Electronic Supplementary Material (ESI) for Nanoscale.

Maximizing the photo catalytic and photo response properties of multimodal plasmonic Ag/WO_{3-x} heterostructure nanorods by variation of Ag size

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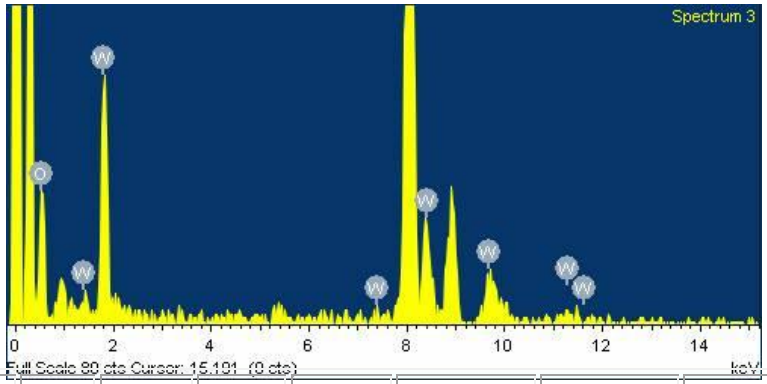

Element	Peak Area	Area Sigma	k factor	Abs Corrn.	Weight%	Weight% Sigma	Atomic%	
O K	179	25	1.810	1.000	14.99	2.02	66.96	
W L	755	54	2.435	1.000	85.01	2.02	33.04	
Totals					100.00			

Fig. S1: EDAX analysis of WO_{3-x} NRs samples shows the appreciable deficiency of oxygen from there stoichiometry.

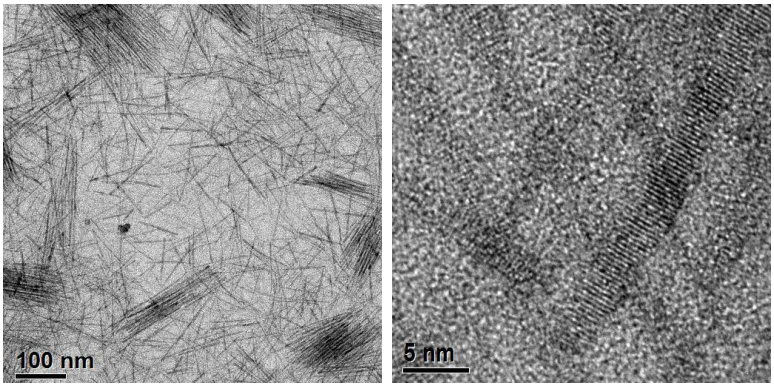

Fig. S2: TEM images of sub stoichiometry WO_{3-x} nanorods synthesized using NMO as the oxidizing agent. (B) HRTEM image of nanorods shows the width of rods < 3 nm with corroded surface.

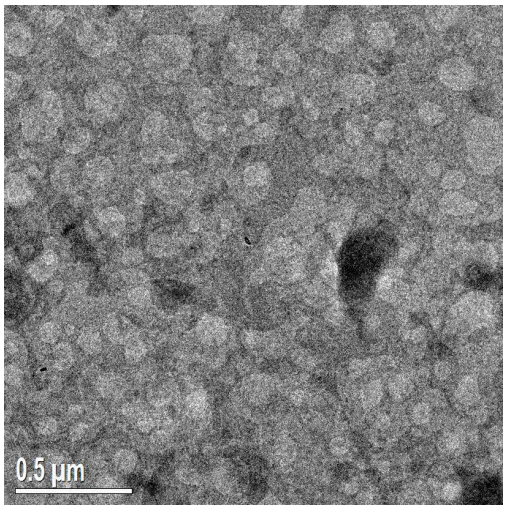

Fig. S3: TEM image of the intermediate blue colored compound after the oxidation of $W(CO)_6$ at 90 ºC by TMNO. The compound was found to be amorphous.

