

Supporting information

Interconnected Osmium Nanoclusters: Preparation and Surface Enhanced Raman Scattering Activity

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Experimental section

Chemicals

OsCl_3 and mercapto pyridine (4-MPy) were obtained from Aldrich, USA. Ascorbic acid (AA) and rhodamine 6G (R6G) were obtained from SD fine chemicals, India. Analytical grade ethanol, acetone and sulfuric acid were obtained from SRL, India. All the glassware were rinsed with aqua regia followed by thorough washing with distilled water. Water with resistivity of 18 $\text{M}\Omega$ cm was used in all the experiments.

Preparation of Os Nanostructures

Os chain-like structures were synthesized by mixing 1:5 molar ratio of aqueous solution of OsCl_3 and AA with stirring at 25°C for 5 minutes followed by heating the solution to 95°C and maintaining it at the same temperature for ninety minutes. The color of the solution changed from brownish red to violet. Subsequently, the Os nanoparticles were washed with ethanol to remove excess capping agent and redispersed in ethanol for further studies.

Characterization

Morphological and structural characterization were carried out using field emission scanning electron microscope (SEM, Sirion, FEI) and transmission electron microscope (TEM,

T20, FEI) attached to selected area electron diffraction (SAED) accessory. The sample for TEM was prepared by slow evaporation of dilute colloid in ethanol on a copper grid, while for SEM, the sample was prepared by drop coating the colloid on doped Si wafer. The X-ray diffraction (XRD) was performed using Bruker D8 diffractometer with graphite-monochromatized Cu-K α radiation source. X-ray photoelectron spectroscopy (XPS) measurements were carried out on Thermo-Fischer Multilab 2000 instrument with MgK α as X-ray source. Optical absorption spectra were recorded on PerkinElmer UV-Vis-NIR spectrophotometer. IR spectroscopy was carried out using thermo scientific FTIR instrument under ambient conditions.

Sample preparation for SERS

The SERS substrates were prepared by drop coating 10 μ L of Os colloid in ethanol on glass slides and dried under vacuum. The dried glass slides were washed well with ethanol and subsequently immersed in ethanolic solution of the analyte of different concentrations, for thirty minutes. The glass slides were then taken out and washed with ethanol to remove any physisorbed analyte and dried. Raman spectral measurements were carried out using two different excitation lasers of 514 and 633 nm [LabRAM HR, Horiba Jobin Yvon equipped with CCD detector]. A 50 X long working distance objective with numerical aperture of 0.5 was used and the acquisition time was kept at 20 seconds.

