Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Thin Silica Shell on Ag_3PO_4 Nanoparticles Augments Stability and Photocatalytic Reusability

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1.0 Experimental Details

All chemicals and reagents were purchased from sigma Aldrich, Merck, Nice chemicals, Isochem and were used as received without any further purification. All the glasswares were used after washed and cleaned with distilled water.

1.1 Instrumentation

UV-Vis experiments were conducted on T90+ UV-VIS Spectrophotometer. P-XRD patterns were acquired using PANALYTICAL,Aeris Research, Cu Kαas the source. Solid-state absorption spectra are recorded on Ocean optics Maya 2000 Pro-UV Compact Spectrometer which is taken by coating the photocatalyst on a glass surface and dried at 100^0C for 1 hr. $BaSO_4$ is used as reflectance standard. High resolution- TEM analysis recorded on FEI-TECNAI-G2 F30.S-TWIN-TEM 300 kV in which sample is well sonicated and taken on a carbon coated Cu grid. Chemical composition of the prepared photocatalyst by X-ray Photoelectron spectroscopywhich is carried out in Omicron nanotechnology Ltd, Germany. Total organic carbon (TOC) analysis carried out by Analytica Jena, multiN/C 3100 instrument. Electrochemical studies (Cyclic Voltammetry) were carried out by CH Instruments Electrochemical Analysis.

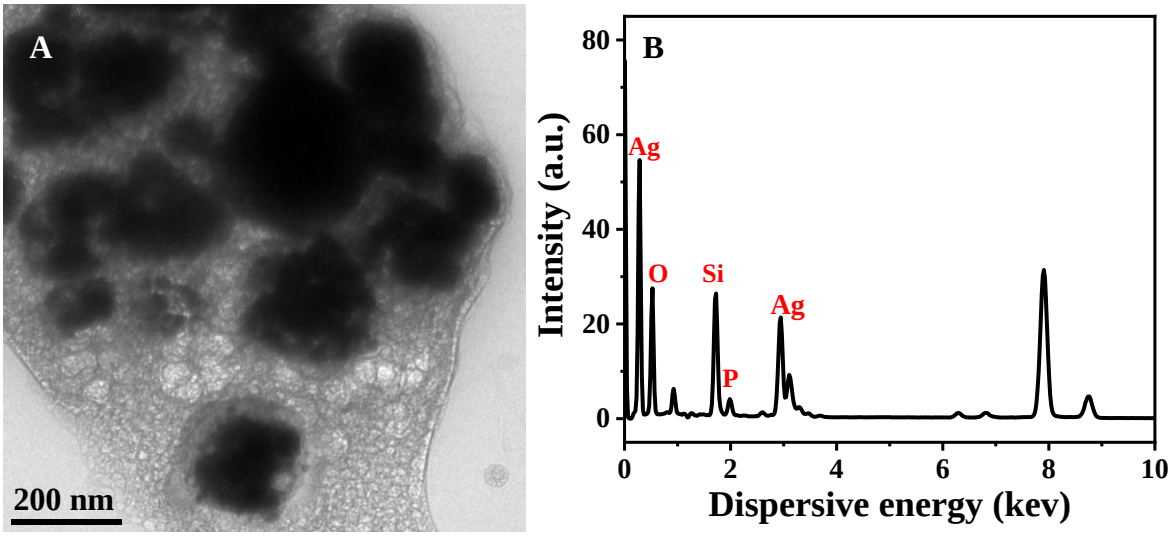


Figure S1. (A) HR-TEM image of $Ag_3PO_4@SiO_2$**. (B)** EDX spectra of $Ag_3PO_4@SiO_2$

