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ARTICLE TYPE

Spontaneous Assembly of Iridium Nanochain-Like Structures: Surface Enhanced Raman Scattering Activity Using Visible Light

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A facile, environmentally friendly approach to synthesize branched Ir nanochain-like structures under mild conditions, using polyfunctional capping molecules in aqueous medium is reported; the nanostructures exhibit surface plasmon resonance peak (SPR) in the visible region and serve as active substrate for surface enhanced Raman scattering studies.

Assemblies based on nanomaterials are of considerable interest for fundamental research and applications since these structures act as bridge between particles and bulk materials.¹⁻³ Different synthetic strategies that include *in-situ* assembly of metal colloids using bifunctional surfactants and polydentate ligands have been developed using bottom up approach either by employing linear templates or template-free methods. Synthesis of interconnected nanochains of different noble metals like Au, Ag, Pt, Rh, Os etc. have been reported.⁴⁻¹³ Due to its reactivity, stability, selectivity under different conditions, iridium (Ir) is an attractive element and possesses good catalytic and electrocatalytic activity for various reactions.¹⁴⁻¹⁷ Compared to other platinum group metals, synthesis of Ir nanostructures is not well-explored and most of the reported procedures that have been successfully employed yield spherical particles.¹⁸⁻²⁰ There is a need to explore synthetic procedures in environmentally friendly conditions, to obtain different shapes and morphologies of Ir nanostructures. The theoretically calculated plasmonic band of spherical 10 nm sized Ir particles lies close of 350 nm²¹ and it is likely that the position of this band may get shifted to visible region when the shape/morphology of the nanostructures are different and conducive. If it does, another application that can be added to the plethora of uses of Ir, will be its property related to surface enhanced Raman scattering (SERS).

SERS which has seen a spurt of activity in recent years is a versatile tool for studies on various surface interactions. The enhancement in Raman spectral signals observed in SERS is primarily attributed to electromagnetic mechanism. Charge transfer and molecular transitions based on Herzberg-Teller type transitions have also been proposed to contribute to the enhancement.^{22,23} Coinage metals like Au, Ag and Cu are the commonly used substrates for SERS studies.²⁴ Other anisotropic nanostructures based on Pd, Os, Rh, and Ru have recently attracted attention, particularly due to advancement in the

synthetic procedures to obtain anisotropic nanostructures.^{10,13,25,26}

The present study explores the synthesis, characterization and plausible mechanism of formation of Ir nanochain-like structures under mild conditions in aqueous medium. The use of branched Ir structures as SERS substrates is explored as well. Ir nanostructures are prepared using sodium borohydride as the reducing agent in the presence of different capping molecules (table S1, Supporting Information). Briefly, an aqueous solution of 0.1 mM IrCl₃ is stirred in the presence of ascorbic acid (AA) (molar ratio of precursor to AA is maintained at 1:3) followed by the addition of freshly prepared sodium borohydride solution (20 mg in 10 mL water), and the mixture is stirred at 80°C for 360 minutes. The colour of the solution changes from light pale yellow to light brown colour during the reaction.

The TEM images (figure 1) of as-synthesized Ir nanostructure using ascorbic acid as the capping agent show that the nanoparticles are connected together forming large extended networks of length, few hundred nm to microns. At low magnifications (figure 1a), the structures are observed to be chain-shaped interconnected particles while at high magnifications, the nanostructures are observed to consist of individual nanoparticles of size 3.8 ± 0.3 nm (figure 1b). High resolution TEM (HRTEM) image (figure 1c) shows lattice constant of 0.225 nm corresponding to (111) spacing of fcc Ir. Selected area electron diffraction pattern (SAED) (figure S2, Supporting Information) shows reflections corresponding to (111), (200), (220) and (311) facets of fcc Ir. When the same reaction is carried out at 25°C instead of 80°C, the formation of interconnected particles takes 24 hours (figure S3, Supporting Information) revealing that the kinetics of formation of Ir is very slow. The absence of AA results in aggregated Ir nanoparticles (figure S4 [a,b], Supporting Information). Similarly, experiments carried out in the presence of polyvinylpyrrolidone (PVP) as the capping agent (figure S4 [c,d], Supporting Information) reveals individual 2 nm sized Ir nanoparticles.