Figures

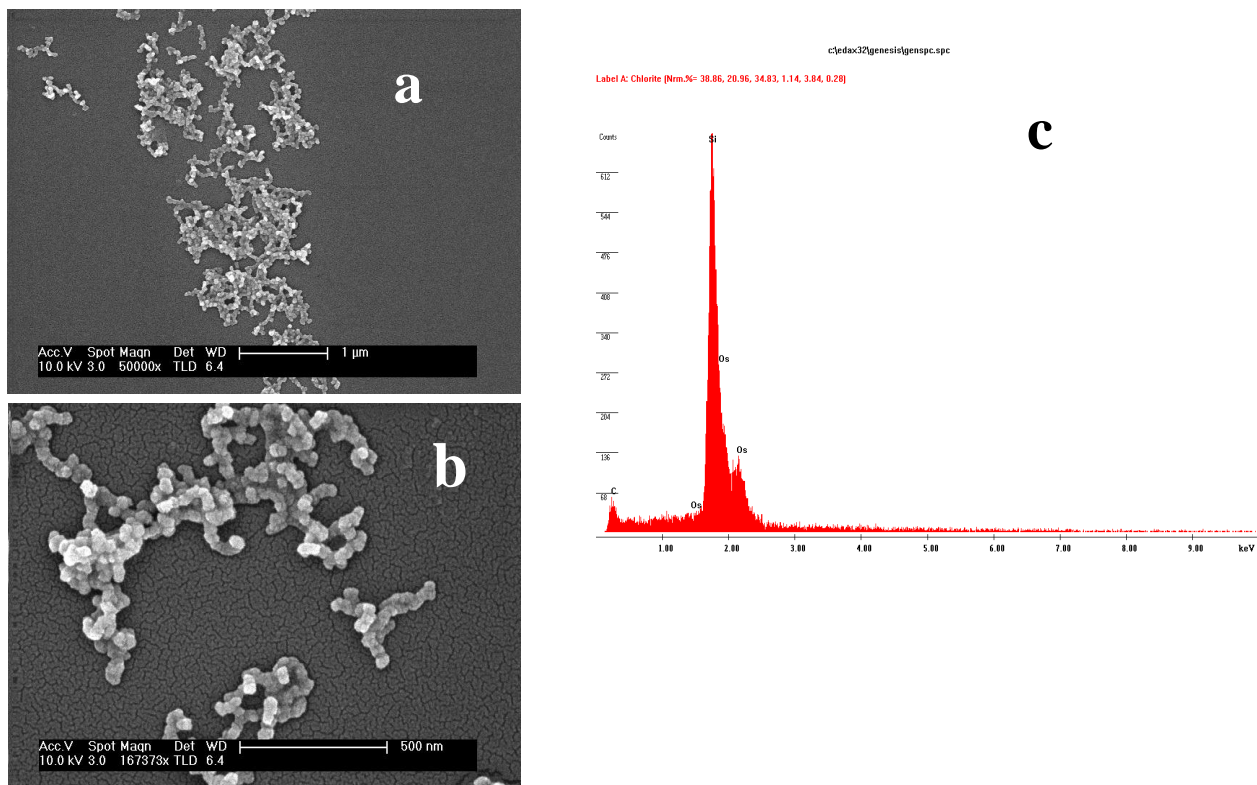


Figure S1. (a,b) Scanning electron microscopic images of Os nanochains under different magnifications and (c) corresponding EDS pattern.

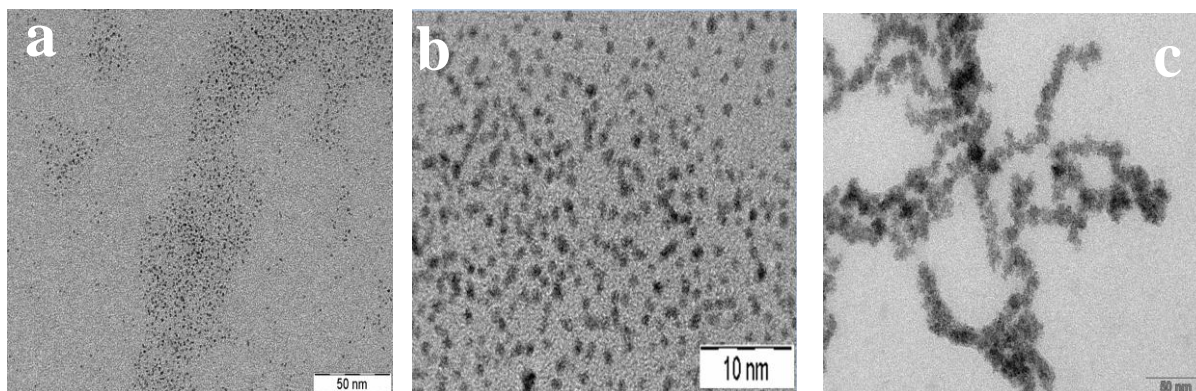


Figure S2. TEM images of Os nanostructures. The reaction mixture is frozen at (a, b) 5 minutes and (c) 90 minutes of the reaction and the nanostructures are subsequently imaged.

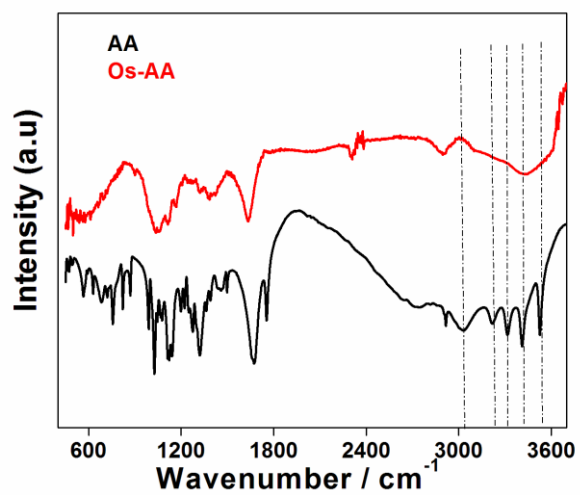


Figure S3. FTIR spectra of pure AA and AA capped Os nanochains. The marked band positions are explained in the text.