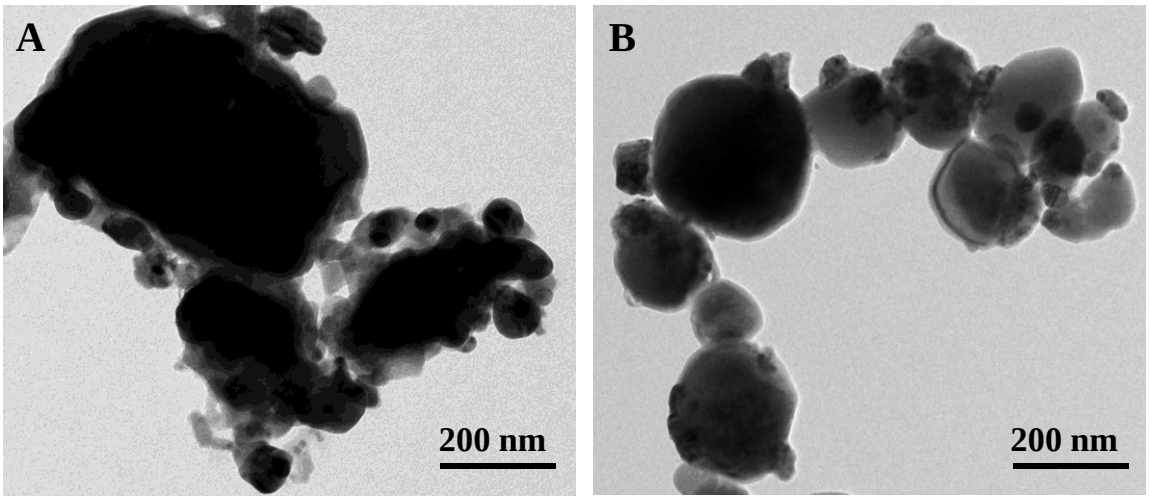


Fig S2- TEM images of **A)** Bare Ag_3PO_4 and **B)** $Ag_3PO_4@SiO_2$ after photocatalytic degradation.

