Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Highly-reactive AgPt nanoferns composed of {001}-faceted nanopyramidal spikes for enhanced-heterogeneous photocatalysis application

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Supporting Data

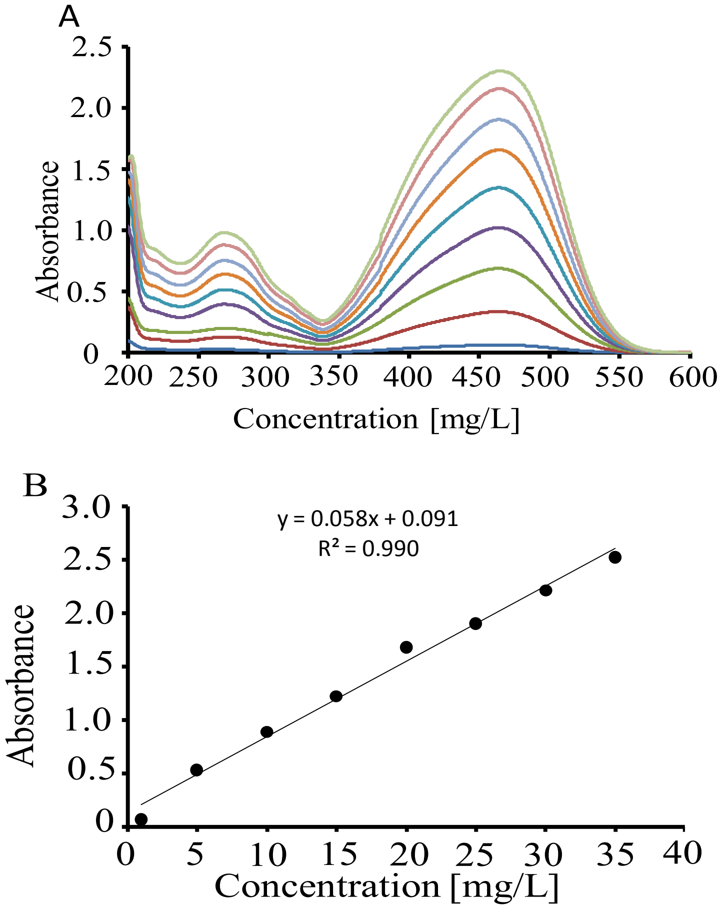

Figure S1. (A) Methyl orange optical absorption spectra with varing concentration (1-35ppm) (B) plotting of the absorbance standard calibration graph of methyl orange at the center of the absorption band.

