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Supporting Information

Large-scale synthesis of uniform silver orthophosphate colloidal nanocrystals exhibiting high visible light photocatalytic activity

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Experimental Section

Chemicals: All chemicals were used as received; silver nitrate ($AgNO_3$), methylene blue (MB), oleylamine (OM), phosphoric acid (H_3PO_4), ammonium hydroxide (NH_4OH) were purchased form Aldrich. Absolute ethanol and toluene solvents were of analytical grade and were also purchased form Aldrich.

Synthesis of 8 nm Ag_3PO_4 nanocrystals: Typically, for the synthesis of about 10 g of 8 nm Ag_3PO_4 NCs, silver nitrate (0.1 mole) and OM (0.2 mole) were dissolved in 300 ml of toluene. To this mixture, H_3PO_4 (0.1 mole) dissolved in 100 ml of ethanol was then gradually added under stirring. The solution changed from colorless to yellow, indicating the formation of Ag_3PO_4 NCs. After 30 minutes of stirring, excess ethanol was added to precipitate Ag_3PO_4 NCs. The obtained NCs were then re-dispersed in 300 ml toluene and reprecipitated in ethanol. This process was repeated three times to remove all unreacted reagents.

Synthesis of Ag_3PO_4 nanocrystals with different sizes: The procedures for the synthesis of 10 nm, 12 nm, 14nm and 16 nm Ag_3PO_4 NCs were similar to that of 8 nm Ag_3PO_4 NCs, except that 2.5 g, 5.0 g, 7.5 g, and 10 g of water was added, respectively, to the H_3PO_4 solution in ethanol before it was added to the solution containing silver ions and OM.

Removing OM surfactant from Ag_3PO_4 NCs surface: The as-synthesized Ag_3PO_4 NCs were treated with dilute NH_4OH solution to remove OM surfactant. Typically, 10 mmol of as-synthesized Ag_3PO_4 NCs was dispersed in 100 ml toluene. To this solution, a mixture containing 1 mmol NH_4OH, 25 ml ethanol and 25 ml toluene was gradually added under stirring. After 1 h of additional stirring, the mixture was centrifuged to obtain a precipitate of Ag_3PO_4 NCs which was then redispersed in 100 ml of ethanol. To this mixture was gradually added a solution of 50 ml ethanol containing 1 mmol NH_4OH. After 1 h of stirring, the Ag_3PO_4 NCs obtained through centrifugation was dispersed in water and ready for photocatalytic tests.

Synthesis of micron-sized Ag_3PO_4 and N-doped TiO_2-P25: Ag_3PO_4 particles with micrometer size was synthesized as previously reported.[1] Briefly, appropriate amounts of Na_3PO_4 and $AgNO_3$ were thoroughly mixed until the initial white color changed to yellow. The mixture was then washed with distilled dried at 70 C in air overnight. Ndoped TiO_2-P25 was obtained by heat treating TiO_2-P25 at 550 oC under a flow of NH_3 for 3h.[2]

Characterization: Transmission electron microscopy (TEM) images of Ag_3PO_4 NCs were obtained on a JOEL JEM 1230 operated at 120kV. Samples were prepared by placing a drop of a dilute toluene dispersion of NCs onto a 200 mesh carbon coated copper grid and evaporated immediately at ambient temperature. The NC size analysis was carried out by manually digitizing the high magnification TEM images with Image Tool. XPS measurements were carried out in an ion-pumped chamber (evacuated to 10-9 Torr) of a photoelectron spectrometer (Kratos Axis-Ultra) equipped with a focused X-ray source (Al Ka, hv = 1486.6 eV). The binding energy of the samples was calibrated by setting the C 1 s peak to 285 eV. Peak deconvolution were performed by means of a standard CasaXPS software (v.2.3.13; product of CasaXPS Software Ltd., USA) to resolve the separate constituents after background subtraction. Powder X-ray diffraction patterns of the samples were obtained on a Bruker SMART APEXII X-ray diffractometer equipped with a Cu Ka radiation rource

(l=1.5418 Å). The UV-visible absorbance spectra were recorded on a Cary 300 Bio UV-visible spectrophotometer. Specific surface areas of the samples were measured by BET method (N2 adsorption) with a Quantachrome Autosorb-1 system.