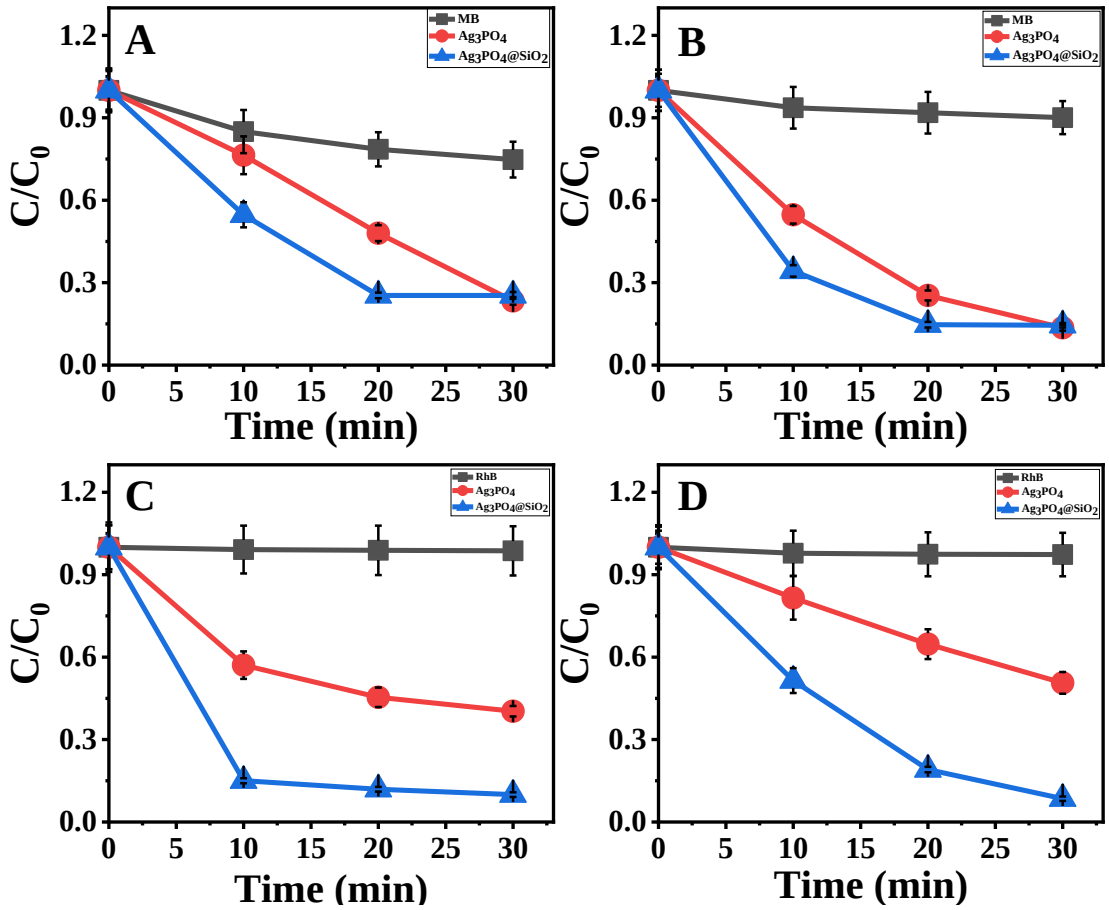


Fig S3- Photocatalytic degradation of methylene blue alone, with bare Ag_3PO_4 , and $Ag_3PO_4@SiO_2$.**A)** under 365 nm light **B)** under 450 nm light. Photocatalytic degradation of Rhodamine B alone , with bare Ag_3PO_4 and $Ag_3PO_4@SiO_2$. **C)** under 365 nm light **D)** under 450 nm light.

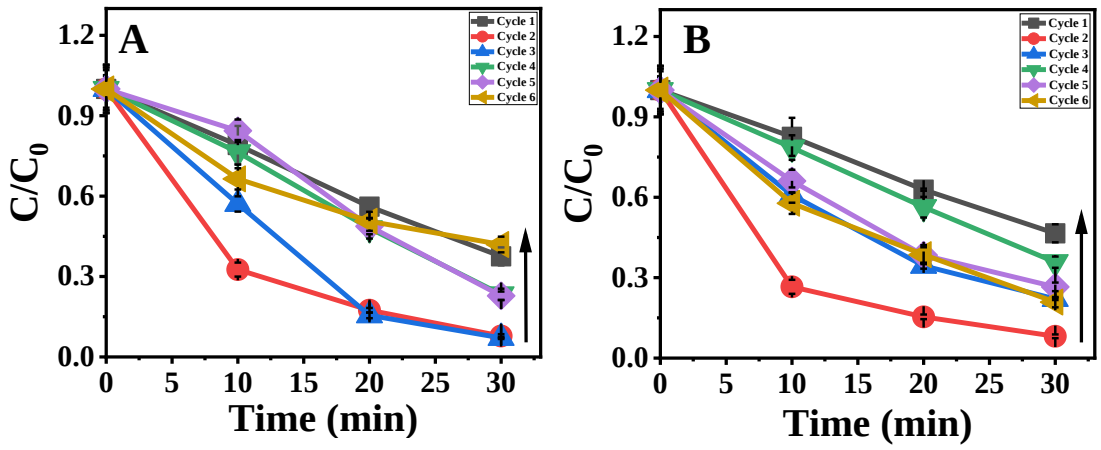


Fig S4. Photocatalytic degradation of methylene blue (MB) (**A)** Bare Ag_3PO_4 and **(B)** $Ag_3PO_4@SiO_2$ under 365 nm light having power of 125 W.

2. Photophysical studies

1.6 x 10^{-5}M of methylene blue and Rhodamine B solutions were prepared in water.0.86 mg of catalyst were added to the solution. All the photophysical experiments were carried out at room temperature in a glass cuvette having a path length of 1 cm.Absorption spectra were recorded on T90+ UV-VIS Spectrophotometer. The solution is magnetically stirred for 30 minutes under dark for establishing adsorption-desorption equilibrium.