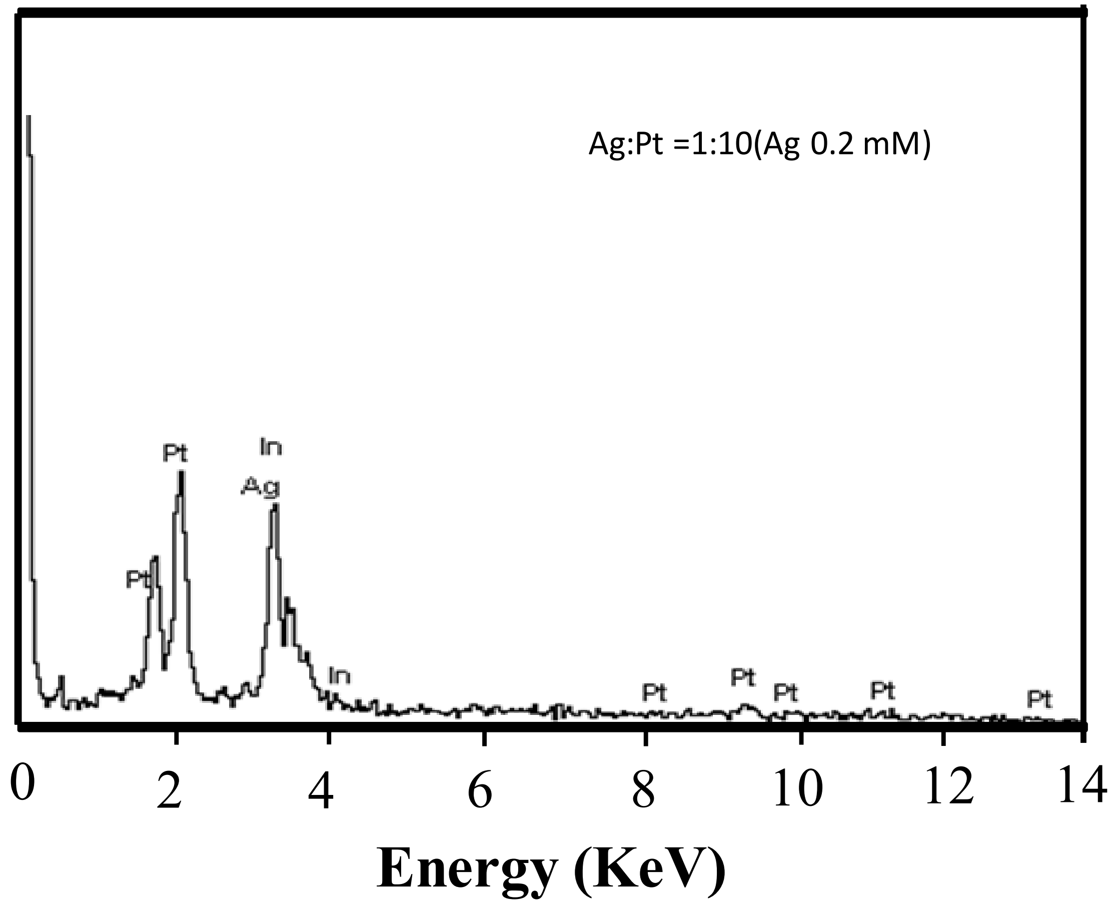

Figure S2. EDX spectrum of AgPt nanofern prepared using a growth solution containing 1 mM potassium cloroplatinate (IV), 0.2 mM silver (I) nitrate, 10 mM sodium dodecylesulfate and 5.0 mM formic acid. The growth times was 30 min