It is likely that AA plays an important role in the formation of nanostructures and the presence of multifunctional stabilizing groups such as carbonyl and hydroxyl groups aids this process. To validate this hypothesis, similar experiments are carried out using vitamin P, a polyfunctional biomolecule

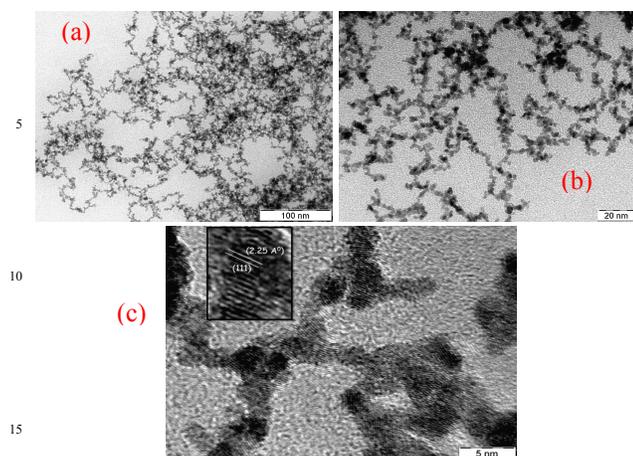


Figure 1 (a,b) TEM and (c) HRTEM images of Ir nanostructures prepared using aqueous IrCl_3 in the presence of AA and sodium borohydride at 80°C for 360 minutes. Inset of figure 'c' shows the lattice spacing.

consisting of different functional groups. The microscopy reveals the morphology of Ir as interconnected nanoparticles (figures S1, S4 [e,f], Supporting Information). Hence, it is clear that the interconnected Ir chain-like structures are obtained in the presence of polyfunctional stabilizing agents such as AA and vitamin P.

The growth of Ir structures is followed by microscopy, zeta potential and dynamic light scattering (DLS) measurements (figure 2, Table S2 & S3, Supporting Information). At the initial stages, large number of irregular nanoparticles is observed (5 minutes), that spontaneously approach each other (15 minutes) resulting in the formation of chain-like structures. Homogeneous nucleation of Ir clusters form aggregates and self-assemble in the presence of AA (or vitamin P) to form interconnected nanostructures (figure S5, Supporting Information).²⁷ Table S2 shows the variation of zeta potential as the function of reaction time and the value is observed to be ~ -32 mV at 5 minutes that decreases to ~ -24 mV after ~ 60 minutes and remains constant thereafter. A decrease in interparticle repulsion results in the decrease in zeta potential values as a function of time. DLS measurements have been performed to understand whether the assemblies are formed in solution or as a result of drying the sample. Table S3 shows the variation of hydrodynamic size as a function of reaction time. The hydrodynamic size of the particles increases from ~ 24 nm (5 minutes) to 478 nm (~ 60 minutes) suggesting that the assemblies are formed in the solution. The intentionally aggregated Ir colloid by the addition of an electrolyte (KCl) reveals completely different morphology (Figure S6, Supporting Information). Figure S7 (supporting information) shows the XRD pattern of as-prepared Ir nanostructures and the diffraction peaks observed at 2θ values of 40.8° , 47.2° , 69.1° and 83.6° correspond to (111), (200), (220) and (311) facets of Ir fcc structure. The XPS analysis reveals two (figure S8, Supporting Information) peaks at 61.1 eV and 64.1 eV corresponding to Ir $4f_{7/2}$ and $4f_{5/2}$ of Ir in zero oxidation state. Weak doublet observed at high binding energies (62.3 and 65.1eV) correspond to surface oxidized Ir(IV). Figure S8

(supporting Information) shows the deconvoluted C 1s and O 1s spectra and the O 1s spectrum shows peaks located at binding energy values of 532.1 and 533.2 eV corresponding to $-\text{C}=\text{O}$ and $-\text{O}^\ominus$ of the hydroxyl groups while the C-1s spectrum reveals peaks at 285.1 eV and 286.7 eV corresponding to C-C- linkages of AA

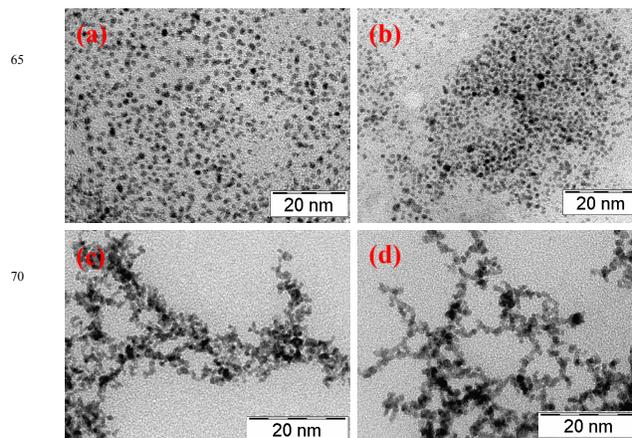


Figure 2 TEM images recorded at different time intervals during the formation of chain-like structures (a) 5; (b) 15; (c) 120 and (d) 240 min. Other preparation conditions are as given in figure 1.

and C-O linkages of carbonyl group respectively. Figure S9 (Supporting Information) shows the FTIR spectra of pure AA and AA capped Ir. The asymmetric stretching of $-\text{OH}$ region (3100 to 3500 cm^{-1}) of AA, disappears after capping the nanostructures.