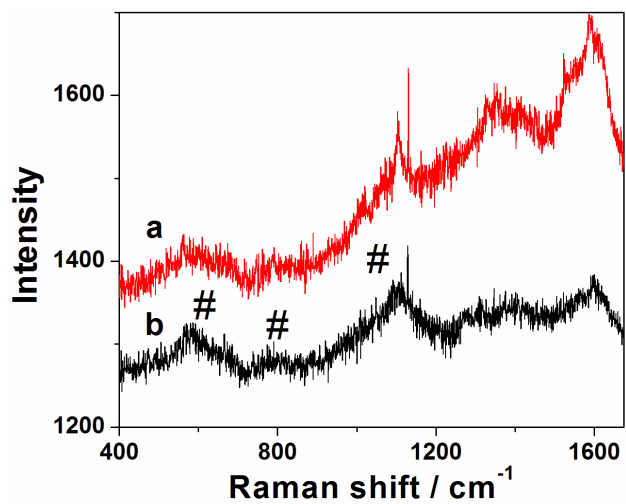


Figure S4. SERS spectra of 4-MPy adsorbed on Os nanochains from (a) 100 nM and (b) 20 nM solutions. The excitation wavelength used is 514 nm.

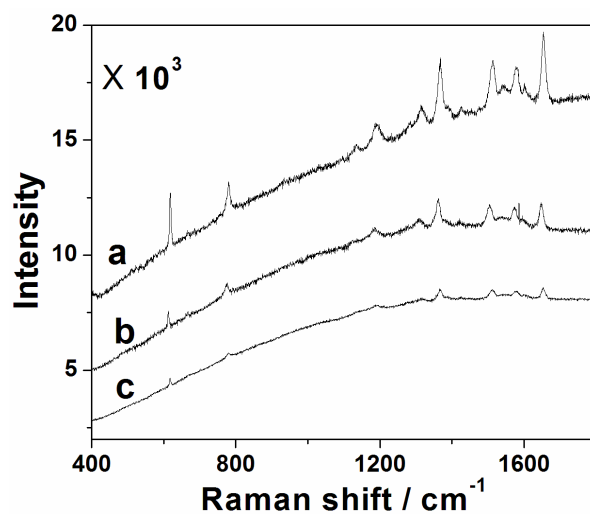


Figure S5. SERS spectra of R6G adsorbed on Os nanochains from (a) 1mM, (b) 100 μM and (c) 10 μM solutions. The excitation wavelength used is 514 nm.

Table S1: Vibrational band assignments for 4-MPy analyte. Vibrational bands for neat analyte are given along with SERS bands observed using 514 nm and 633 nm excitation sources.

Vibrational mode	<u>Band position, cm⁻¹</u>		
	<u>neat 4-MPy</u>	<u>(SERS) 514 nm</u>	<u>(SERS) 633 nm</u>
v(CC)	1614	1615	1608
v(CC)	1595	1589	1586
v (C=N)/ v (C=C)	1456,1475	1479	1451
v(CC)	1392	1411	1402
β(C-H)	1285	1286	1308
β(C-H)	1247		1258
β(C-H)/ δ(N-H)	1197	1222	1225
ring breathing/ C-S	1100	1107	1104
β(C-H)	1076	1069	1066
γ (C-H)	786	787	789

Table S2: Vibrational band assignments of R6G. Vibrational bands for pure analyte are given along with SERS bands observed using 514 nm excitation source.

Vibrational Mode	<u>Band position, cm⁻¹</u>	
	<u>neat R6G</u>	<u>SERS (514 nm)</u>
Inplane C-C-C bending.	610	614
Out of plane C-H bending.	768	774
C-H bending, N-H bending, Inplane xanthene ring deformation.	1182	1184
Inplane xanthene ring breathing, NH bending, CH ₂ wagging	1313	1315
Xanthene ring stretching, inplane C-H bending	1361	1364
Aromatic C-C stretching, C-N stretching, N-H bending, C-H bending	1517	1508
Xanthene ring stretching, inplane C-H bending	1574	1577
In plane C-H bending	1650	1653

Table S3: Variation of zeta potential of the reaction mixture as function of time of the reaction.

Time (min)	Zeta potential, ζ (mV)
5	-34.3
10	-28.5
15	-25.7
30	-23.5
45	-22.1
60	-21.3
90	-20.4
120	-20.2