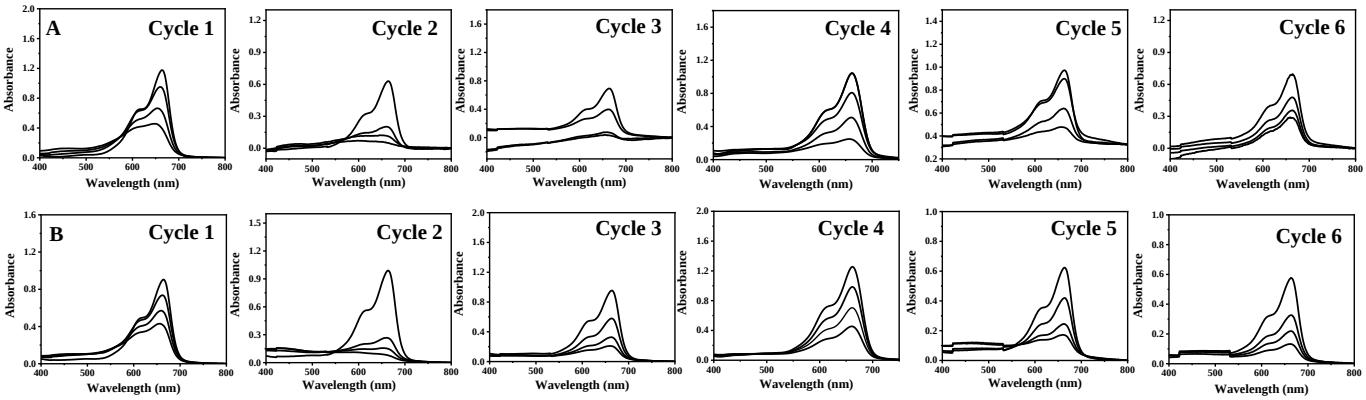
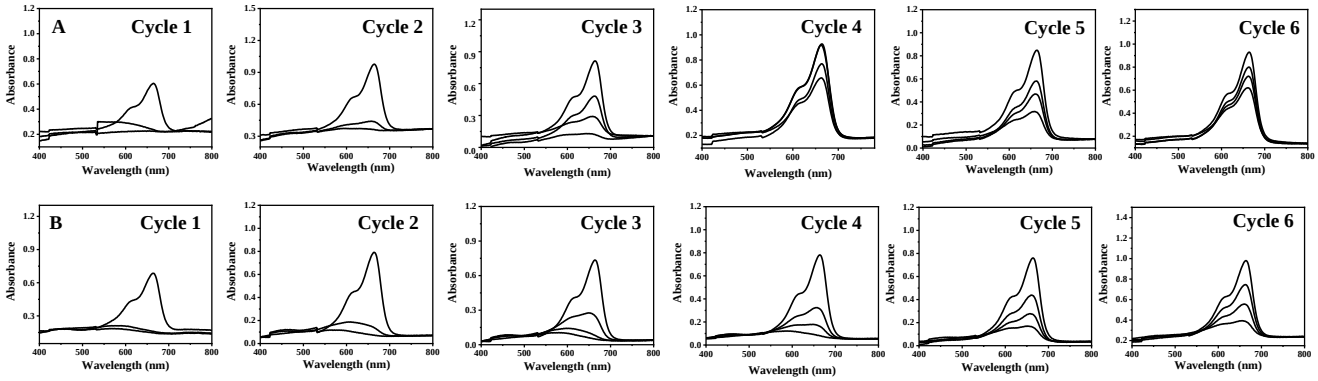


Fig S5. UV-Vis absorption spectra of Methylene blue under 365 nm light **A)** Ag_3PO_4**B)** $Ag_3PO_4@SiO_2$