Photocatalysis: Photocatalytic activities of the samples were evaluated by the photocatalytic decomposition of Methylene Blue (MB). A mixture of MB aqueous solution (15 ppm, 100 ml) and the given photocatalyst (30 mg) was magnetically stirred in absence of light for 60 minutes to ensure adsorption-desorption equilibrium between the photocatalyst and MB. The mixture was then stirred under visible light irradiation using a 40W compact fluorescent lamp. At given time intervals, 3 ml of the suspension was collected and centrifuged to remove photocatalyst particles. UV-vis adsorption spectrum of the centrifugated solution was recorded using a Cary 300 Bio UV-visible spectrophotometer to determine the conversion of the reaction.

1. Z. Yi, J. Ye, N. Kikugawa, T. Kako, S. Ouyang, H. S-. Williams, H. Yang, J. Cao, W. Luo, Z. Li, Y. Liu and R. L. Withers, *Nature Mater.*,2010, **9**, 559.
2. J. Wang, D. N. Tafen, J. P. Lewis, Z. Hong, A. Manivannan, M. Zhi, M. Li and N. Wu, *J. Am. Chem. Soc.*, 2009, **131**, 12290.

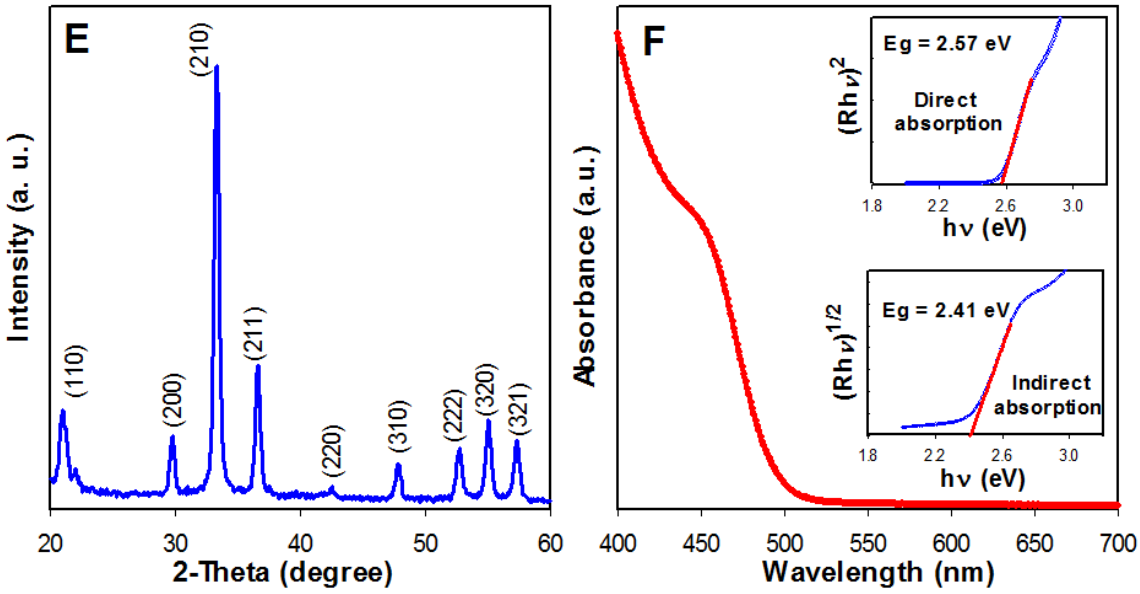

Figure S1. (E) powder XRD pattern and (F) UV-visible spectra of 8 nm Ag_3PO_4 NCs. (Insets in F: plots for determining the band gap of Ag_3PO_4 NCs).