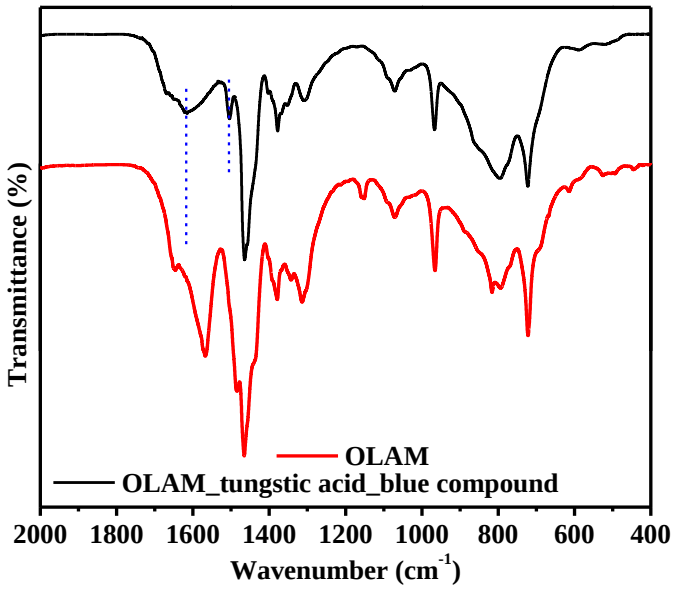

Fig. S4: Two new peaks at 1508 cm^{-1} and 1617 cm^{-1} in the isolated blue compound which is the mixture of OLAM and as-formed tungstic acid are related to $–NH_3^+$ species[1]. Which also indicate the formation of C_{18}-NH_3^+-H_2WO_4 complex (blue colored intermediate compound in the reaction).

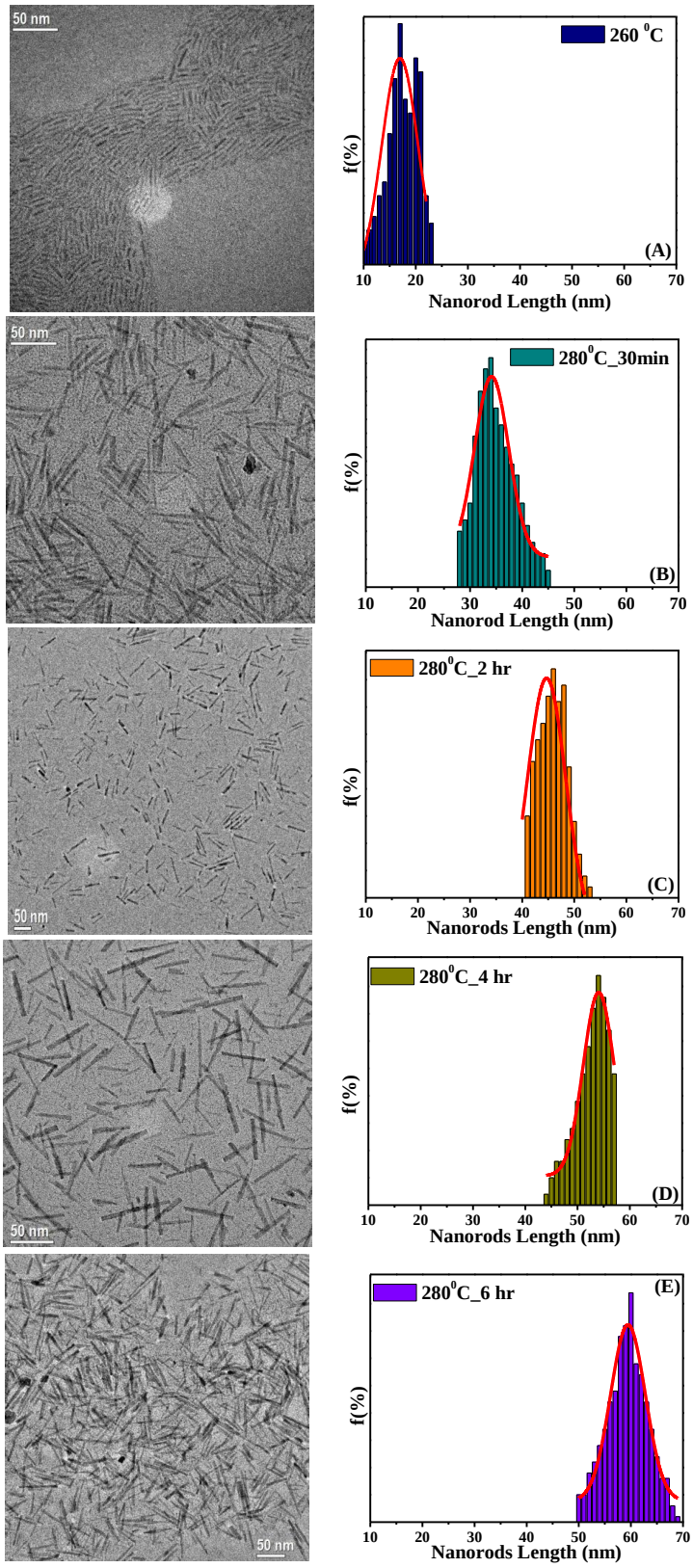

Fig. S5: Temporal growth evolution of WO_{3-x} nanorods at different time intervals.