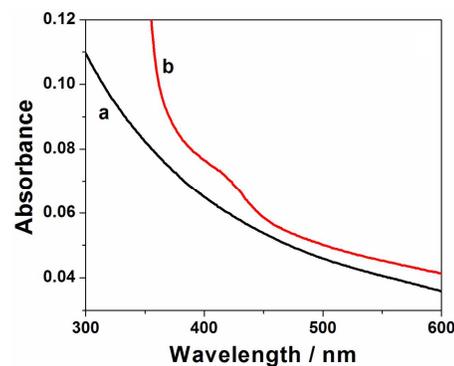


Figure 3 Absorption spectra of (a) Ir nanoparticles and (b) Ir nanochain-like structures in aqueous media. The nanoparticles are prepared using PVP while nanostructures are prepared using AA as the capping agent.

Absorption spectrum of Ir nanostructures reveals a weak plasmonic band observed at ~ 425 nm with a tail extending in to visible region while for the nanoparticles, only continuous change in absorption is observed (figure 3). The absorbance spectra as a function of reaction time (figure S10, supporting information) shows that the peaks corresponding to IrCl_3 disappear in about 5 minutes and a broad hump develops around 402 nm after 15 minutes of the reaction. This hump further shifts to 405 nm after 30 minutes of reaction and stabilizes at 425 nm after 120 minutes and remains constant thereafter (table S4, supporting information). The microscopy reveals irregular shaped nanoparticles after 5 minutes which undergo self-assembly after 30 minutes resulting in red shift in the absorption peak. The

surface plasmon band observed around 425 nm may be due to coupled plasmons from the interconnected Ir structures.

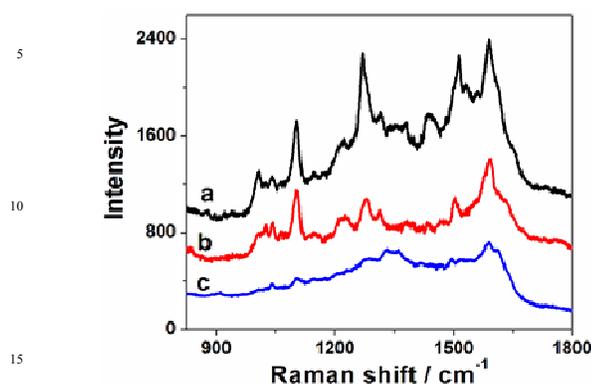


Figure 4. SERS spectra of 4-MPy adsorbed on Ir nanostructures from (a) 1 mM, (b) 100 μM and (c) 10 μM solutions. The excitation wavelength used is 533 nm. Details of sample preparation are given in the Supporting Information.

SERS activity of Ir nanostructures is explored using 4-mercaptopyridine as the analyte.^{10,13,25,26} Figure 4 shows the Raman spectra of 4-Mpy adsorbed on Ir nanostructures with excitation wavelength of 533 nm. Raman band intensities are enhanced in the presence of nanostructures and the band assignments are given in table S5. The peaks observed at 1594, 1223, 1065 and 1011 cm^{-1} are assigned to the ring stretching modes, C-H deformation, -NH stretching and -CH deformation and ring breathing modes respectively.²⁸⁻³⁰ It should be noted that the excitation wavelength is away from the plasmon peak and still enhancement in Raman signals is observed. This is similar to spherical silver particles that generally show plasmon around 420 nm and still reveal very good enhancement for excitation wavelength of 514 nm laser. The Ir nanostructures show a tail extending in to visible region as shown in figure S10 (supporting information). It has also been demonstrated both theoretically and experimentally that strong electromagnetic field enhancements would arise at the interparticle junctions in nanoparticle aggregates upon interaction with visible radiation.^{31,32} Concentration dependent studies have been carried out by dipping the Ir modified glass substrate into 2 mL of different concentrations of the analyte (1 mM to 0.1 μM) for 30 minutes and subsequently drying the substrate before Raman spectral measurements are carried out. The detection limit for 4-MPY in the present studies is observed to be 0.1 μM .

In summary, Ir nanochain-like structures synthesized under mild conditions in aqueous medium possess surface plasmon peak in the visible region which make them useful as SERS substrates. The interparticle plasmon coupling in the case of Ir seems to be weak and the absorption cross section being low probably does not result in clear maxima for the coupled plasmons at longer wavelength regions. However, the evolution of chain-like structures is clearly indicated based on TEM studies.

Notes and references

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†Electronic Supplementary Information (ESI) available: Detailed experimental procedures for the preparation of Ir nanostructures. SAED pattern, TEM images under different conditions, zeta potential values at different time intervals, XRD, IR, UV-Vis and XPS data, Details of enhancement factor determination and Raman band assignments.