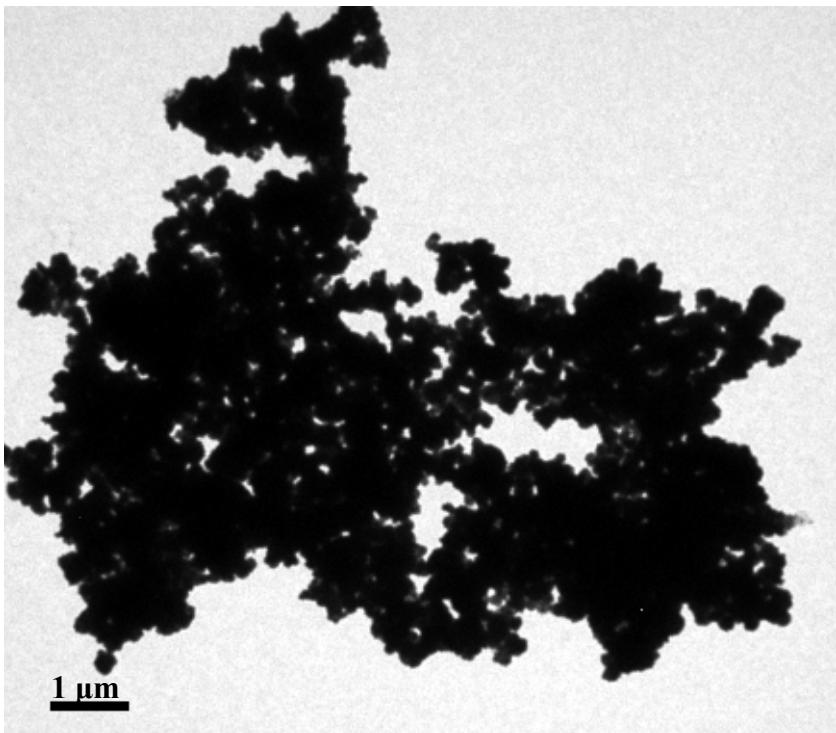

Figure S2. TEM image of Ag_3PO_4 synthesized without OM.