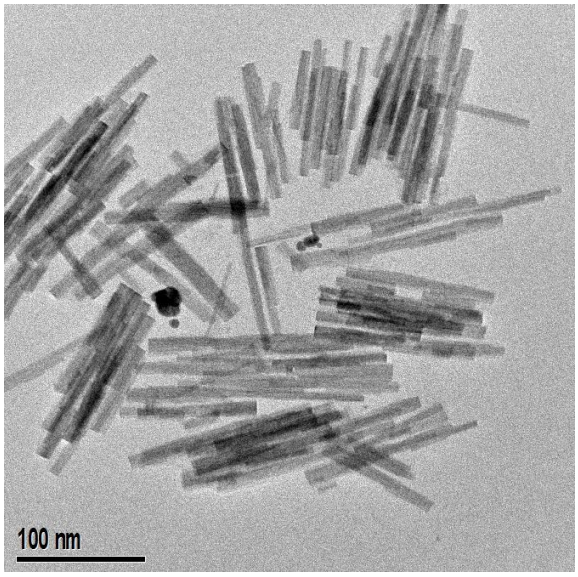

Fig. S6: TEM image of WO_{3-x} NRs using hexadecylamine instead of OLAM in similar reaction condition. Nanorod thickness was found to be increased 3-4 times than OLAM used nanorods.

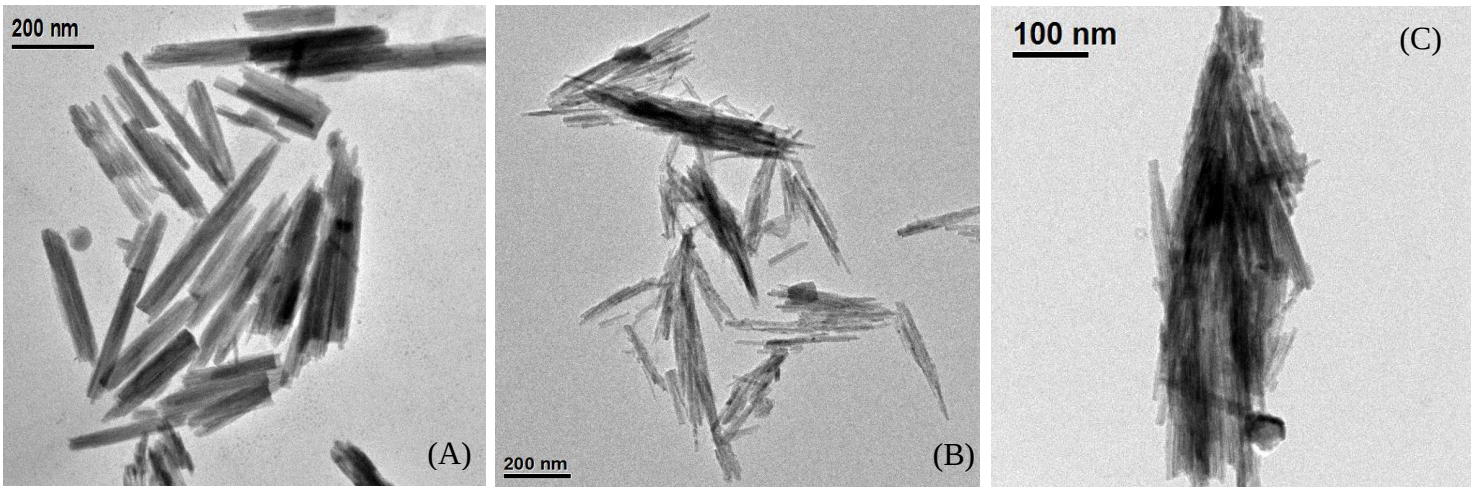

Fig. S7: TEM images of WO_{3-x} products using (A) 14 mmol OLAM + 7 mmol OLAC (oleic acid); (B) 10.5 mmol OLAM + 10.5 mmol OLAC; (C) 7 mmol OLAM + 14 mmol OLAC.

We fitted the experimental absorbance spectra of WO_{3-x} nanorods based on semiclassical Drude model.

The LSPR frequencies predicted by the classical Drude model are given by:

$$\omega_p = \left[\left\{\frac{N_e e^2}{\varepsilon_0 m_e(\varepsilon^{/}+2\varepsilon_m)}\right\} - \gamma^2\right]^{1/2} \quad (1)$$

Where, N_e is the free electron density, e is the electron charge, ε_0 is the permittivity of vacuum, ε_m is the dielectric constant of the medium (2.656 for CS_2), m_e= 1.2 m_0 is the mass of an electron in WO_3, $\varepsilon^{/}$ is high frequency dielectric constant (5.88 for WO_3)[2] and $\gamma = \gamma_{bulk}$ is the bulk scattering frequency.

The scattering frequency is modified by the size –dependent surface scattering as follows:

$$\gamma = \gamma_{bulk} + \frac{AV_F}{r} \quad (2)$$

Here, V_F is the Fermi velocity, r is the size of nanocrystals obtained from the TEM images and A is an empirical constant whose value is debated in the literature.

