

Electronic supplementary Information

Fabrication of Tungsten Nanocrystals and silver-tungsten nanonets: a potent reductive catalyst

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Section-I

Experiment Details:

Materials: All chemicals were used directly without further purification. Hexacarbonyl Tungsten[W(CO)₆, 97%], 1- Octadecene [ODE, tech. 90%], n- Octadecane [99%], 1- Octadecylamine [97%], Tri-octyl phosphine oxide [98%] were purchased from Alfa-Aeser. Oleylamine [OLAM, tech., 97%] was purchased from Sigma-Aldrich. Other Chemicals like n-hexane, Tetrachloroethylene (TCE), Silver Nitrate [AgNO₃], Ethanol, acetone etc were purchased from Merck chemicals, India.

Synthesis:

All the reaction might be carried out in fume hood with expert personnel. W(0) NCs synthesis discussed in main article. The as-synthesized product was washed by centrifugation process using hexane as solvent and acetone as non-solvent for several times.

Ag NC seeds: Ag seeds were synthesized using AgNO₃ and degassed OLAM. Typically 11.25 ml degassed OLAM and 0.5 gm AgNO₃ were mixed in a 25 ml round bottom three neck flask and degassed for 30 min in room temperature. The system was backfilled with dry Ar, heated to 160 °C and reaction was carried out for 1 hr. The product was collected using hexane as solvent and ethanol as non-solvent by centrifugation for several times. The as-synthesized Ag NCs were dried in vacuum and used as seeds for AgW heterostructure formation.

Characterization:

Fourier transform infrared (FT-IR) spectra of the samples were taken by using a Perkin Elmer spectrochem 100 FT-IR spectrometer. The crystalline phases of the products were determined by X-ray powder diffraction (XRD) by using Bruker AXS D8SWAX diffractometer with Cu K α radiation ($\lambda = 1.54 \text{ \AA}$), employing a scanning rate of 0.5° S^{-1} in the 2θ range from 20° to 80° . For XRD measurement the hexane solution of the NCs was drop cast over amorphous silicon sample holder till a naked eye visible thin layer was formed. Transmission electron microscopy (TEM) images, high angle annular dark field scanning TEM (HAADF STEM) images and energy dispersive spectrum (EDS) were taken using an Ultra-high resolution field emission gun transmission electron microscope (UHR-FEG TEM, JEM-2100F, Jeol, Japan) operating at 200 kV. For the TEM observations, the sample dissolved in hexane was drop cast on a carbon coated copper grid. The room temperature optical absorbance of the samples was recorded by a Varian Cary5000 UV-VIS-NIR spectrophotometer. Valence state analysis was carried out by using an X-ray photoelectron spectroscopic (XPS, Omicron, model: 1712-62-11) method. XPS measurement was done using an Al-K α radiation source under 15 kV voltage and 5 mA current. For XPS measurement the hexane solution of the NCs was also drop cast over glass slide (2mm \times 2mm) till a naked eye visible thin layer was formed.

Catalytic activity study:

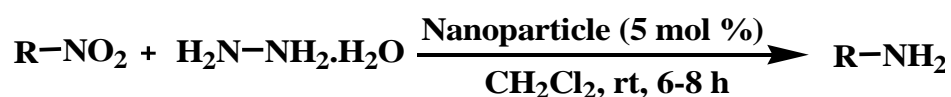
1. Materials and Methods

All the reaction were carried out in presence of solar light source, KRATOS, Analytical instruments, universal Arc lamp supply-250 watt, 150 XE, model no 1152. The light intensity was standardized using a photometer.

All reagents were purchased from commercial suppliers and used without further purification, unless otherwise specified. Commercially supplied ethyl acetate and petroleum ether were distilled before use. CH $_2$ Cl $_2$ was dried by distillation over P $_2$ O $_5$. Petroleum ether used in our experiments was in the boiling range of 60° - 80° C. Column chromatography was performed on silica gel (60-120 mesh, 0.120 mm-0.250 mm). Analytical thin layer chromatography was performed on 0.25 mm extra hard silica gel plates with UV254 fluorescent indicator. Melting points are reported uncorrected. ^1H NMR and ^{13}C NMR spectra (Bruker Advance 300) were recorded at ambient temperature using 300 MHz spectrometers

(300 MHz for ^1H and 75 MHz for ^{13}C). Chemical shift is reported in ppm from internal reference tetramethylsilane and coupling constant in Hz. Proton multiplicities are represented as s (singlet), d (doublet), dd (double doublet), t (triplet), q (quartet), and m (multiplet). Infrared spectra were recorded on FT-IR spectrometer (Perkin Elmer Spectrum 100) in thin film on NaCl window (liquid sample). HR-MS data were acquired by electron spray ionization technique on a Q-tof-micro quadrupole mass spectrophotometer (Bruker).

2. General procedure for nanoparticle mediated reduction of nitro-compound:



R = aromatic and aliphatic group

To a solution of nitro-compound (1 mmol) in dichloromethane (5 ml) hydrazine hydrate (1.5 mmol, 75 mg) was added. Then under vigorously stirring condition at room temperature synthesized nanoparticle was added. After that completeness of the reaction was confirmed by thin layer chromatography (TLC). The post reaction mixture was filtered and washed with DCM and water respectively. The solid residue i.e. nanoparticle was collected and reused for further reaction. The filtrate was washed with H_2O (30 mL) and the organic layer was dried over anhydrous Na_2SO_4 , filtered and evaporated in a rotary evaporator under reduced pressure at room temperature. Thus, the reaction with p-nitrotoluene (**1a**, 107 mg, 1.0 mmol) afforded p-toluidine (**2a**) after purification by column chromatography on silica gel (60-120 mesh) with ethyl acetate-petroleum ether (1:5, v/v) as an eluent in a yield of 78% (83 mg, 0.78 mmol). The synthesized amines were characterized using spectroscopic techniques.

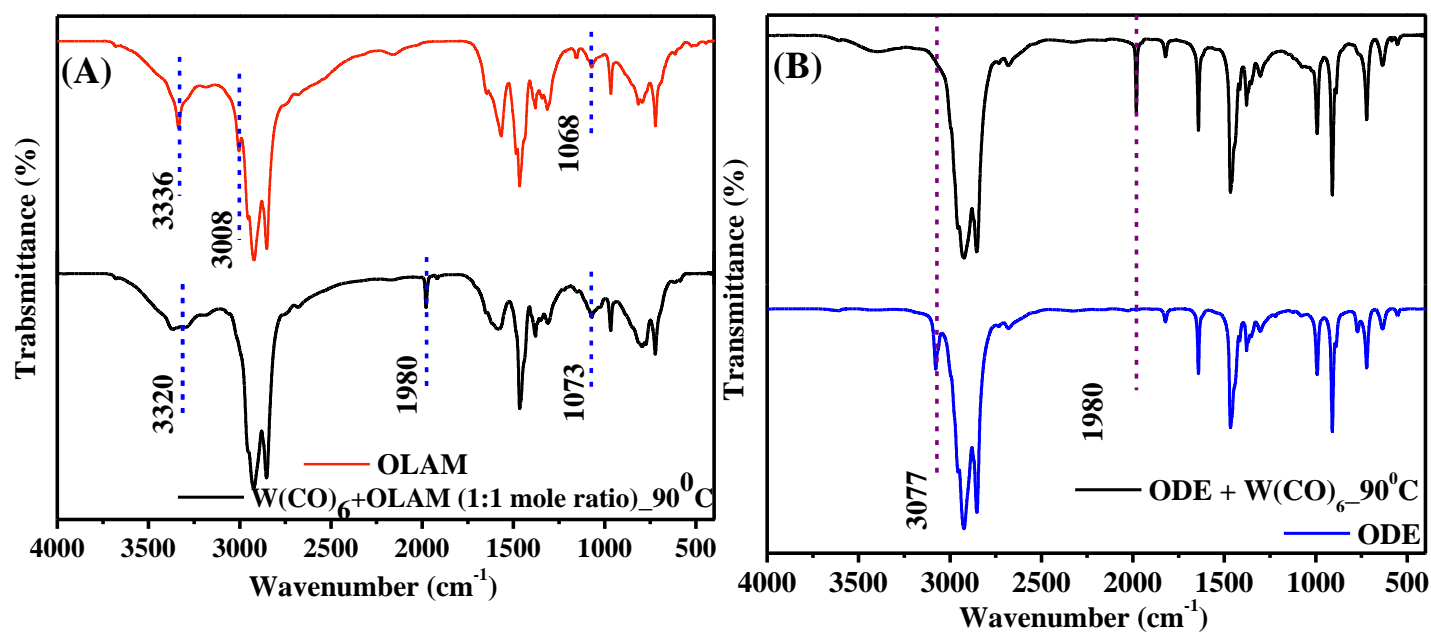


Fig. S1: (A) FTIR spectra of OLAM and $W(CO)_6$ -OLAM complex (the transparent solution obtained after heating the reaction mixture in 1:1 molar ratio at 90 °C). (B) FTIR spectra of ODE and $W(CO)_6$ -ODE (1:1 molar ratio) complex.