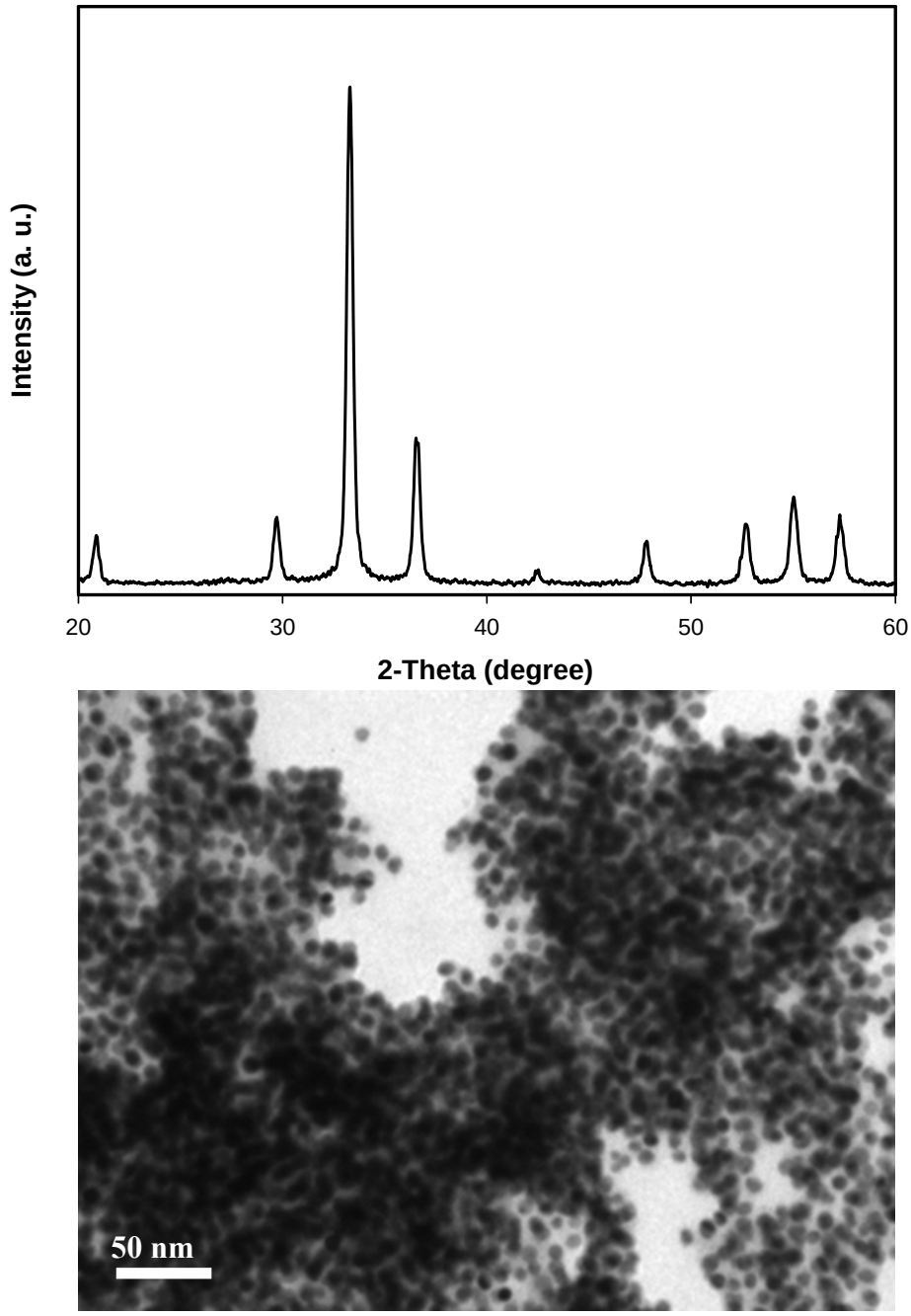

Figure S3. XRD pattern (upper) and TEM image (lower) of 8 nm Ag_3PO_4 NCs after being treated with NH_4OH.

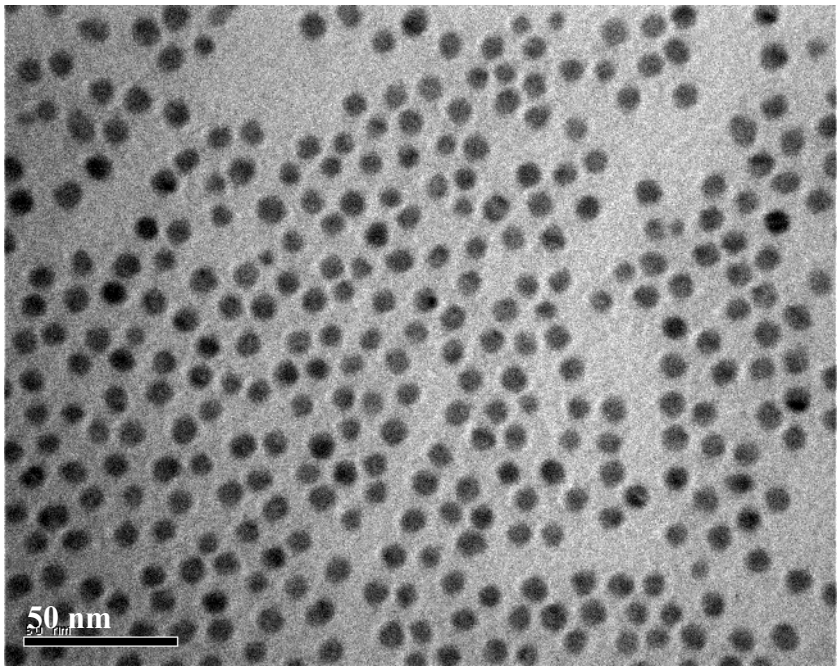

Figure S4. TEM image of 10 nm Ag_3PO_4 NCs synthesized by adding 2.5 g water to the H_3PO_4 solution