The absorbance due to Plasmon resonance is given by

$$A = \varepsilon_m^{3/2}\omega \sum_i \frac{\frac{Im(\varepsilon)}{P_i^2}}{\left(Re(\varepsilon) + \frac{(1-P_i)\varepsilon_m}{P_i}\right)^2 + Im(\varepsilon)^2} \quad (3)$$

where ω is the angular frequency of incident light, ε_m is the dielectric constant of the medium, ε is the dielectric function of WO_3, and the P_j are the depolarization factors for axis x, y, and z of the three dimensional system .

Where ε can be given by,

$$\varepsilon = 1 - \frac{\omega_p^2}{\omega^2 + j\gamma\omega} \quad (4)$$

The de-polarization factor in a direction can be given by,

$$P_x = \frac{(1-S^2)}{S^2}\left[\frac{1}{2S}\ln\left(\frac{1+S}{1-S}\right) - 1\right] \quad (5)$$

And

$$P_y = P_z = \frac{(1-P_x)}{2} \quad (5a)$$

And the geometric factor appeared in equation (5) S is defined as,

$$S = \left(1 - \frac{1}{R^2}\right)^{\frac{1}{2}}$$

Where R is the aspect ratio which is taken to 18.

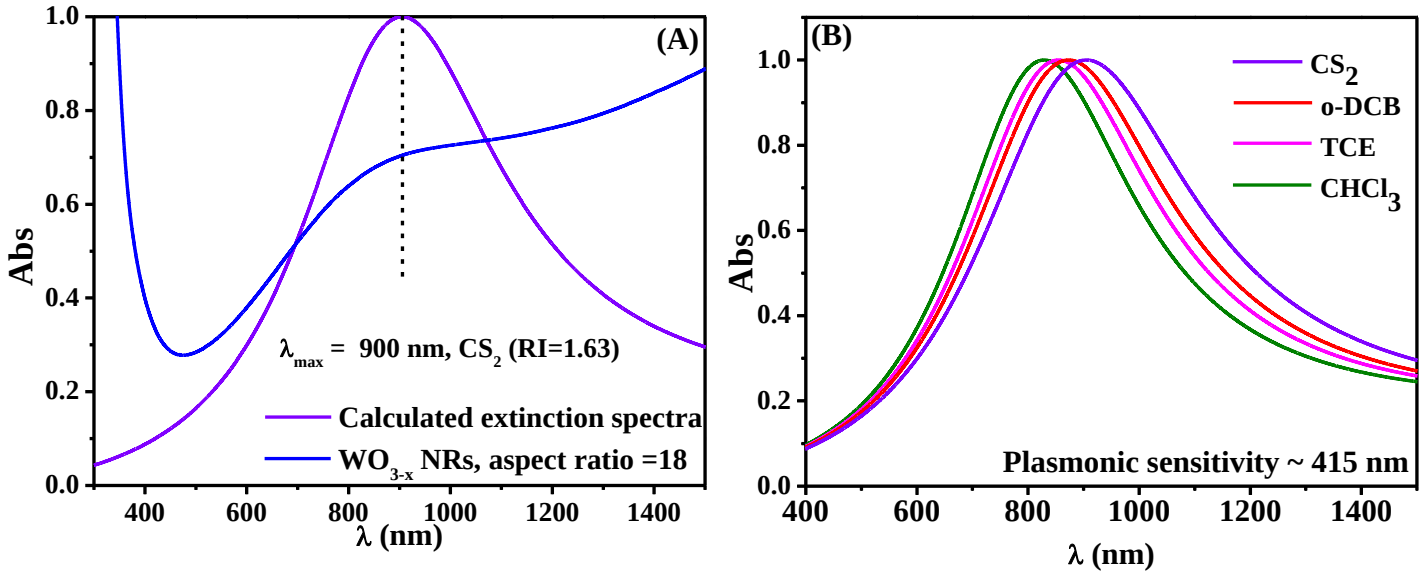

Fig. S8: (A) plot of calculated extinction spectra of WO_{3-x} NRs in CS_2 solvent from the above formulae using MATLAB program taking aspect ratio =18 (from TEM image) and experimental observed spectra in same solvent.

(B) Calculated extinction spectra of WO_{3-x} NRs in different solvent ($N_e = 6.1\times 10^{27}$ m^{-3}).