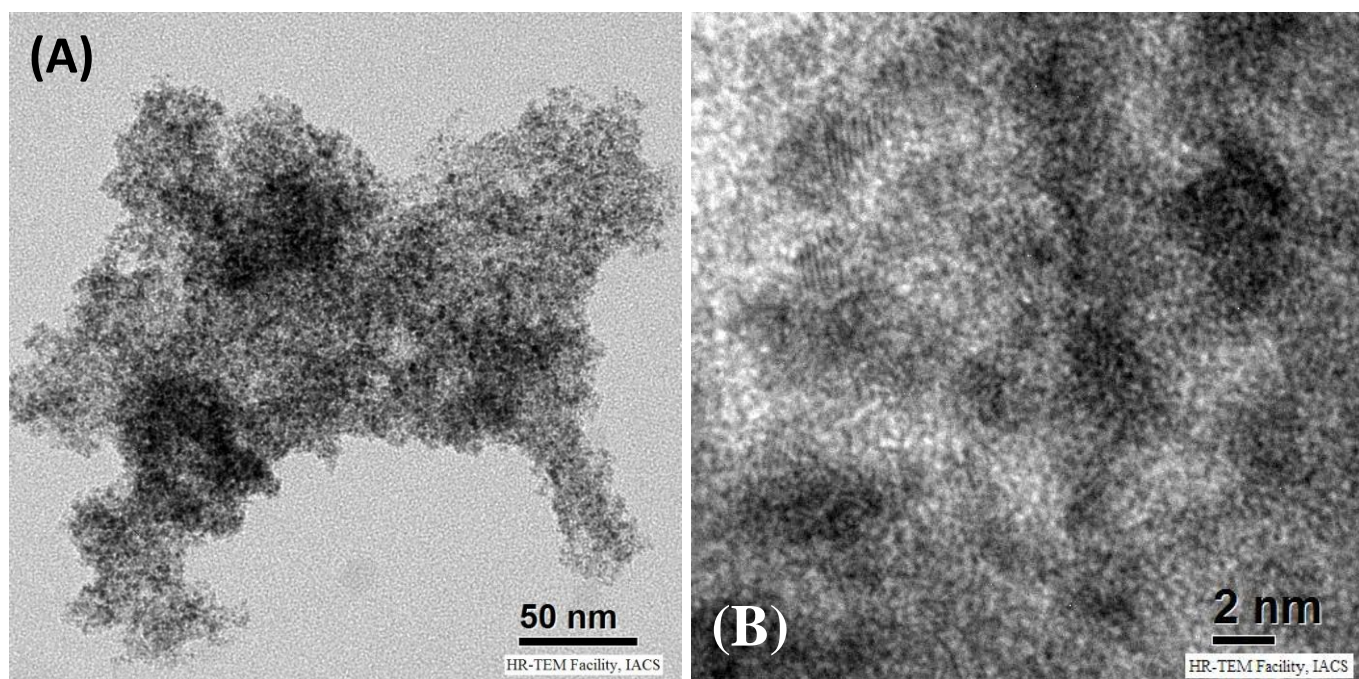


Fig. S2 : (A) TEM image of $W(0)$ NC obtained by decomposing $W(CO)_6$ in ODE at 320 °C for 2 hrs in absence of OLAM shows highly agglomerated nature of $W(0)$ NCs. (B) HRTEM image of $W(0)$ NCs shows the poor crystalline nature of the product.

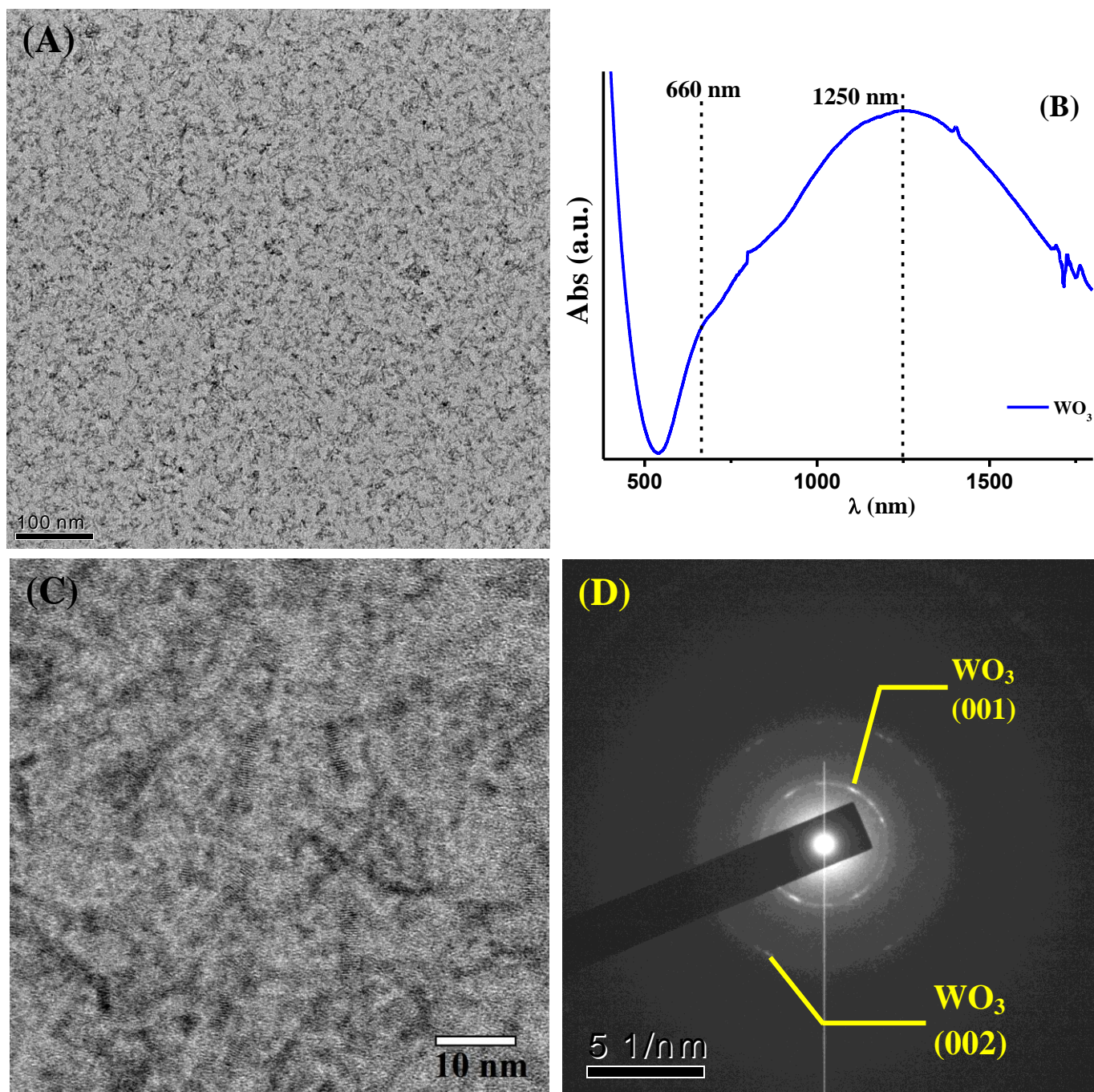


Fig. S3: (A) Formation of tungsten oxide nanorods when tri-n-octylphosphine oxide was used as surfactant with ODE. (B) Absorbance spectra of the WO_3 colloids in TCE shows two absorbance mode for the localized surface Plasmon resonance ; lower wavelength absorbance for short axis and higher λ absorbance for long axis LSPR mode respectively.(C) HRTEM image. (D) SAED patterns confirm the formation of WO_3 .