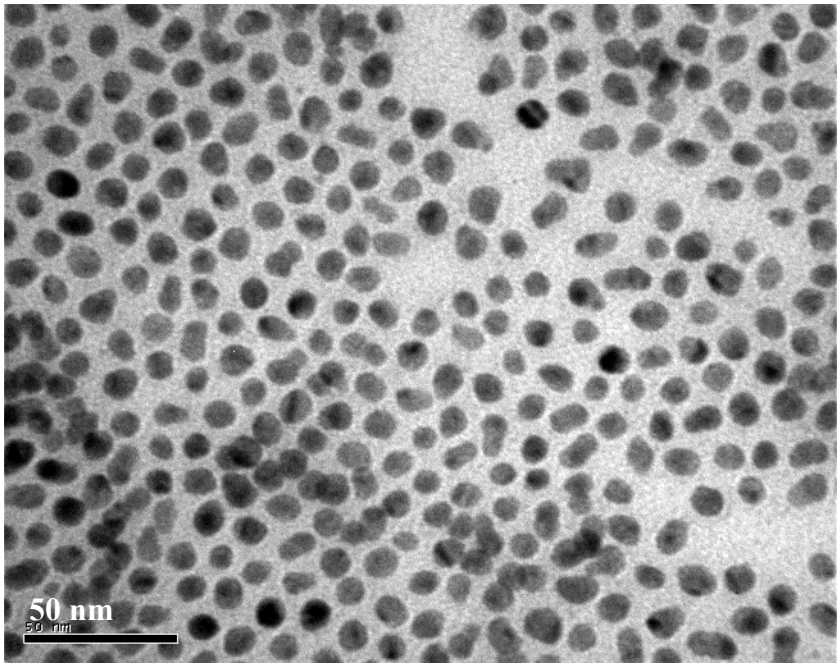

Figure S5. TEM image of 12 nm Ag_3PO_4 NCs synthesized by adding 5.0 g water to the H_3PO_4 solution

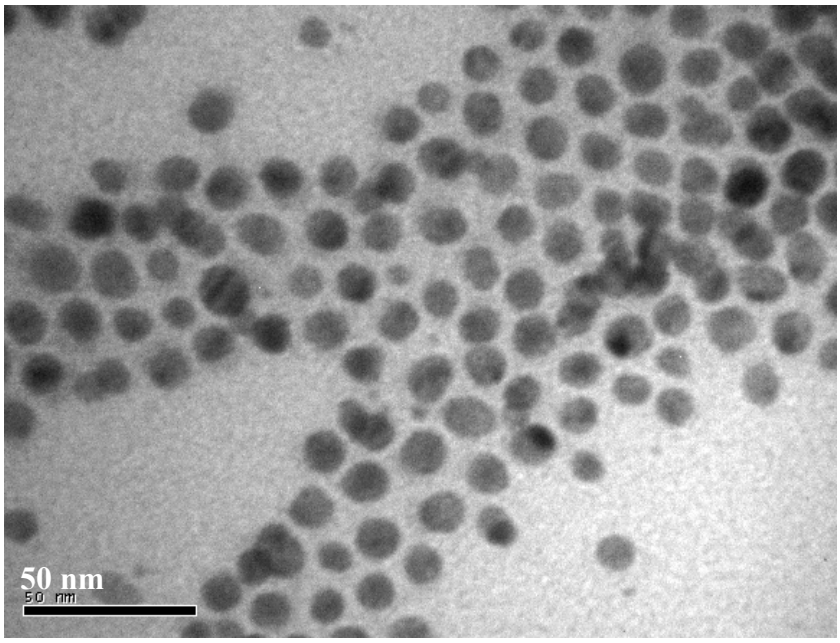

Figure S6. TEM image of 14 nm Ag_3PO_4 NCs synthesized by adding 7.5 g water to the H_3PO_4 solution