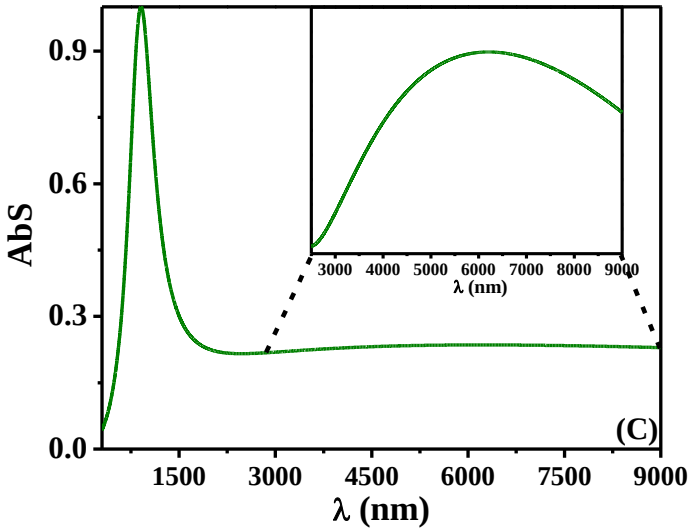

Fig. S8: (C) calculated extinction spectra of WO_{3-x} NRs in UV to IR region. Inset shows the enlarged view of spectra in 3000 nm to 9000 nm with peak maxima ~ 6000nm.

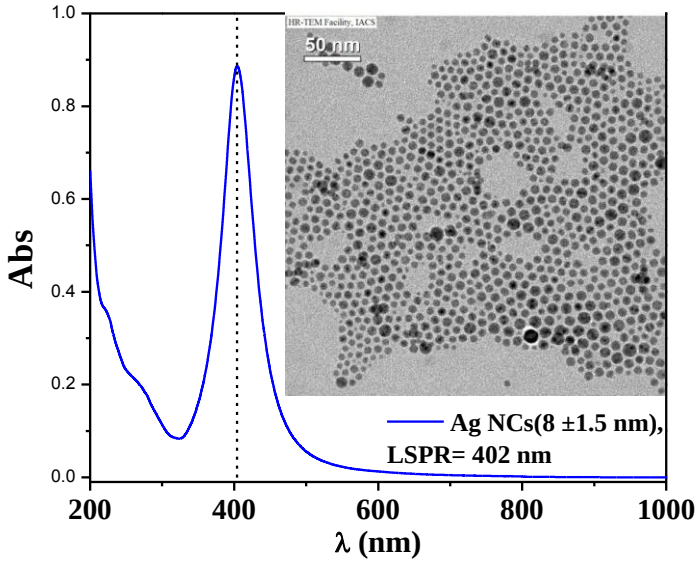

Fig. S9: Absorbance spectra of OLAM capped Ag NCs (Size 8 ± 1.5 nm) dispersed in CS_2. Inset shows the TEM image of the Ag NCs.

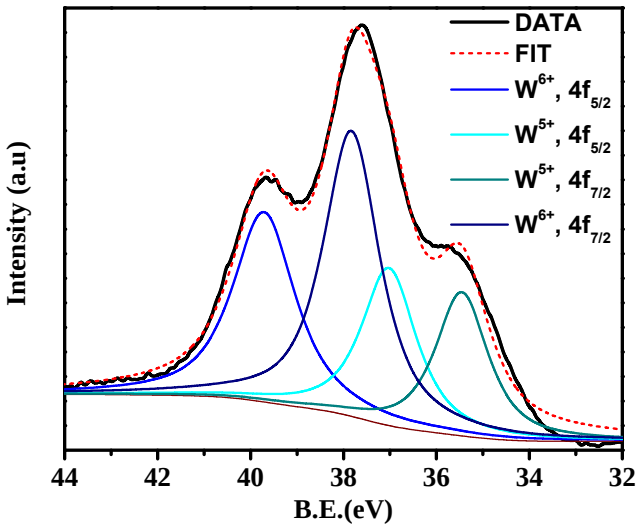

Fig. S10: Deconvulated HRXPS spectra of Ag(2nm)/WO_{3-x} NRs shows the presence of both W+5 and W+6 states of tungsten[3].