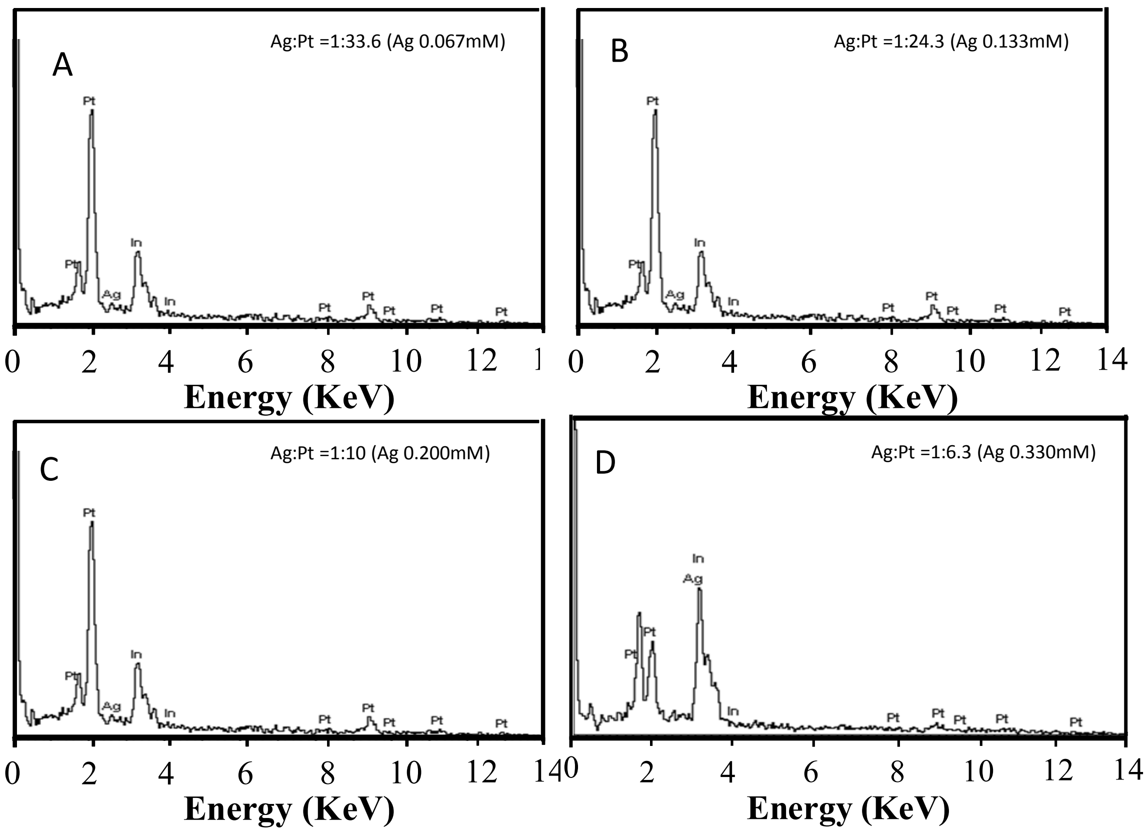

Figure S3. EDX spectra of AgPt nanofern prepared using different concentration of Ag ions in the reaction, namely 0.067 (A), 0.133 (B), 0.200 (C) and 0.330 mM (D). The Ag:Pt atomic ratio for every sample are shown in the corresponding graph.

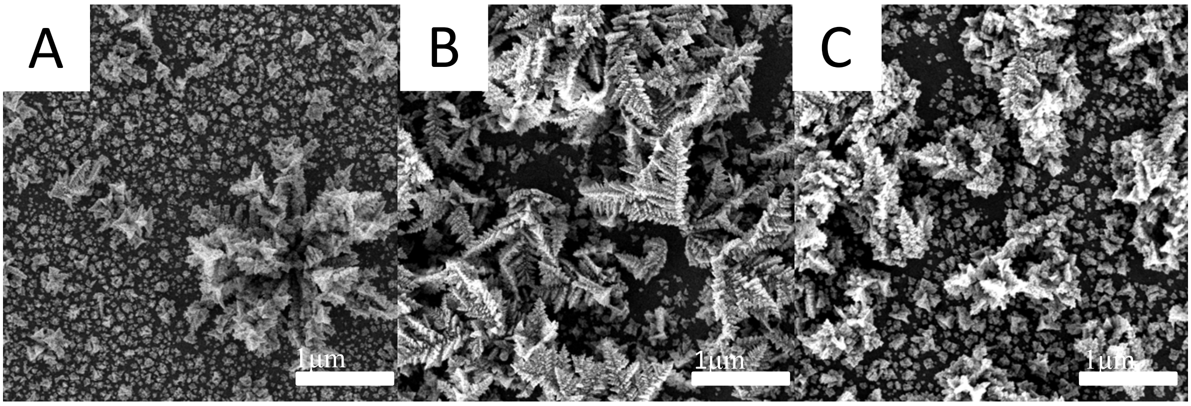

Figure S4. AgPt nanofern prepared using different formic acid concentration, namely 3 (A), 5 (B) and 10 mM (C). Other reactant concentration is fixed at the optimum condition namely, 1.0, 2.0, and 10.0 mM for potassium cloroplatinate (IV), silver (I) nitrate and sodium dodecyl sulphate, respectively. The growth time was 30 min.

