The different nitro compounds tested and the expected time for the full reduction are summarized.