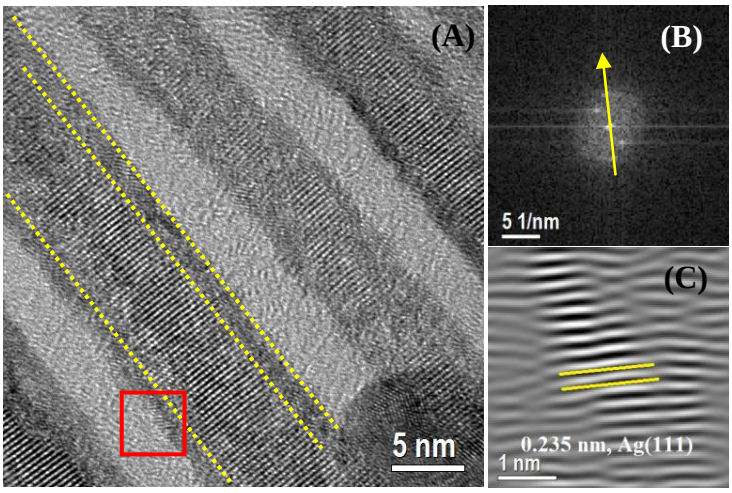

Fig. S11: (A) TEM image of Ag(5nm)/WO_{3-x} heterostructure NRs upon annealing at 170°C for 10 min. Shows a change of surface structure of almost all nanorods upon exposure of electron beam for 10 s. (B) FFT pattern of red circle are in Fig (A). The value obtained from the spots (along the yellow arrow) is 0.235 nm. (C) The simulated HRTEM image masking the yellow arrowed spots. They are the lattice fringes of Ag(111) plane. The surface of other rods also shows the presence of Ag(111) plane.