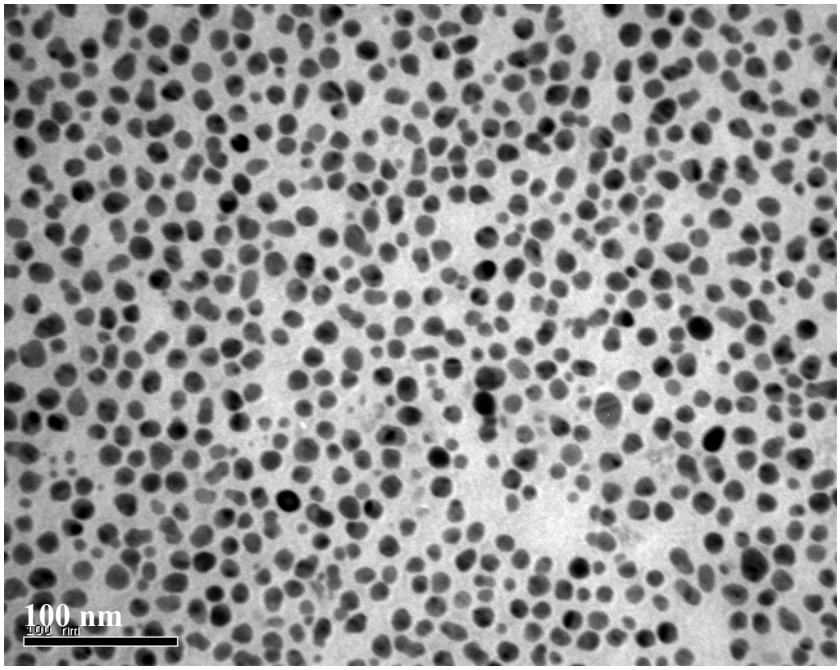

Figure S7. TEM image of 16 nm Ag_3PO_4 NCs synthesized by adding 10 g water to the H_3PO_4 solution

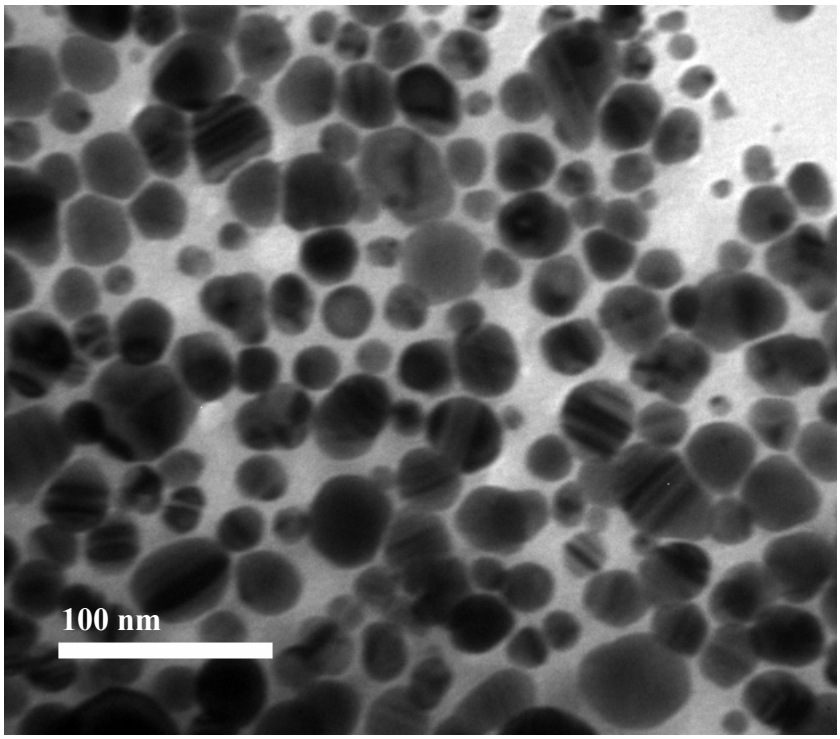

Figure S8. TEM image of Ag_3PO_4 NCs synthesized by adding 20 g water to the H_3PO_4 solution.

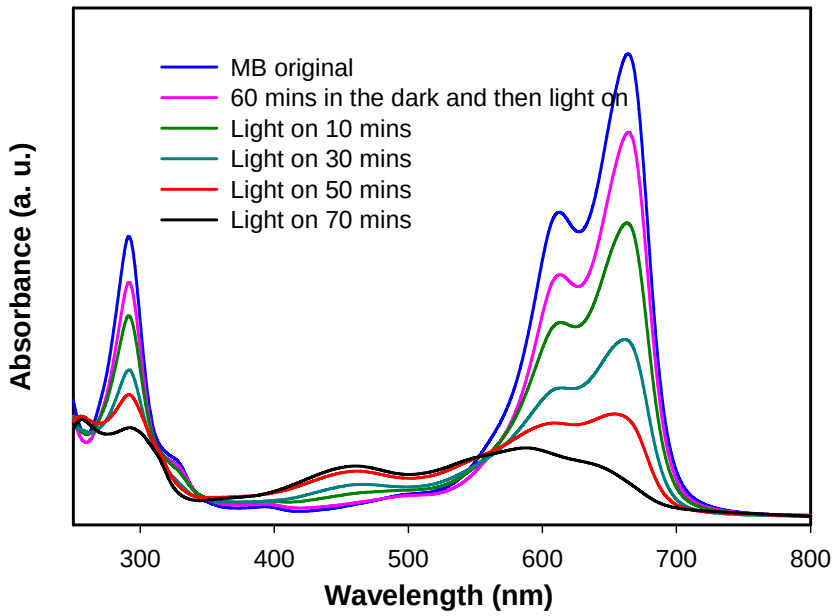

Figure S9. UV-vis absorption spectra of MB solution separated from catalyst suspensions during illumination using Ag_3PO_4 NCs photocatalysts