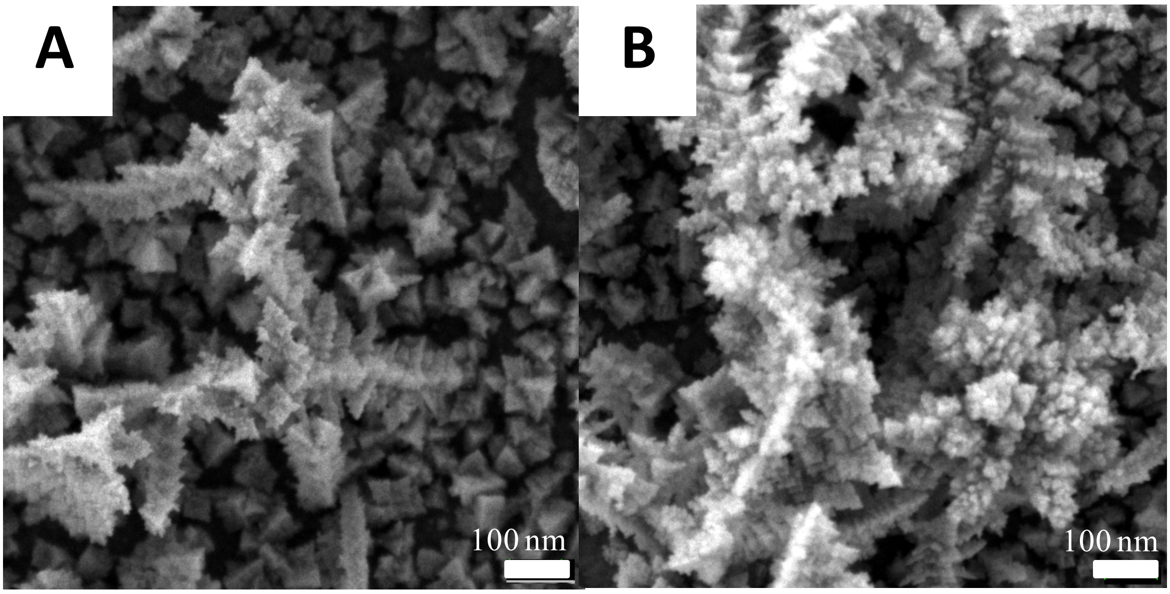

Figure S5. AgPt nanofern prepared using sodiumdodecyl sulphate (SDS) concentration of 5 mM (A) and 15 mM (B). Other reactant concentration is fixed at 1.0, 0.2, and 5.0 mM for potassium cloroplatinate (IV), silver (I) nitrate and formic acid, respectively. The growth time was 30 min.