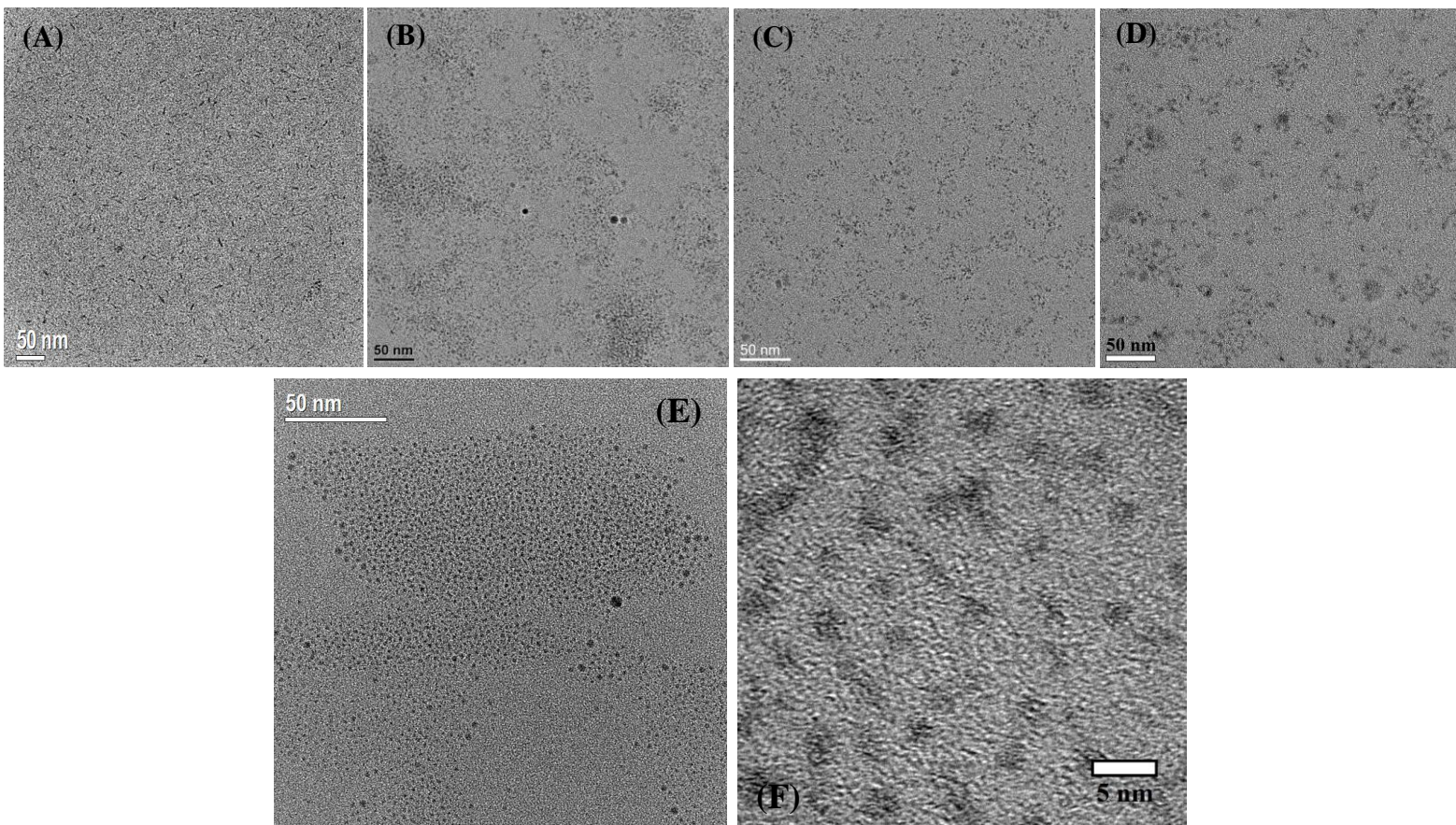


Fig. S4: TEM images of (A) 5 min, (B) 15 min, (C) 30 min, (D) 60 min and (E) 90 min reaction products. (F) HRTEM image of 90 min reaction products shows the appearance of crystalline nature.

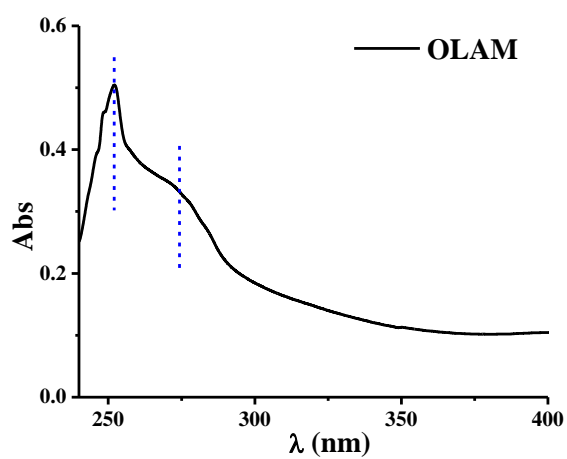


Fig. S5 : Absorbance spectra of oleylamine in hexane.

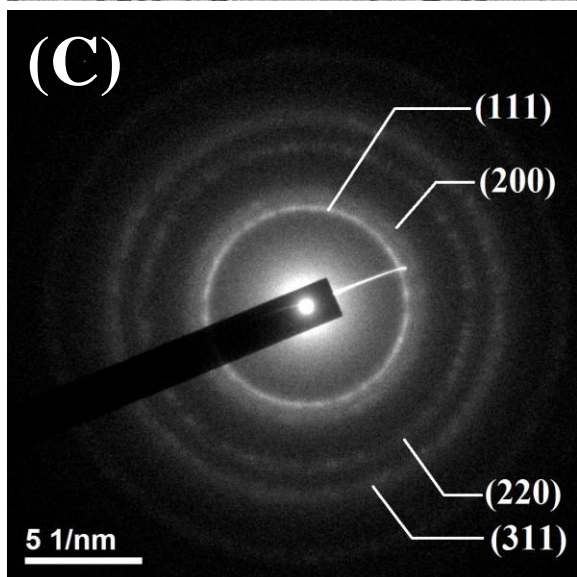
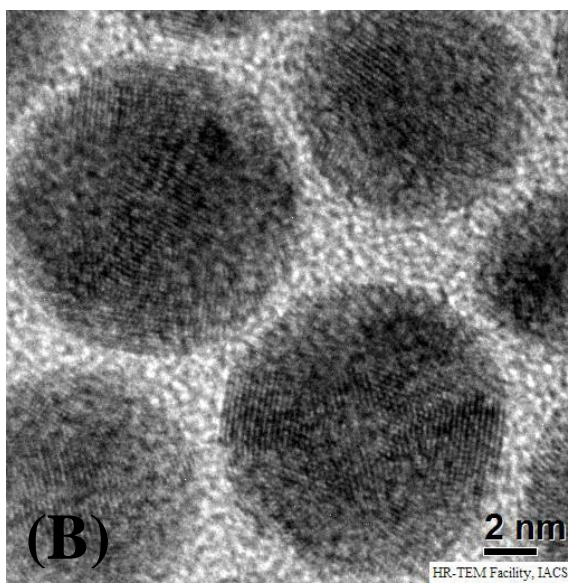
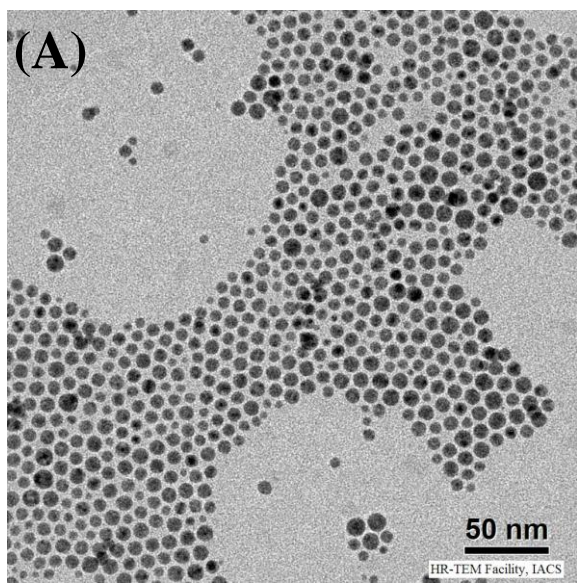


Fig. S6 : (A) TEM image of monodisperse Ag NCs used as seeds (9.6 ± 1.7 nm). (B) HRTEM image of an Ag NC showing the (111) planes. Particles are mainly decahedral and dodecahedral shaped. (C) SAED pattern of Ag NCs. Assigned planes confirm the FCC crystal phase.

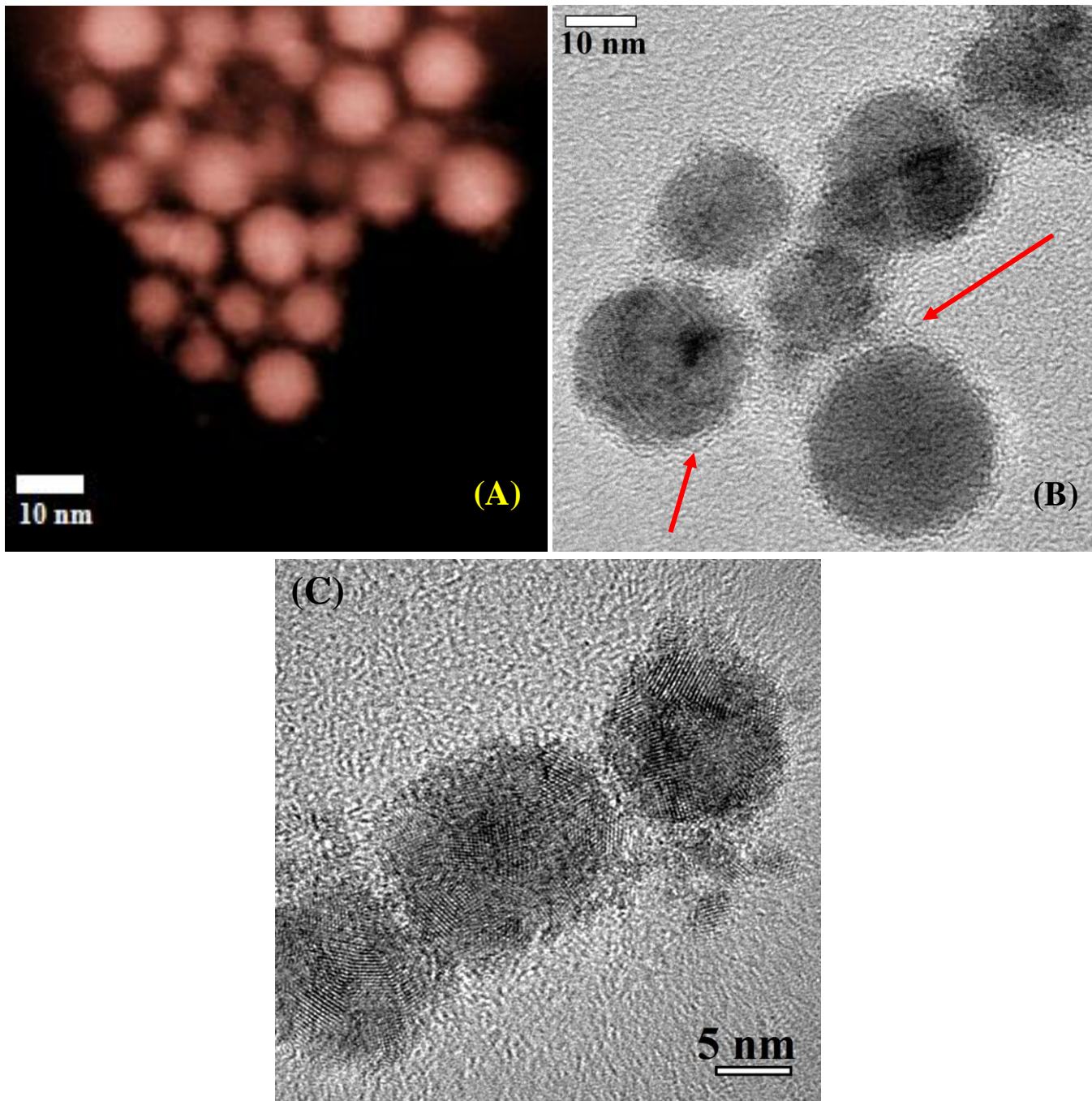


Fig. S7 : (A) STEM image of Ag-W NCs (AgW1) where Ag:W = 2:1 mole ratio. Presence of W(0) NCs on the Ag surface and started connecting the Ag moiety. (B) Formation of amorphous shell around the surface of Ag NC when reaction was quenched at 280 °C. (C) HRTEM image of AgW1 NCs shows the formation of crystalline W(0) onto Ag NCs after completion of reaction.