FigS6. A) UV-Vis absorbance spectra of MB dye under 450 nm light of bare Ag_3PO_4**B)** $Ag_3PO_4@SiO_2$

Table 1- Total organic carbon analysis (TOC)

Initial concentration (mgL^{-1})		Percentage of mineralization after photodegradation (%)
4.38	Ag_3PO_4	92 %
	$Ag_3PO_4@SiO_2$	92 %

Table 2. Photodegradation efficiency of Ag_3PO_4 and $Ag_3PO_4@SiO_2$ in methylene blue and Rhodamine B under 450 nm light.

Methylene blue degradation efficiency (%)						
	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5	Cycle 6
Ag_3PO_4	92%	98%	96%	75%	51%	49%
$Ag_3PO_4@SiO_2$	92%	91%	91%	94%	96%	85%
Rhodamine B degradation efficiency (%)						
Ag_3PO_4	82%	73%	61%	50%	20%	11%
$Ag_3PO_4@SiO_2$	98%	98%	98%	92%	58%	47%

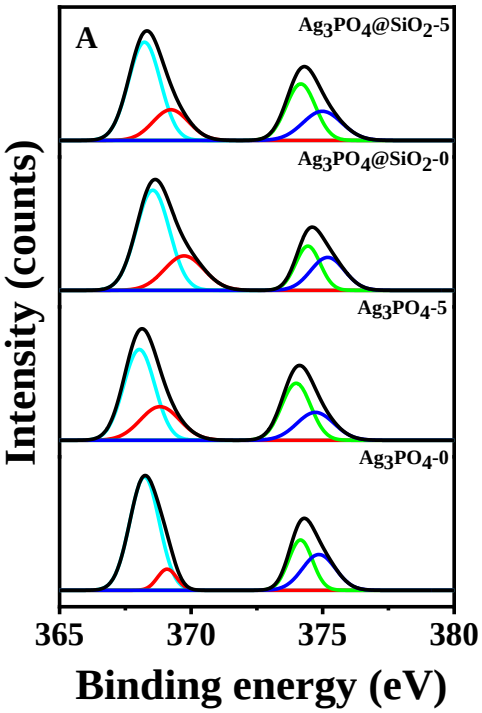


Fig S7 –A) XPS analysis of Ag_3PO_4 and $Ag_3PO_4@SiO_2$ before and after 5 cycles of photodegradation. Deconvoluted spectra of Ag $3d_{5/2}$ and Ag $3d_{3/2}$ peaks of Ag^+ and Ag^0 in the bare Ag_3PO_4-0 and Ag3PO4@SiO2-0 (before photodegradation), Ag_3PO_4-5 and $Ag_3PO_4@SiO_2$-5 (5 cycles of photodegradation).

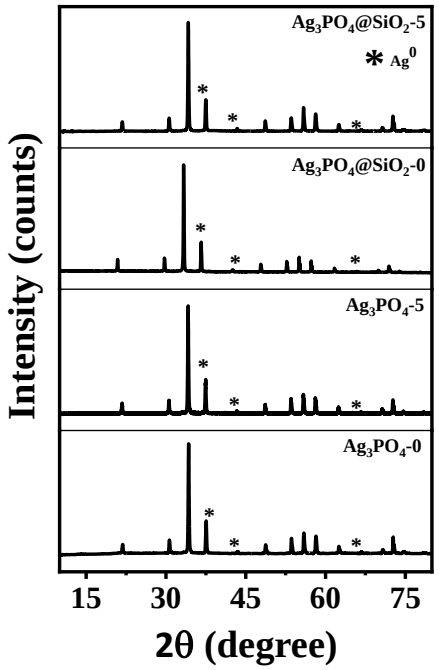


Fig S8- XRD patters of Ag_3PO_4 and $Ag_3PO_4@SiO_2$ before (Ag_3PO_4-0 and $Ag_3PO_4@SiO_2$-0) and after 5 cycles of photodegradation (Ag_3PO_4-5 and $Ag_3PO_4@SiO_2$-5). The peaks corresponding to Ag^0 is marked.