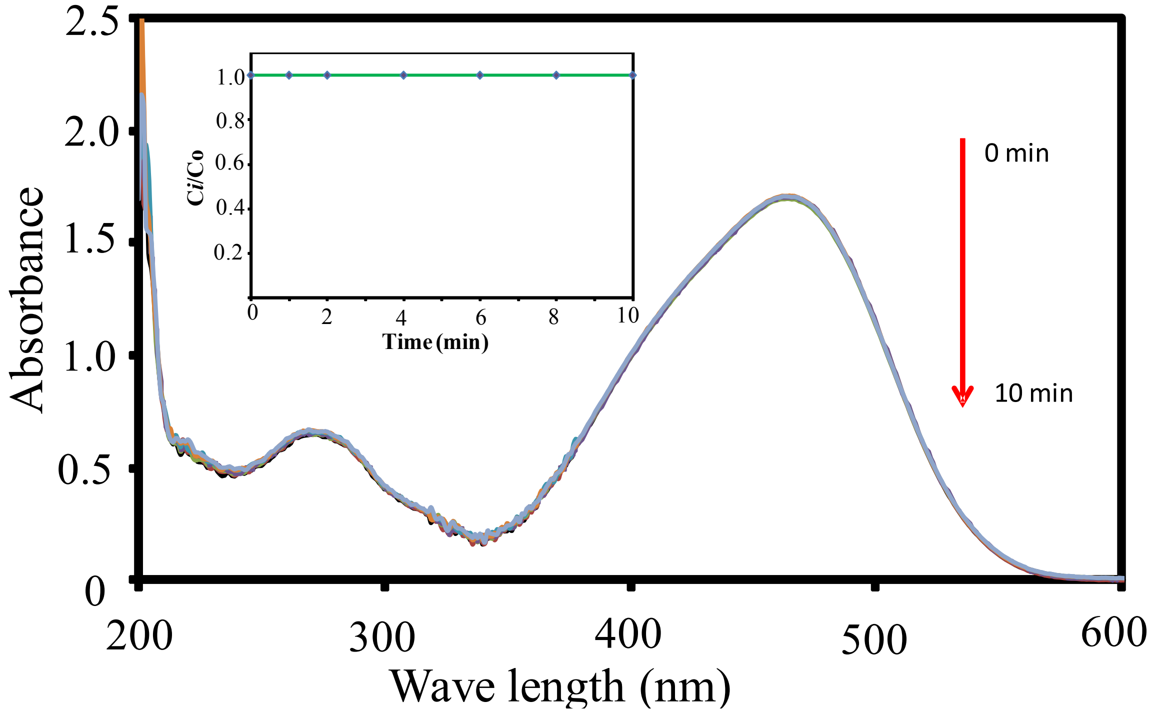

Figure S6. Degradation kinetic of MO in the presence of single slide AgPt nanofern but in the absence of light irradiation.