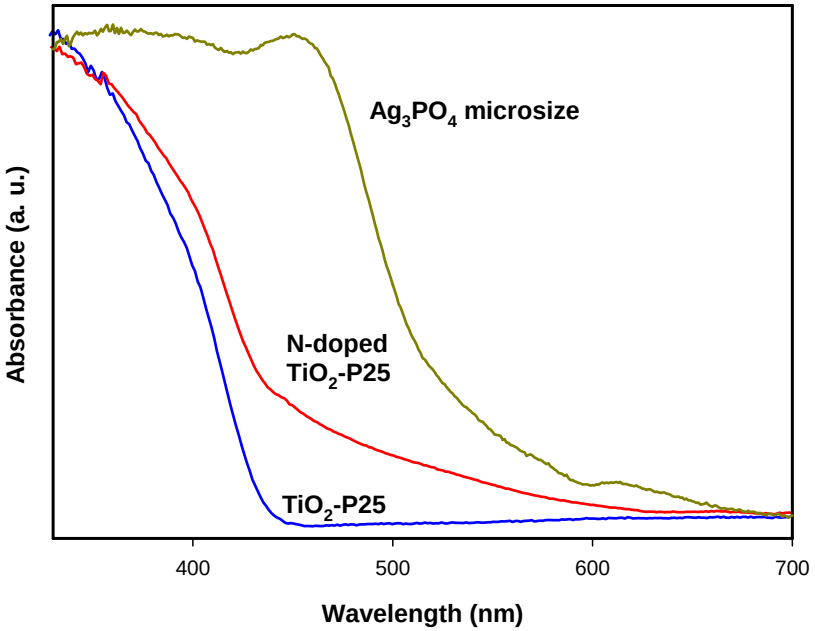

Figure S10. UV vis spectra of TiO_2-P25, N-doped TiO_2-P25 and Ag_3PO_4 microsized used for photocatalytic tests.

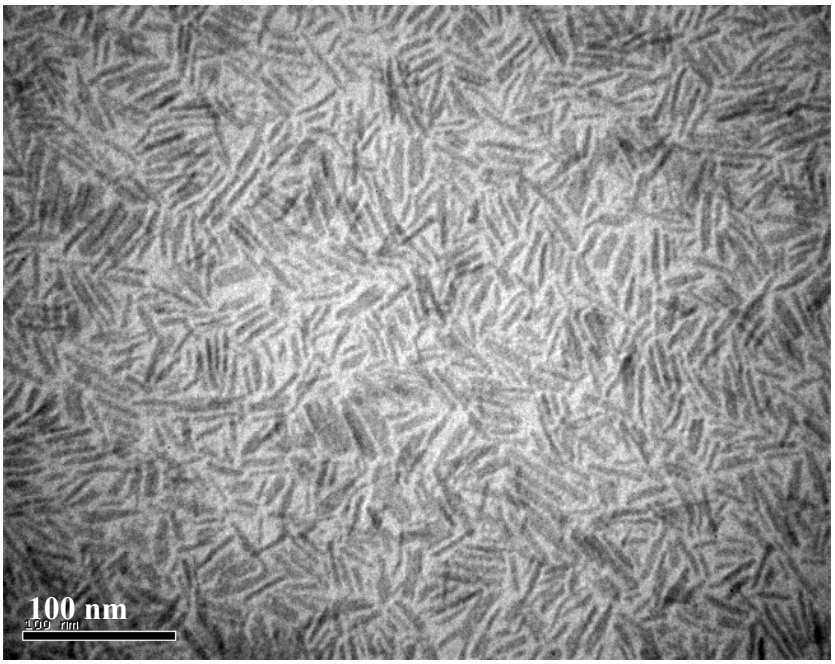

Figure S11. TEM image of $Ca_3(PO_4)_2$ nanorods obtained by simultaneous reactions of phosphoric H_3PO_4 with Ca^{2+} ions and OM in toluene at 80 ^oC.