- Z. Tang and N. A. Kotov, *Adv. Mater.*, 2005, **17**, 951.
- X. Ting, W. Q. Han, W. Ku, and M. Hucker, *Angew. Chem. Int. Ed.*, 2008, **47**, 2055.
- H. Jia, X. T. Bai, and L. Q. Zheng, *CryEngComm*, 2012, **14**, 2920.
- L. Polavarapu and Q. H. Hu, *Nanotechnology*, 2008, **19**, 075601.
- R. Sardar and J. S. Shumaker-Parry, *Nano. Lett.*, 2008, **8**, 731.
- S. Lin, M. Li, E. Dujardin, C. Girard and S. Mann, *Adv. Mater.*, 2005, **17**, 2553.
- J. Xu, G. Fu, Y. Tang, Y. Zhou, Y. Chen and T. Lu, *J. Mater. Chem.*, 2012, **22**, 13585.
- Y. Song, R. M. Garcia, R. M. Dorin, H. Wang, Y. Qiu, E. N. Coker, W. A. Steen, J. E. Miller and J. A. Shelnutt, *Nano. Lett.*, 2007, **7**, 3650.
- M. J. Shiers, R. Leech, C. J. Carmalt, I. P. Parkin and A. J. Kenyon, *Adv. Mater.*, 2012, **24**, 5227.
- C. Feng, R. Zhang, P. Yin, L. Li, L. Guo and Z. Shen, *Nanotechnology*, 2008, **19**, 305601.
- B. R. Sathe, B. K. Balan and V. K. Pillai, *Energy Environ. Sci.*, 2011, **4**, 1029.
- J. Wang, Y. Chen, H. Liu, R. Li and X. Sun, *Electrochem. Commun.*, 2010, **12**, 219.
- K. Chakrapani and S. Sampath, *Chem. Commun.*, 2013, **49**, 6173.
- M. Zahmakiran, *Dalton Trans.*, 2012, **41**, 12690.
- E. Bayaram, M. Zahmakiran, S. Ozkar and R. G. Finke, *Langmuir*, 2010, **26**, 12455.
- Y. Zhang, H. Zhang, Y. Zhang, Y. Ma, H. Zhong, and H. Ma, *Chem. Commun.*, 2009, 6589.
- V. Kiran, T. Ravikumar, N. T. Kalyanasundaram, S. Krishnamurthy, A. K. Shukla and S. Sampath, *J. Electrochem. Soc.*, 2010, **157**, B1201.
- M. Rueping, R. M. Koenigs, R. Borrmann, J. Zoller, R. M. Weirich and J. Mayer, *Chem. Mater.*, 2011, **23**, 2008.
- Y. M. Lopez-De Jesus, A. Vincente, G. Lafaye, P. Marecot and C. T. Williams, *J. Phys. Chem. C*, 2008, **112**, 13837.
- S. Kundu and H. Liang, *J. Colloid Interface Sci.*, 2011, **354**, 597.
- J. A. Creighton and D. G. Eadon, *J. Chem. Soc. Faraday Trans.*, 1991, **87**, 3881.
- J. Kneipp, H. Kneipp and K. Kneipp, *Chem. Soc. Rev.*, 2008, **37**, 1052.
- J. R. Lombardi, R. L. Birke and G. Haran, *J. Phy. Chem. C*, 2011, **115**, 4540.
- H. Ko, S. Singamaneni and V. V. Tsuruk, *Small*, 2008, **4**, 1576.
- N. Zettsu, J. M. McLellan, B. Wiley, Y. Yin, Z. Y. Li and Y. Xia, *Angew. Chem. Int. Ed.*, 2006, **45**, 1288.
- A. X. Yin, W. C. Liu, J. Ke, W. Zhu, J. Gu, Y. W. Zhang and C. H. Yan, *J. Am. Chem. Soc.*, 2012, **134**, 20479.
- F. Vines, F. Illas and K. M. Neyman, *Angew. Chem. Int. Ed.*, 2007, **46**, 7094.
- Y. Wang, Z. Sun, H. Hu, S. Jing, B. Zhao, W. Xu, C. Zhao and J. R. Lombardi, *J. Raman Spectrosc.*, 2007, **38**, 34.
- Z. Wang and L. J. Rothberg, *J. Phy. Chem. B*, 2005, **109**, 3387.
- W. Song, Y. Wang and B. Zhao, *J. Phy. Chem. C*, 2007, **111**, 12786.
- K. L. Wustholz, A. L. Henry, J. M. McMahon, R. G. Freeman, M. E. Valley, M. J. Natan, G.C. Schatz and R. P. Van Duyne, *J. Am. Chem. Soc.*, 2010, **132**, 10903.
- K. L. Nagashree, R. Lavanya, C. Kavitha, N. S. Venkata Narayanan and S. Sampath, *RSC Advances*, 2013, **3**, 8356.

TOC graphic