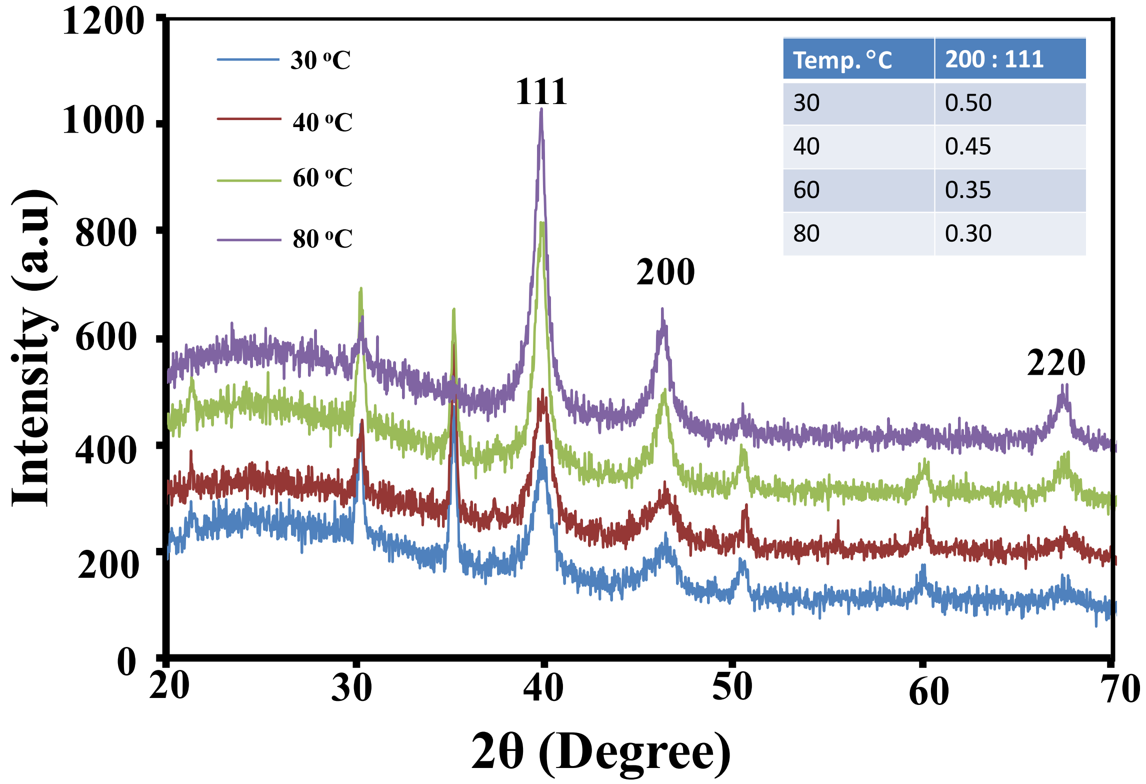

Figure S7. XRD spectra of AgPt nanofern prepared using optimum growth solution concentration with different growth temperatures. The inset table shows the peak intensity ratio of (200) and (111) planes.

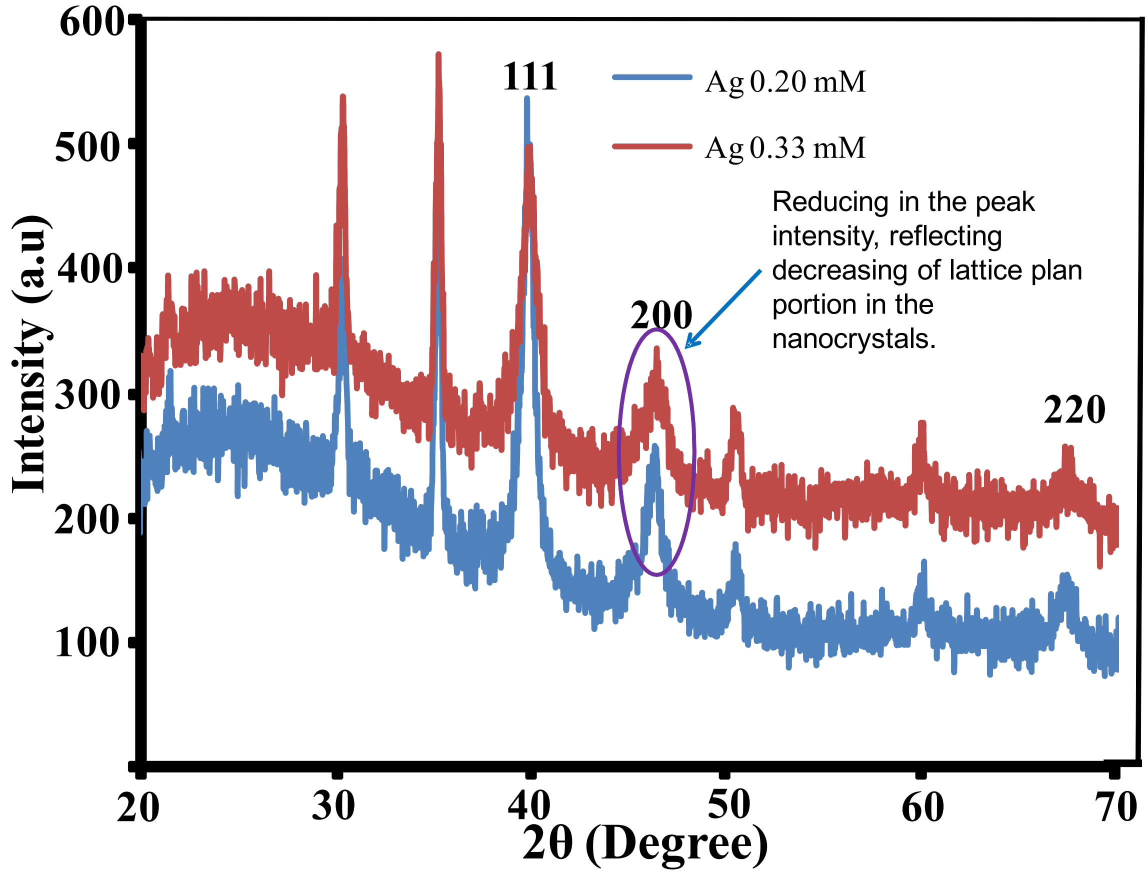

Figure S8. XRD spectra of AgPt nanofern prepared at high-concentration of Ag, namely 0.33 mM. The (001) peak is little bit lower compared to the sample prepared at 0.20 mM, implying lower surface reactivity.