Kinetic Data

Table 3- Kinetic data of of Ag_3PO_4 and $Ag_3PO_4@SiO_2$ under 450 nm light in methylene blue.

450 nm Xenon lamp (MB)			
No. of Cycles		Slope (min^{-1})	R^2
Cycle 1	$Ag_3PO_4@SiO_2$	-0.0549 ±0.0016	0.9992
	Ag_3PO_4	-0.0651 ± 0.0088	0.9822
Cycle 2	$Ag_3PO_4@SiO_2$	-0.0595±0.0130	0.9077
	Ag_3PO_4	-0.0805 ± 0.0036	0.9980
Cycle 3	$Ag_3PO_4@SiO_2$	-0.0416 ±0.0028	0.9955
	Ag_3PO_4	-0.0380 ± 0.0048	0.9686
Cycle 4	$Ag_3PO_4@SiO_2$	-0.0392 ±0.0010	0.9976
	Ag_3PO_4	$-0.0101 \pm 2.6442*10^{-4}$	0.9986
Cycle 5	$Ag_3PO_4@SiO_2$	-0.0263 ±0.0010	0.9939
	Ag_3PO_4	-0.0102 ± 0.0018	0.9426
Cycle 6	$Ag_3PO_4@SiO_2$	-0.0228±0.0020	0.9747
	Ag_3PO_4	$-0.0071 \pm 5.3023*10^{-4}$	0.9889

Table 4. Kinetic data of of Ag_3PO_4 and $Ag_3PO_4@SiO_2$ under 450 nm light in Rhodamine B.

450 nm Xenon lamp (Rhodamine B)			
No. of Cycles		Slope (min^{-1})	R^2
Cycle 1	$Ag_3PO_4@SiO_2$	-0.0374±0.0172	0.8253
	Ag_3PO_4	-0.0212 ±0.0000	0.9930
Cycle 2	$Ag_3PO_4@SiO_2$		0.9539

		-0.0413±0.0091	
	Ag_3PO_4	-0.0238± 9.685	0.9967
Cycle 3	$Ag_3PO_4@SiO_2$	-0.0391±0.0064	0.9738
	Ag_3PO_4	-0.0194± 8.9489 $*10^{-4}$	0.9979
Cycle 4	$Ag_3PO_4@SiO_2$	-0.0343±0.0039	0.9869
	Ag_3PO_4	-0.0145 ± 6.0497	0.9965
Cycle 5	$Ag_3PO_4@SiO_2$	-0.0204 ±0.0035	0.9720
	Ag_3PO_4	-0.0058 ± 2.0297	0.9976
Cycle 6	$Ag_3PO_4@SiO_2$	-0.0145± 0.0021	0.9794
	Ag_3PO_4	0.0029 ± 1.0344	0.9976

3. Electrochemical studies

Cyclic voltammetry is a three-electrode system. The prepared Ag_3PO_4/SiO_2 which is coated on a glass plate sandwiched with FTO plate was employed as working electrode. A platinum electrode and Ag/AgCl electrode was used as counter electrode and reference electrode respectively. 0.1M of tetra butyl ammonium hexafluorophosphate in 10 ml acetonitrile is used as electrolyte. The cyclic voltammogramm is measured between -1V to +1V at a scanrates of 0.1 V/Sec and 0.05V/Sec. All Cyclic voltammograms were taken after degassing the electrolyte with N_2 gas. All electrochemical experiments were carried out at room temperature.