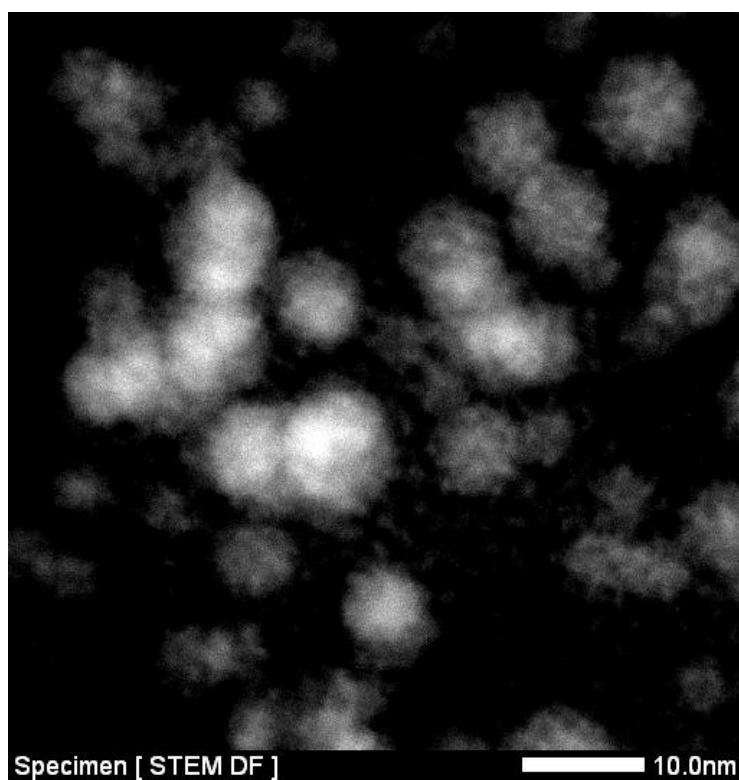


Fig. S8 : STEM image of Ag-W heterostructure NCs (AgW2) where Ag:W = 1:2. Formation of some free-standing W(0) NCs was found which is not directly connected to Ag NC.

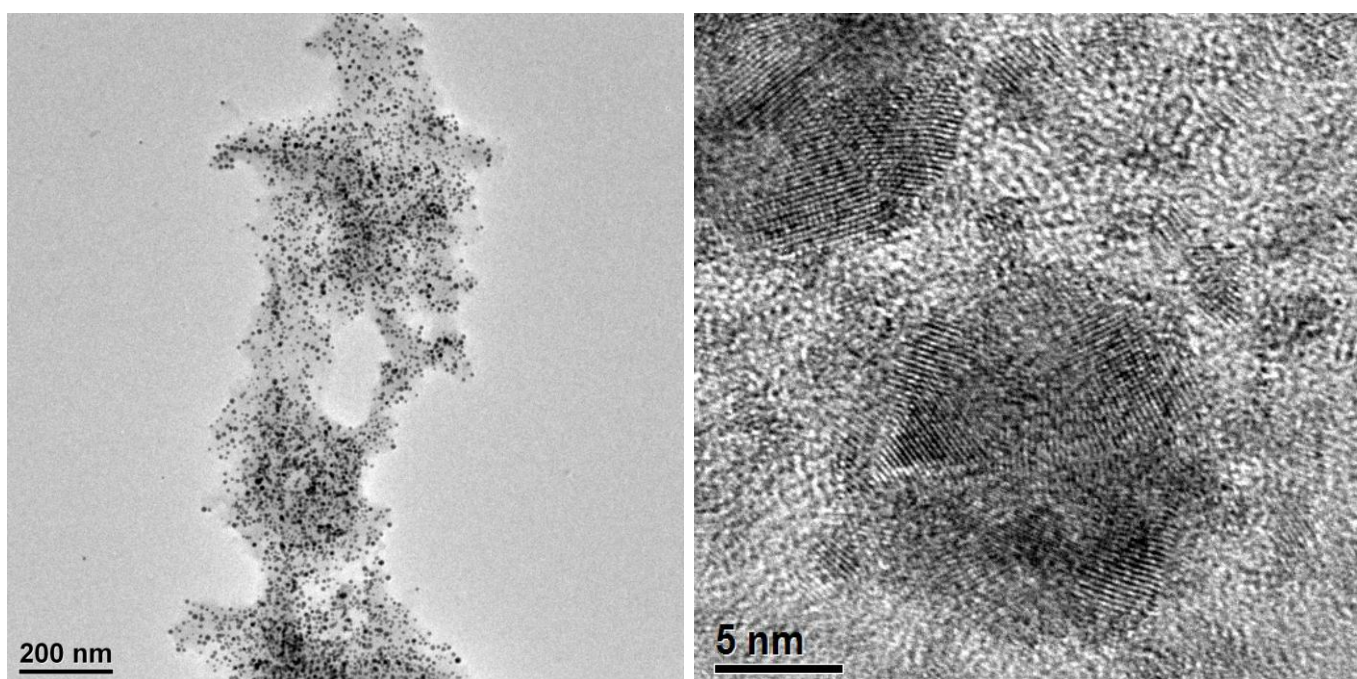


Fig. S9 : (A) Large area TEM image of AgW4 nanonets (Ag:W = 1:10) . (B) HRTEM image of AgW4 nanonets clearly shows network formation around Ag NCs.

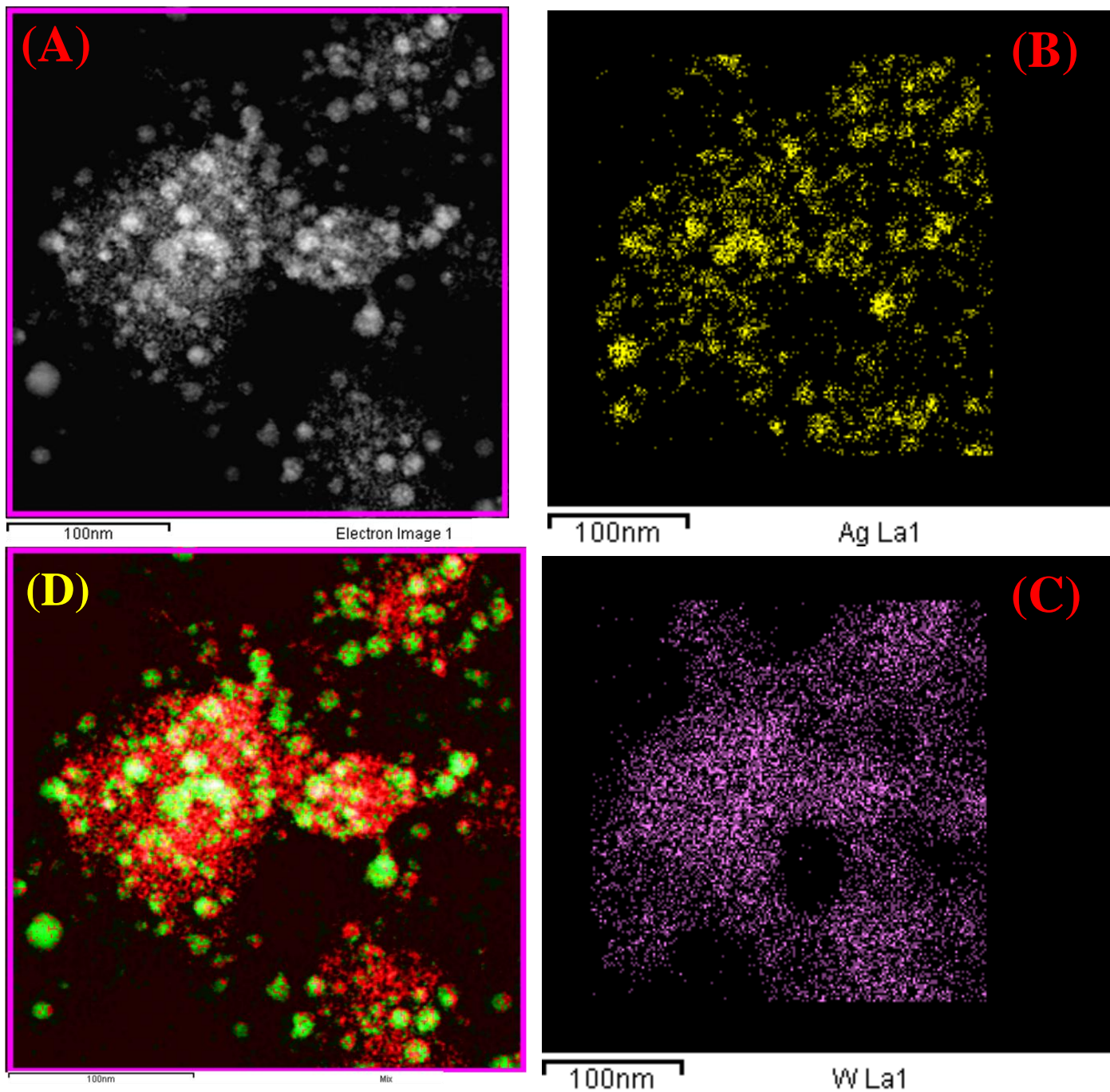


Fig. S10 : (A) HAADF image of AgW5. EDS element mapping of (B) Ag, (C) W and (D) Superposition of Ag and W mapping, where red and green color are symbolic for W and Ag respectively.