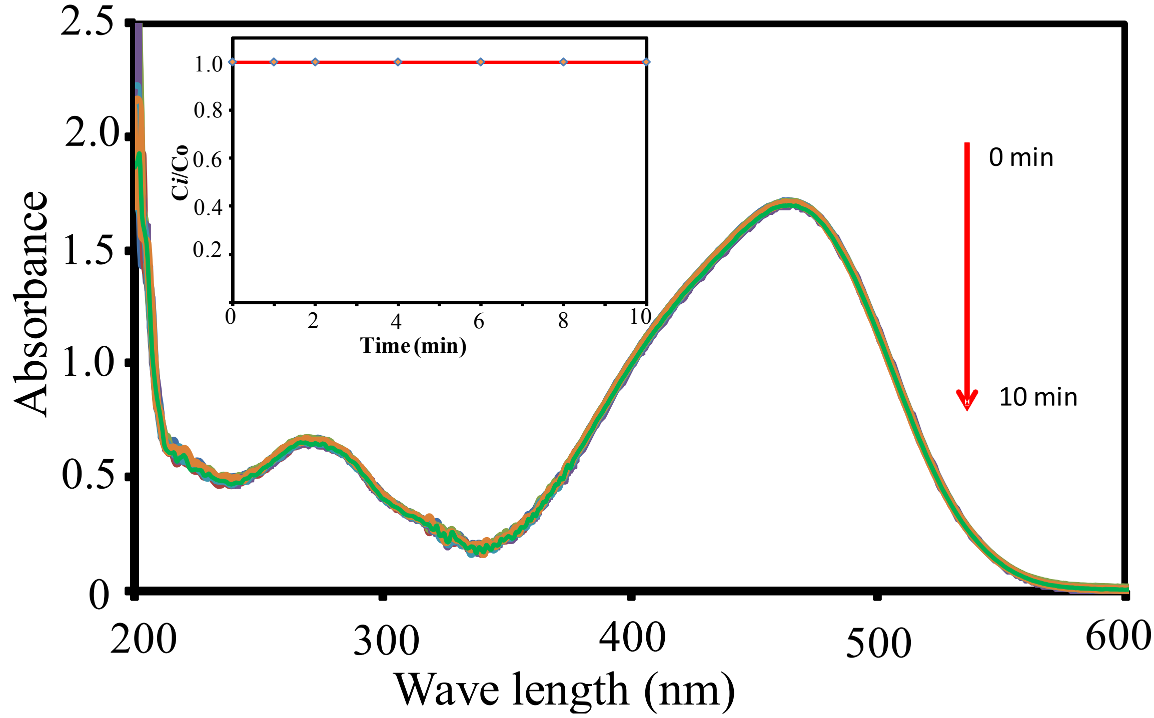

Figure S9. Degradation kinetic of MO under irradiation of light but in the absence of AgPt nanofern catalyst.

BET analysis

BET analysis was carried out to obtain the surface area of AgPt nanofern on the ITO substrate using Micrometics ASAP 2020 apparatus. In typical procedure, ten ITO slides containing AgPt nanofern with dimension of 0.3 cm × 0.5 cm were prepared and used in the BET analysis. By gravimetric method, the mass of AgPt nanofern on 10 ITO slides was found to be 340 μg or equivalent to 34 μg for a single slide. The surface area and porosity properties of all AgPt samples were analyzed using the nitrogen gas adsorption-desorption technique at a temperature of -196 °C.