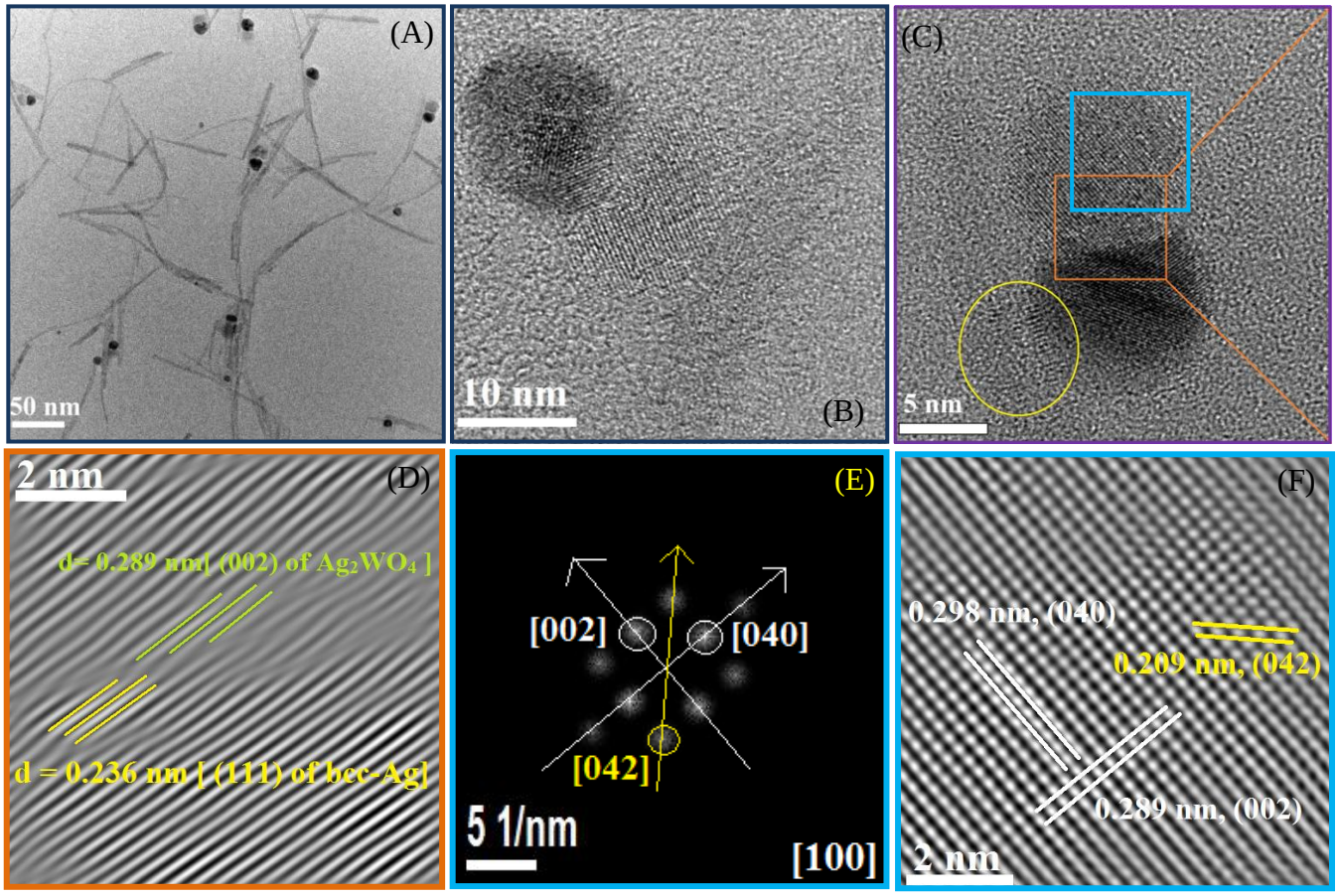

Fig. S12: (A) Large area TEM image of Ag/α-Ag_2WO_4 heterodimer formed by reaction of roughed surface thin WO_{3-x} nanorods or nanowire and Ag-OLAM solution on plasmonic photocatalysis followed by thermal annealing process. (B) and (C) shows the closer view (HRTEM) of two heterodimer. Both the heterodimers are situated with carbon-skin of capping agent (amorphous) which is formed when the crystalline WO_{3-x} converted to Ag_2WO_4. (D) The simulated HRTEM image from orange square area of Fig. (C) shows the formation of epitaxy between (111) Ag with (002) planes of Ag_2WO_4. (E) FFT pattern of blue squared area which is the pure WO_{3-x} part. (F) Simulated HRTEM image shows the presence of mutual perpendicular (040) and (002) planes and (042) plane when viewed along [100] zone axis.(P n 2 n (34) – orthorhombic Ag_2WO_4)[4,5]

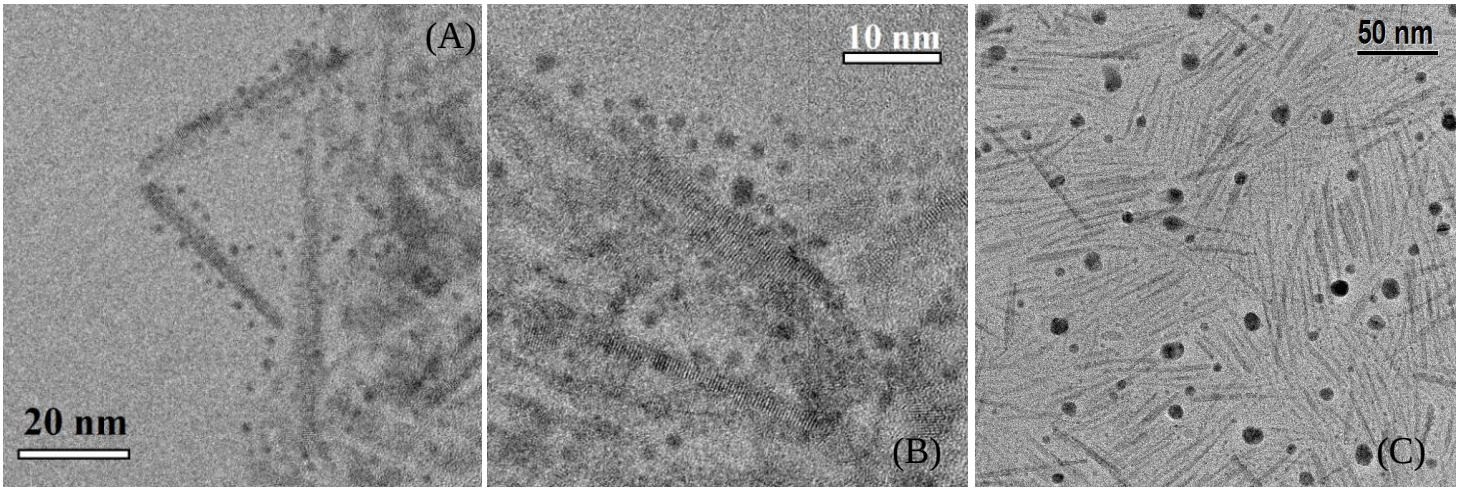

Fig. S13: (A) TEM image of Au/ WO_{3-x} NRs when $HAuCl_4$_OLAM solution and WO_{3-x} NRs irradiated for 30 min in white light. (B) The 60 min product. In both the cases Au cluster was found to be detached from NRs. (C) TEM image of product when the 60 min photocatalysed product was annealed at 170 °C for 30 min

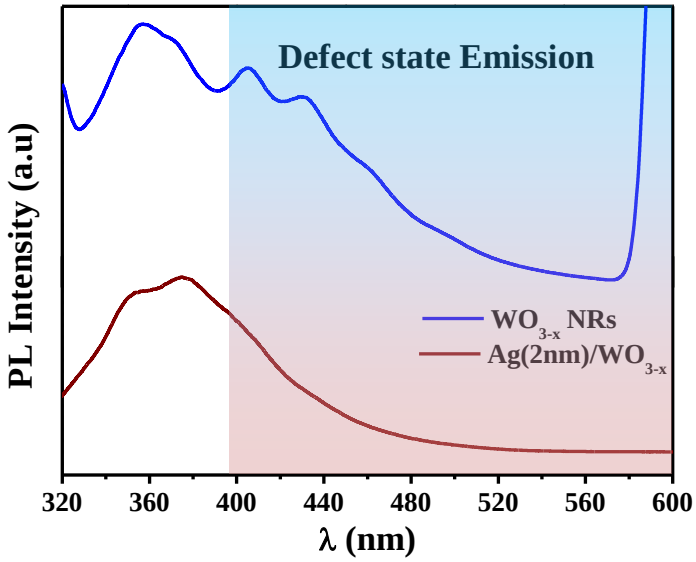

Fig. S14: The photoluminescence spectra of pure WO_{3-x} nanorods and Ag (2nm) decorated WO_{3-x} nanorods. Band edge excitation was found at 350 nm for both the samples. Defect PLs ranging from 380 nm to 560 nm for pure WO_{3-x} was found to be quenched for Ag decorated nanorods.