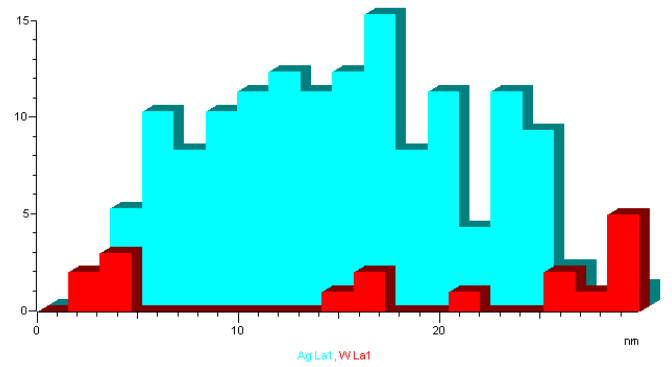
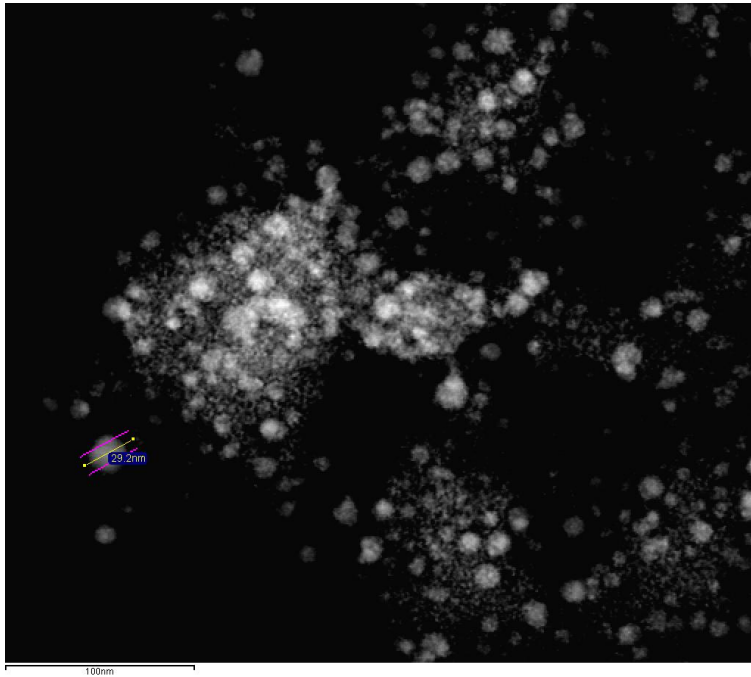


Fig. S11 : Line scan of a free standing Ag NCs which is not involved in Net like structure also shows the presence of W on Ag Surface.

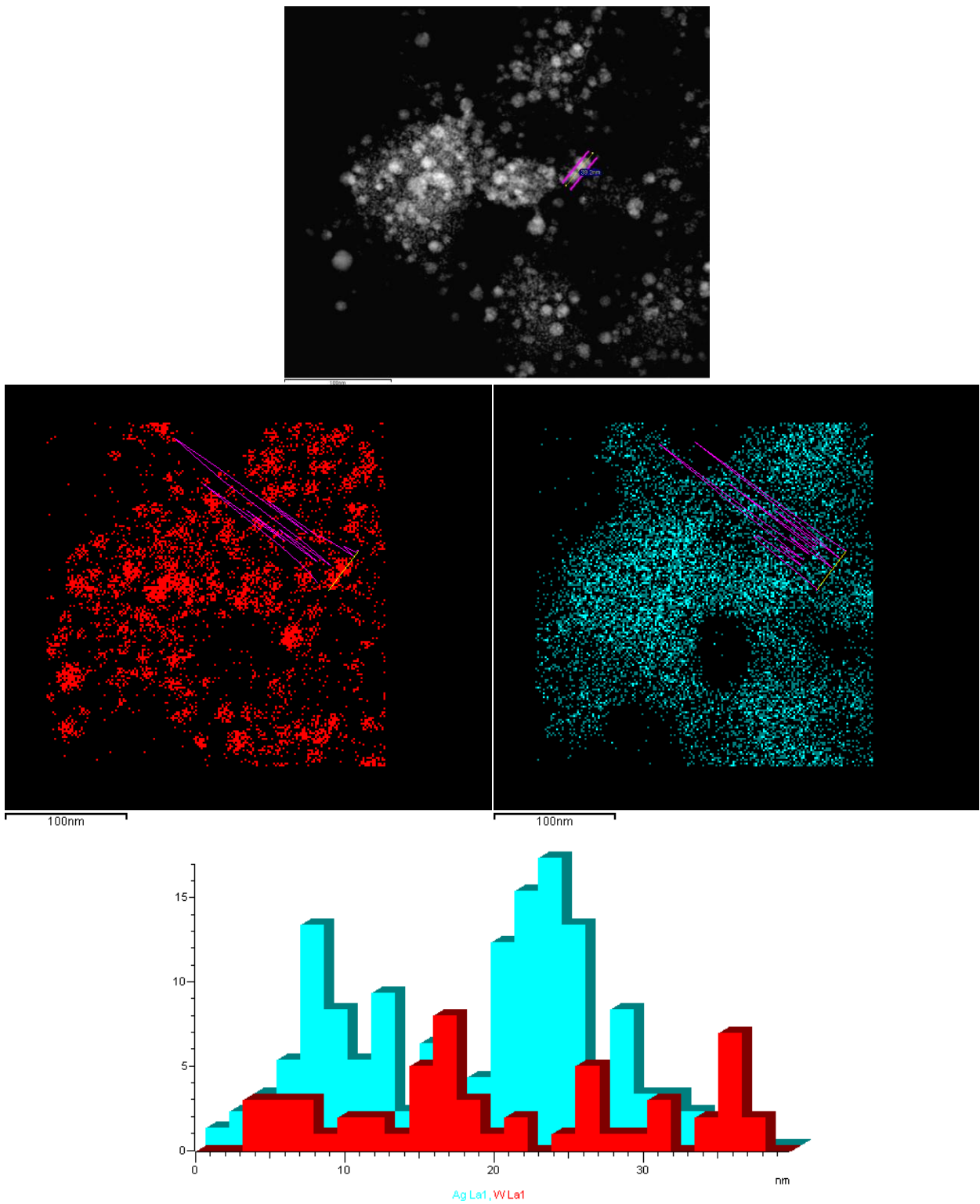


Fig. S12 : Line scan of two adjacent Ag NCs shows the Ag nanocrystals are connected by W(0).