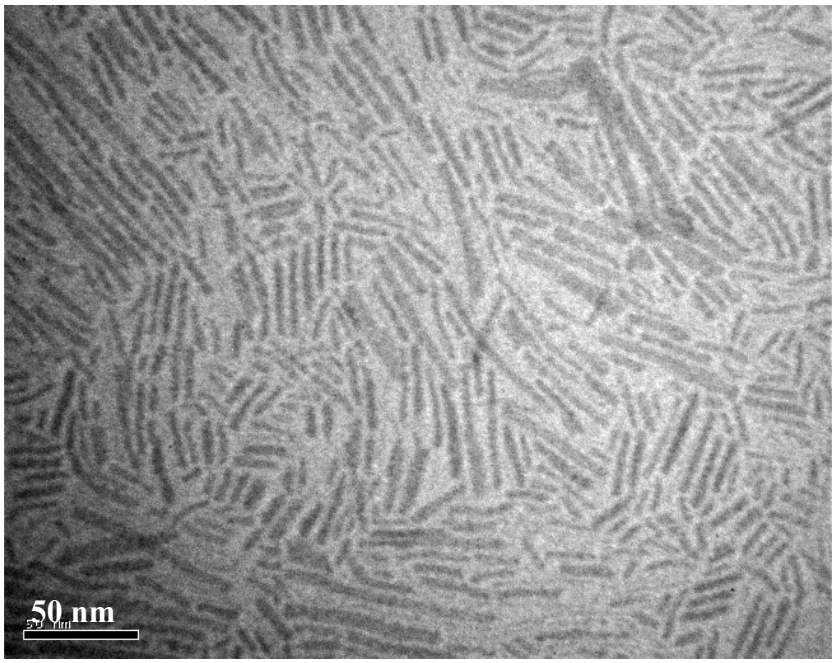

Figure S12. TEM image of $LaPO_4$ nanorods obtained by simultaneous reactions of phosphoric H_3PO_4 with La^{3+} ions and OM in toluene at 80 ^oC.

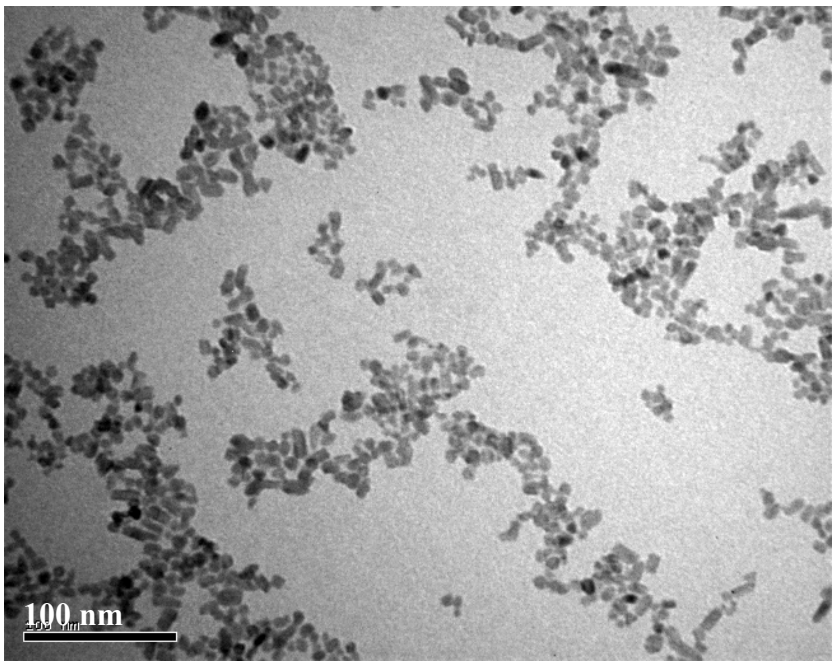

Figure S13. TEM image of $CePO_4$ nanorods obtained by simultaneous reactions of phosphoric H_3PO_4 with Ce^{3+} ions a