From the analysis result, the BET surface area for AgPt nanofern on ITO slide is approximately 51.6 $m^2\ g^{-1}$.

Calculation of TON and TOF.

To obtain the turnorver number (TON) and turnover frequency (TOF) of AgPt nanofern catalyst in the photodegradation of MO, the active sites (AS) number (i.e. the effective site on AgPt nanofern catalyst surface for MO adsorption and heterogeneous catalytic reaction), was firstly calculated. In normal process, the temperature programmed desorption (TPD) of hydrogen analysis is used for active site calculation. However, due to the amount of AgPt nanofern catalyst on the surface is very small, the active site from TPD result could not be obtained. Therefore, we estimated the active site using the obtained BET surface area.

For heterogeneous catalytic reaction, we assumed the entire surface is attached with MO molecules. The amount of MO molecules accommodated on the catalyst surface reflects the number of active site on the catalyst surface. The length of MO molecule is approximately 2.61×10^{-9} m. By considering the MO molecules attachment orientation on the catalyst surface is random, its length can be assumed as the “dynamic diameter” (***D***) of MO. Therefore, cross-section of single MO molecules ($\boldsymbol{MO}_{\mathrm{CS}}$) is equivalent to the area on the catalyst surface occupied by the MO. Thus, :

$$MO_{CS} = 3.14 \times \left(\frac{D}{2}\right)^2 = 3.14 \times \left(\frac{2.61 \times 10^{-9} m}{2}\right)^2 = 5.36 \times 10^{-18} m^2 \text{...(1)}$$

From the BET analysis, the BET surface area ($\boldsymbol{BET}_{\mathrm{SA}}$) is found to be 51.6 $m^2\ g^{-1}$. Because on an ITO substrate there is 34 μg (***MG***) of AgPt nanofern, the specific surface area (***SSA***) of AgPt nanofern become:

$$SSA = BET_{SA} \times MG = 51.6 m^2 g^{-1} \times 34 \times 10^{-6} g = 1.76 \times 10^{-3} m^2$$

The number of active sites (***AS***) on the catalyst surface was calculated by dividing the specific surface area (***SSA***) (1) with the MO cross-section ($\boldsymbol{MO}_{\mathrm{CS}}$) (2).

$$AS = \frac{SSA}{MO_{CS}} = \frac{1.76\times10^{-3}m^2}{5.36\times10^{-18}m^2} = 3.27\times10^{14} \quad ...(2)$$

The TON and TOF of the AgPt nanofern in the degradation of Mo molecules were calculated by dividing the number of MO molecules degraded ($\boldsymbol{MO}_{\mathrm{deg}}$) with the number of active sites (***AS***). For example from the experimental data, at 4 minutes on reaction, 55% of MO molecules have been degraded. Since the initial concentration of MO is 20 ppm (10 mL), the $\boldsymbol{MO}_{\mathrm{deg}}$ is:

$$MO_{\mathrm{deg}} = 55\%\times N_{init} = 55\%\times\left[V_{react}\times\frac{C_0}{Mr_{MO}}\times A_v\right] = 55\%\times\left[10mL\times\frac{20ppm}{327.3}\times6\times10^{23}\right] = 2.02\times10^{17}$$

...(3)

Where $\boldsymbol{N}_{\mathrm{init}}$, $\boldsymbol{V}_{\mathrm{react}}$, $\boldsymbol{Mr}_{\mathrm{MO}}$ and $\boldsymbol{A}_{\mathrm{v}}$ are initial number of MO molecules, volume of reaction, molecular weight of MO molecules and Avogadro number, respectively. The TON was calculated by dividing (2) and (3), while the TOF was obtained by dividing TON with time, respectively. Therefore, TON and TOF at 4 min of reaction become:

$$TON = \frac{2.02\times10^{17}}{3.27\times10^{14}} = 616$$

$$TOF = \frac{TON}{4\min} = \frac{616}{4\min} = 154\min^{-1}$$