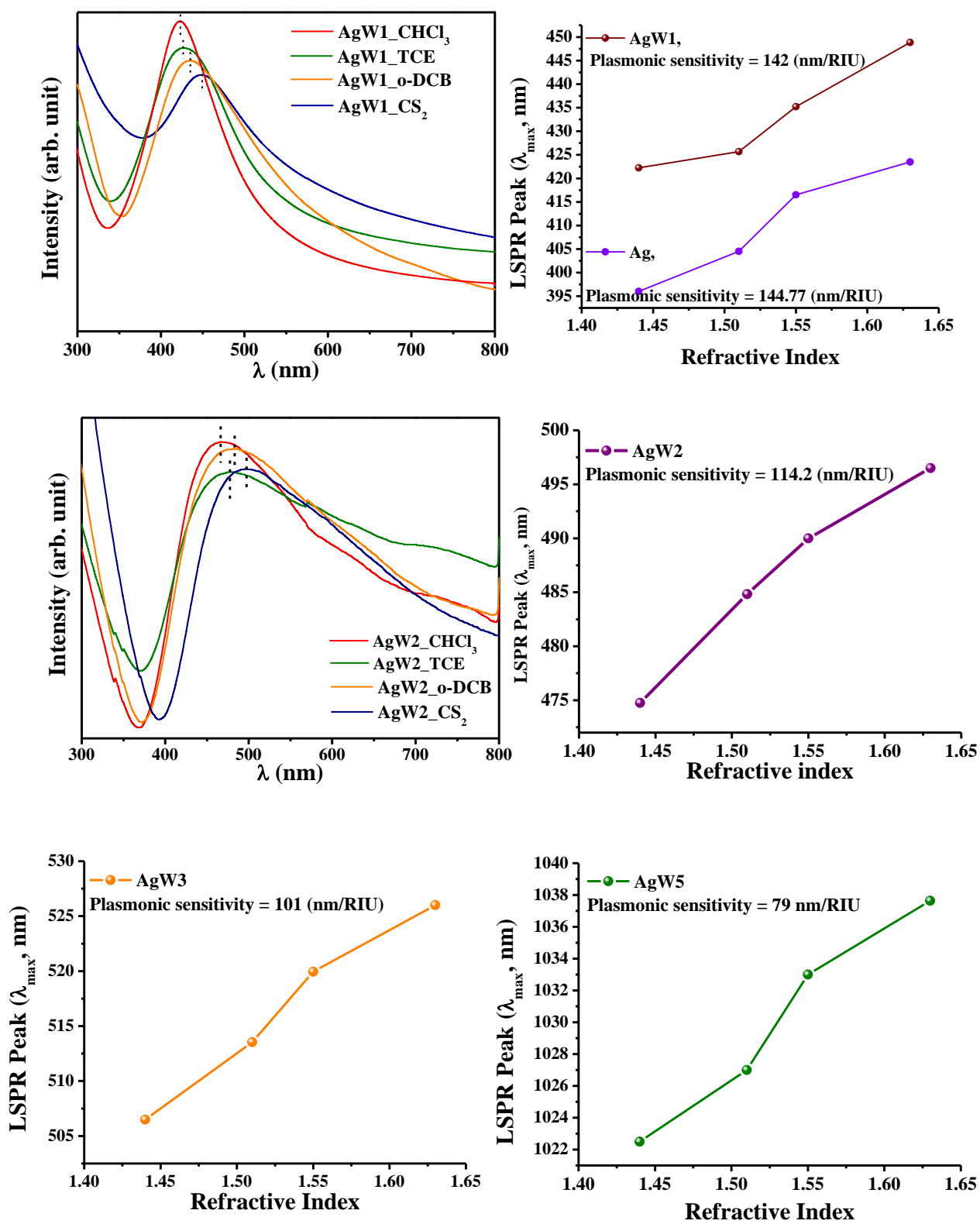


Fig. S13: Plasmonic Sensitivity of Ag and Ag-W heterostructures.

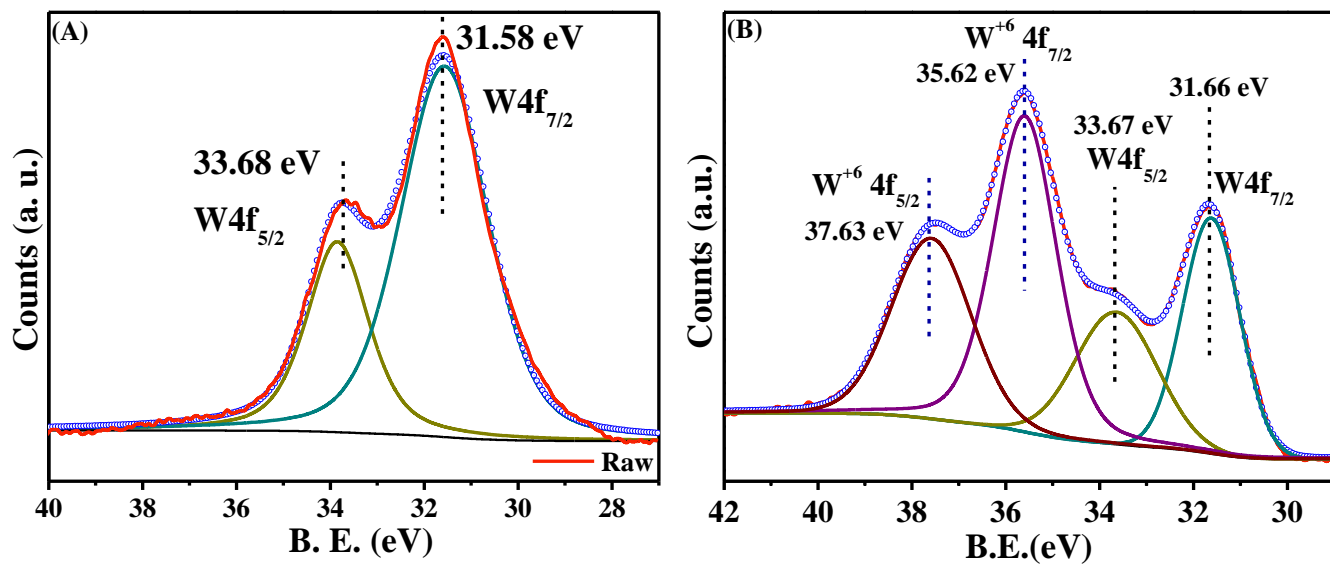
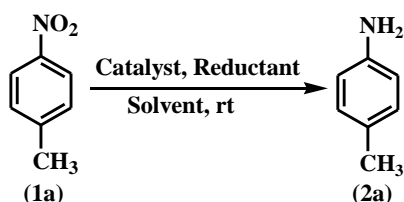


Fig. S14 : (A) W 4f XPS spectrum of AgW5 nanonets before use in catalysis. (B) W 4f XPS spectrum of that after reaction for 15 min.

Development and optimization of the reduction process using AgW₅ nanonet

In this context, we observed that AgW nanonet can catalyze the reduction of nitro compound towards amine in presence of solar illumination under ambient condition (entry 2, table 1.1). During optimization of the reaction condition with *p*-nitro toluene (**1a**), NH₂NH₂.H₂O (1.2 equiv) was found as an effective reductant compared to PPh₃ or ascorbic acid. Moreover, dichloromethane is a good solvent of our choice at room temperature as it provides maximum yield of the product **2a** (entry 2, table 1.1). Whereas other commonly used solvents such as CH₃CN, THF, toluene etc were in vain. Improvement of product-yield was not observed with increment of reaction temperature. Here the required catalyst loading is only 5 mol%. Surprisingly, individual Ag do not catalyze this reduction (Fig. 3 , manuscript).

Table 1.1. Optimization of the reaction condition

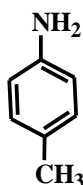


entry	reductant ^b	solvent	time (h)	yield ^a (%)
1	NH ₂ NH ₂ .H ₂ O	THF	24	76
2	NH ₂ NH ₂ .H ₂ O	DCM	1.1	78
3	NH ₂ NH ₂ .H ₂ O	DCM	24	78
4	NH ₂ NH ₂ .H ₂ O	CH ₃ CN	24	75
5	NH ₂ NH ₂ .H ₂ O	Toluene	24	70
6	Ascorbic Acid	DCM	24	-
7	PPh ₃	DCM	24	37
8	NH ₂ NH ₂ .H ₂ O ^c	DCM	1.1	78

^aIsolated yield of **2a**. ^bReductant (1.2 equiv). ^c3.0 equiv

Characterization data of amines

1. *p*-Toludine (2a)



Yield: 78% (83 mg, 0.78 mmol).

Characteristic: Brown solid.

Melting range: 41-43 °C

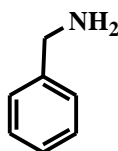
¹H NMR (300 MHz, CDCl₃): δ 2.29 (3H, s), 3.55 (2H, brs), 6.64 (2H, d, *J* = 8.1 Hz), 7.01 (2H, d, *J* = 8.1 Hz).

¹³C NMR (75 MHz, CDCl₃): δ 20.2, 115.1, 127.5, 129.7, 143.7.

FT-IR (KBr, cm⁻¹): 835, 1493, 1505, 1615, 2852, 2986, 3324, 3361.

HR-MS (*m/z*) for C₇H₁₀N (M⁺+H): Calculated 108.0813, found 108.0812.

2. Benzylamine (2b)



Yield: 81% (87 mg, 0.81 mmol).

Characteristic: Yellow oil.

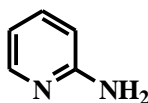
¹H NMR (300 MHz, CDCl₃): δ 1.54 (2H, s), 3.84 (2H, s), 7.21-7.36 (5H, m).

¹³C NMR (75 MHz, CDCl₃): δ 46.5, 126.7, 127.0, 128.5, 143.3.

FT-IR (neat, cm⁻¹): 1385, 1453, 1496, 1586, 1605, 2920, 3027, 3062, 3106, 3290, 3373.

HR-MS (*m/z*) for C₇H₁₀N (M⁺+H): Calculated 108.0813, found 108.0810.

3. 2-Aminopyridine (2c)



Yield: 90% (165 mg, 0.90 mmol).

Characteristic: Brownish solid.

Melting range: 56-60 °C

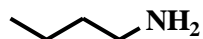
¹H NMR (300 MHz, CDCl₃): δ 4.66 (2H, brs), 6.41-6.45 (1H, m), 6.54-6.59 (1H, m), 7.32-7.38 (1H, m), 8.00-8.02 (1H, m).

¹³C NMR (75 MHz, CDCl₃): δ 108.6, 113.8, 137.6, 148.0, 158.6.

FT-IR (KBr, cm^{-1}): 1253, 1365, 1443, 1482, 1571, 1610, 2959, 3019, 3365, 3080, 3407, 3509, 3676.

HR-MS (m/z) for $\text{C}_5\text{H}_7\text{N}_2$ (M^+H): Calculated 95.0609, found 95.0611.

4. *n*-Butylamine (2d)



Yield: 66% (48 mg, 0.66 mmol).

Characteristic: Yellow oil.

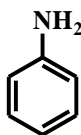
^1H NMR (300 MHz, CDCl_3): δ 0.53 (3H, t, $J = 7.2$ Hz), 0.90-1.09 (4H, m), 2.30 (2H, brs).