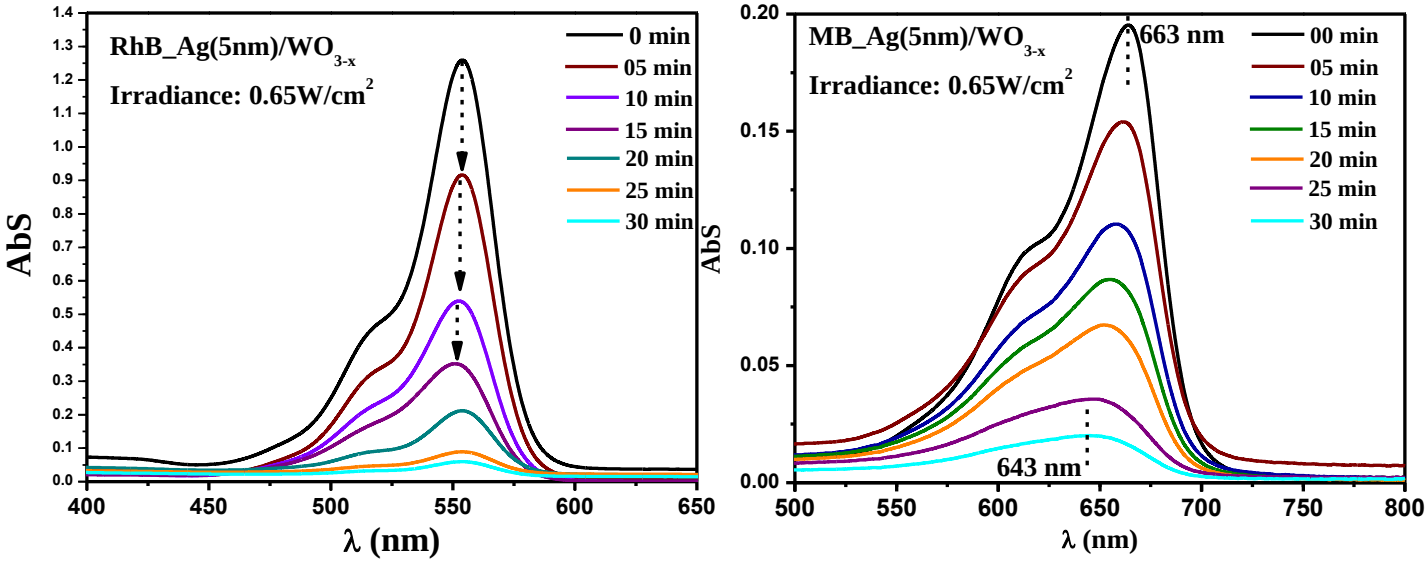

Fig. S15: Change of absorbance intensity of RhB and MB dye in water in presence of $Ag(5nm)/WO_{3-x}$ catalyst with light irradiance of $0.65W/cm^2$.

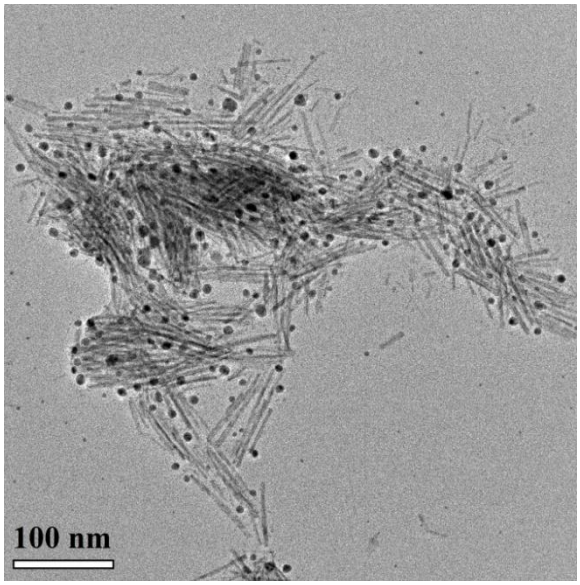

Fig. S16: TEM image of recovered $Ag(10nm)/WO_{3-x}$ NHS catalyst.

References:

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