^{13}C NMR (75 MHz, CDCl_3): δ 13.0, 19.1, 35.1, 40.9.

FT-IR (neat, cm^{-1}): 1290, 1492, 1608, 1700, 2857, 2920, 2972.

HR-MS (m/z) for $\text{C}_4\text{H}_{11}\text{N}$ (M^+): Calculated 73.0891, found 73.0890.

5. Aniline (2j)



Yield: 70% (65 mg, 0.70 mmol).

Characteristic: Yellow oil.

^1H NMR (300 MHz, CDCl_3): δ 3.60 (2H, s), 6.69 (2H, dd, $J = 7.5, 0.9$ Hz), 6.78-6.83 (1H, m), 7.16-7.22 (2H, m).

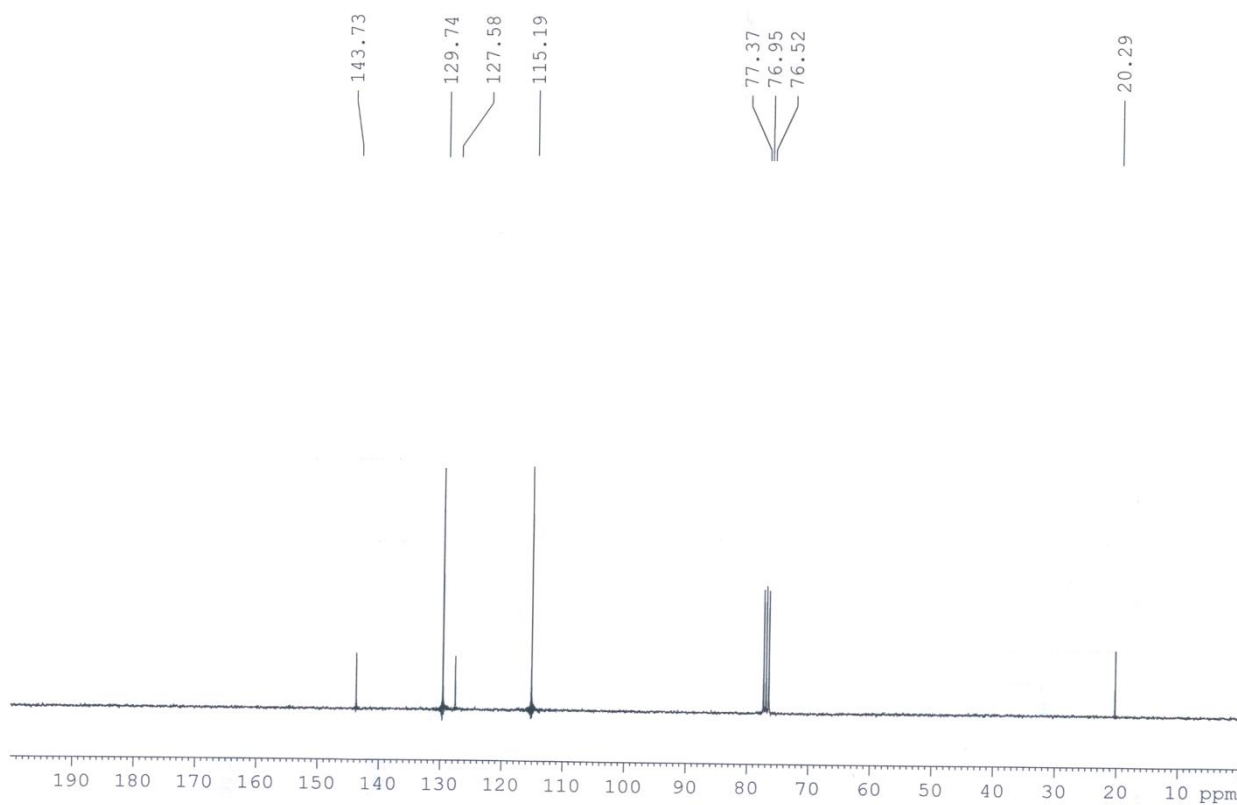
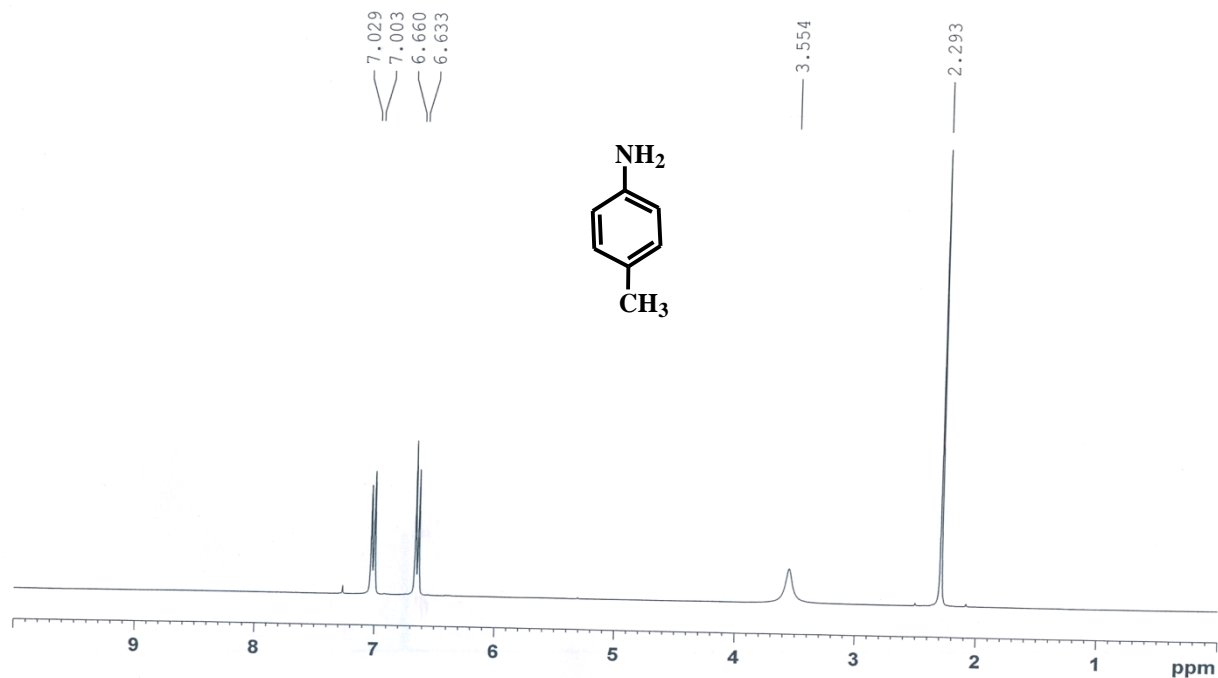
^{13}C NMR (75 MHz, CDCl_3): δ 115.0, 118.4, 129.1, 146.1.

FT-IR (neat, cm^{-1}): 1281, 1496, 1619, 3360, 3442.

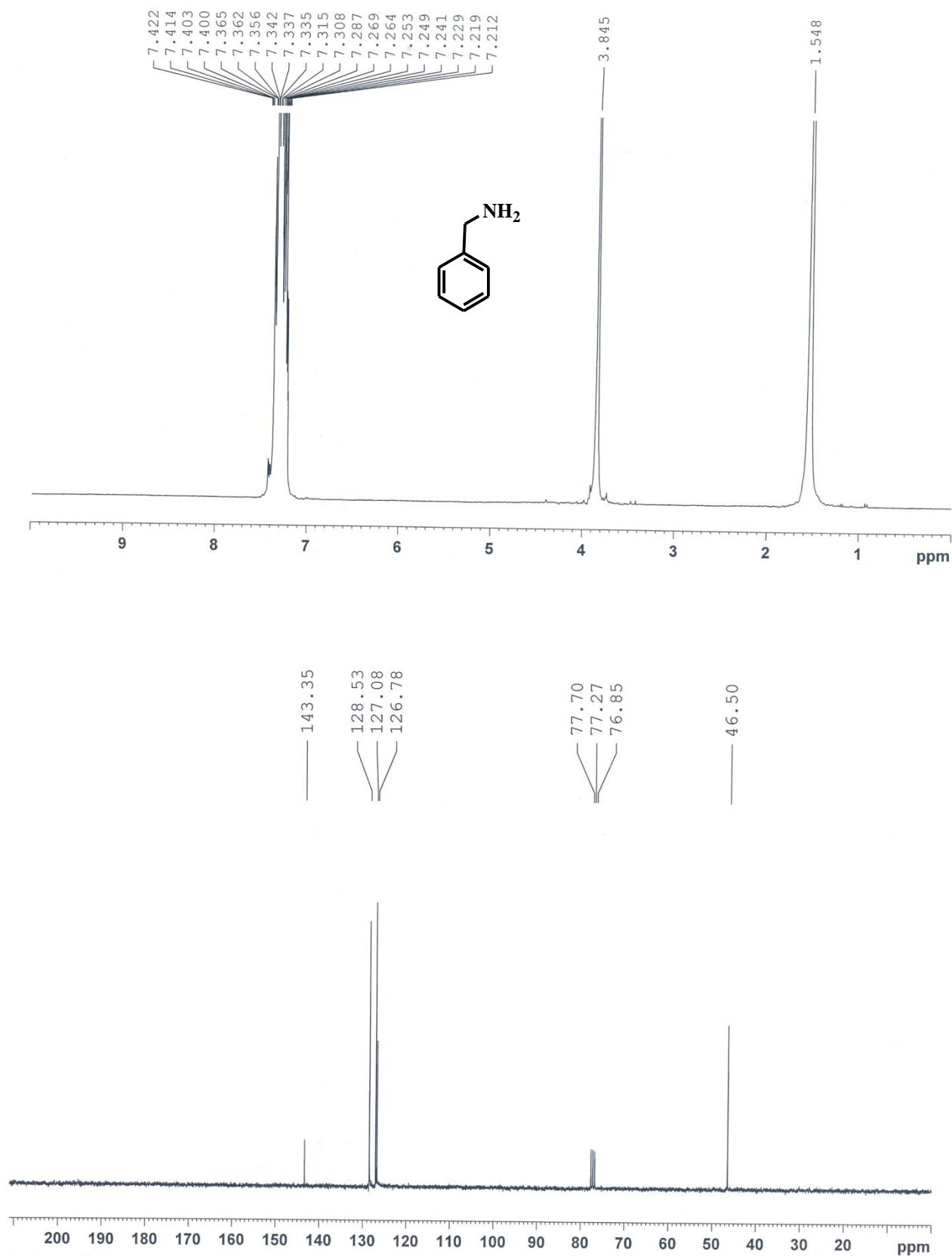
HR-MS (m/z) for $\text{C}_6\text{H}_7\text{N}$ (M^+): Calculated 93.0578, found 93.0578.

^1H and ^{13}C -NMR spectra of the synthesized compounds

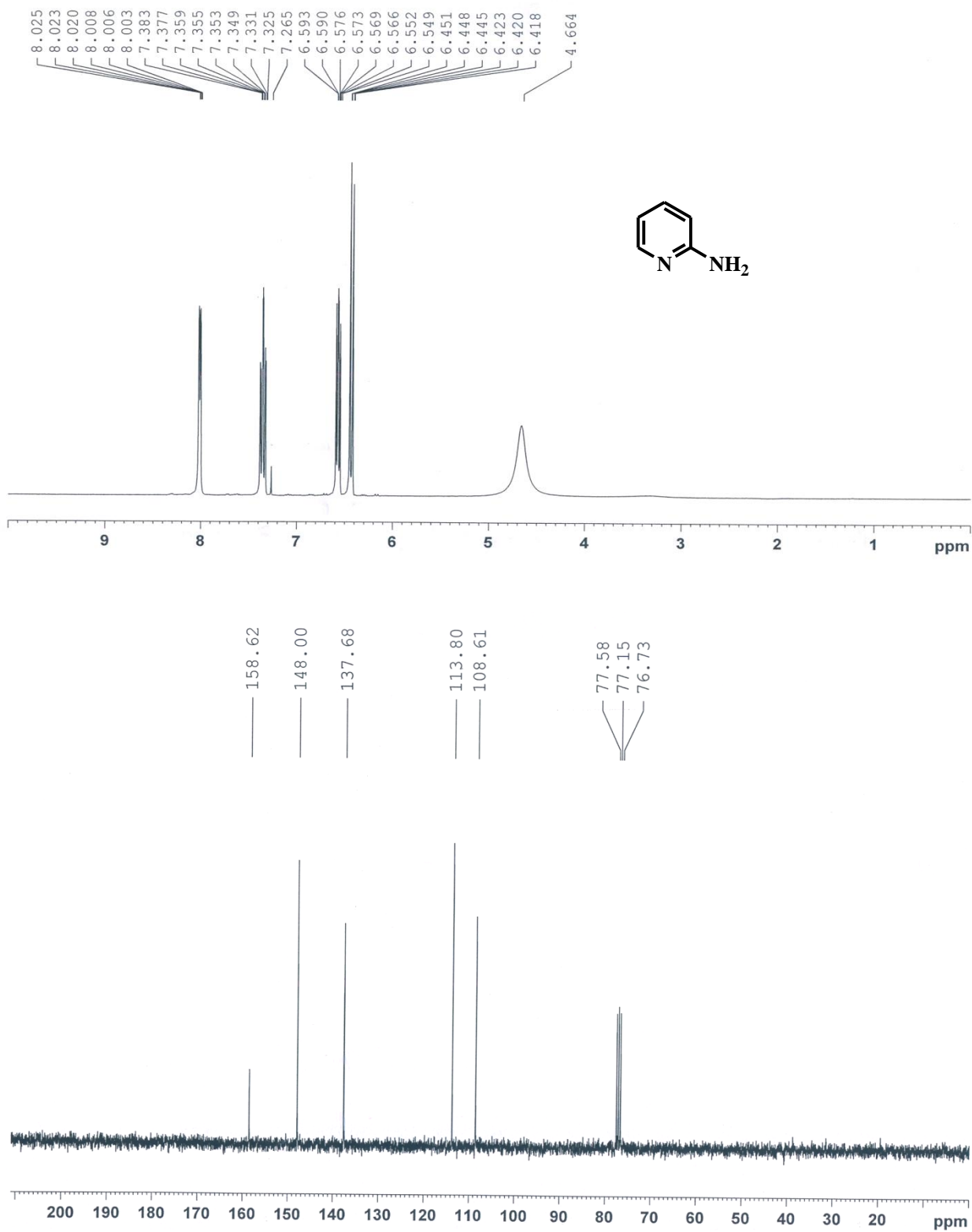
SI Figure 1. ^1H & ^{13}C -NMR spectra 2a



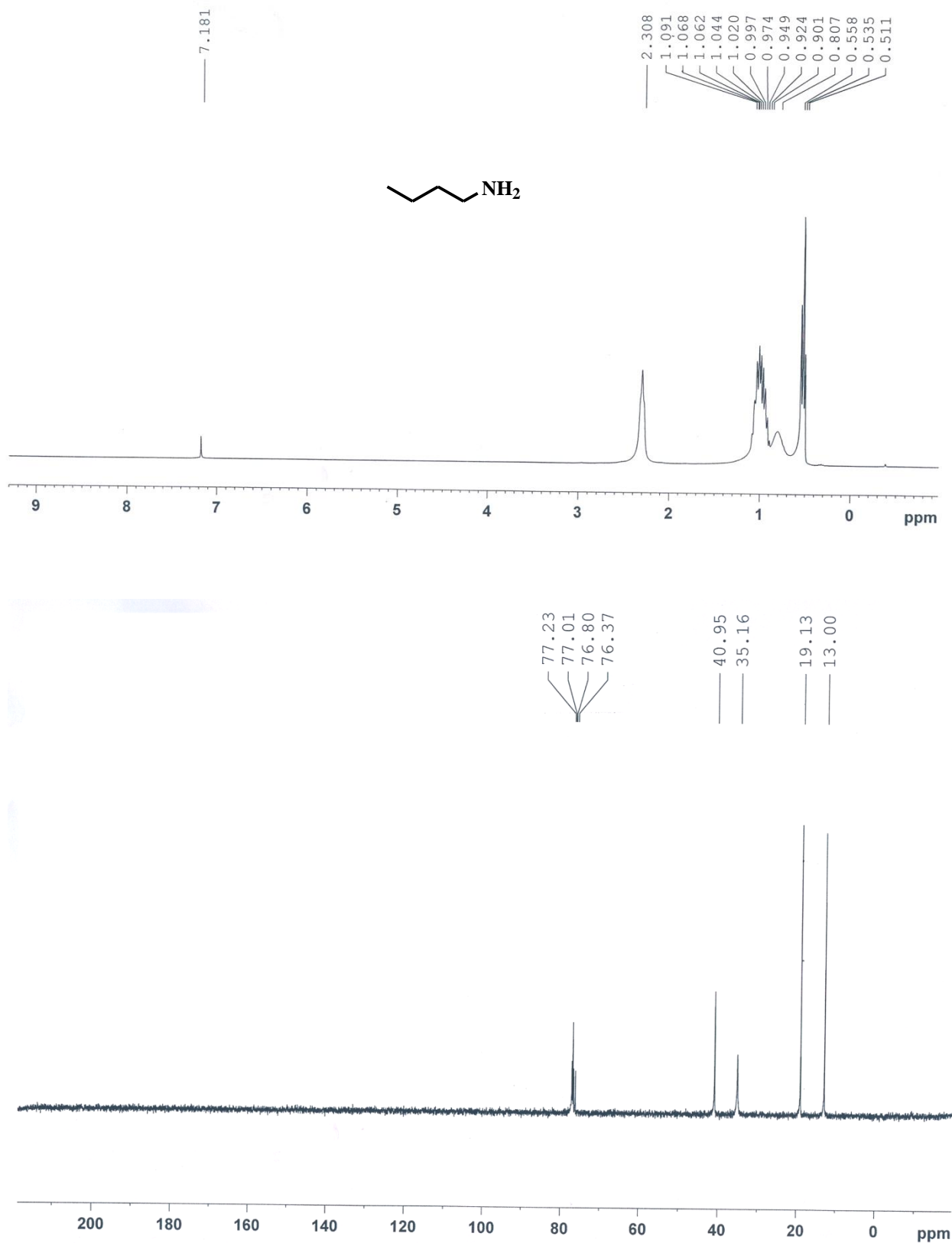
SI Figure 2. ^1H & ^{13}C -NMR spectra of **2b**



SI Figure 3. ^1H & ^{13}C -NMR spectra of **2c**



SI Figure 4. ^1H & ^{13}C -NMR spectra of **2d**



SI Figure 5. ^1H & ^{13}C -NMR spectra of **2j**