Modification of working electrode

Synthesized $Ag_3PO_4@SiO_2$ is dispersed in THF. spin coated on a glass plate of width 1 cmand length 3 cm at 300 rpm. A thin layer of $Ag_3PO_4@SiO_2$ was coated on the glass plate. Spin coated glass plate was dried in hot over at 100o C for 30 minutes. FTO of 1cm width and 5 cm length is washed in acetone and dried. $Ag_3PO_4@SiO_2$ coated glass plate is sandwiched with the conducting side of FTO plate and tied with a Teflon tape.

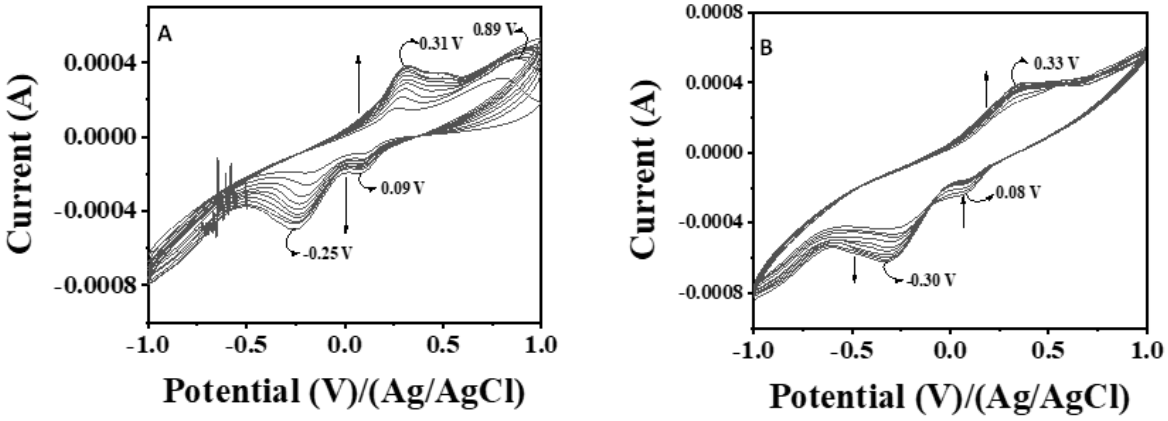
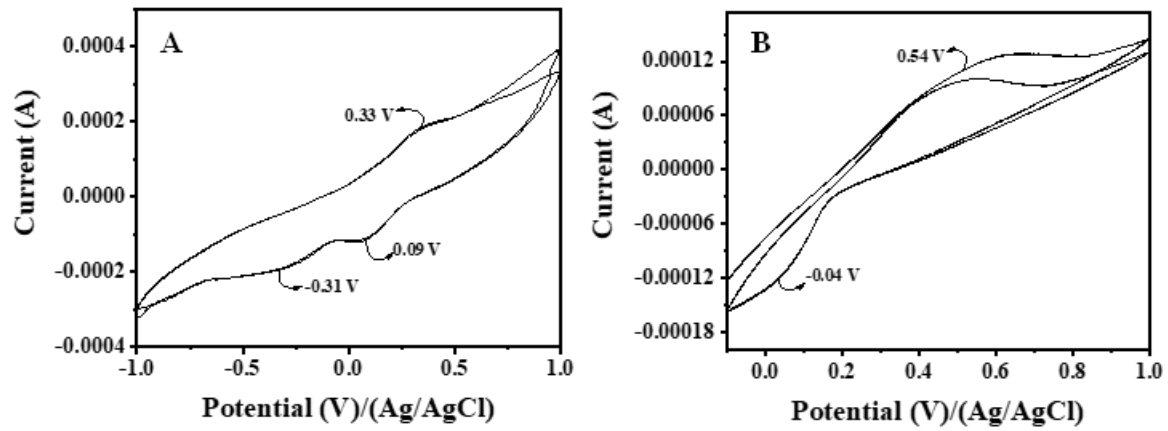


Fig S9. Cyclic voltammogram of $Ag_3PO_4@SiO_2$. **A-** scan rate of 0.05 V/sec,**B-** scan rate of 0.1 V/sec.



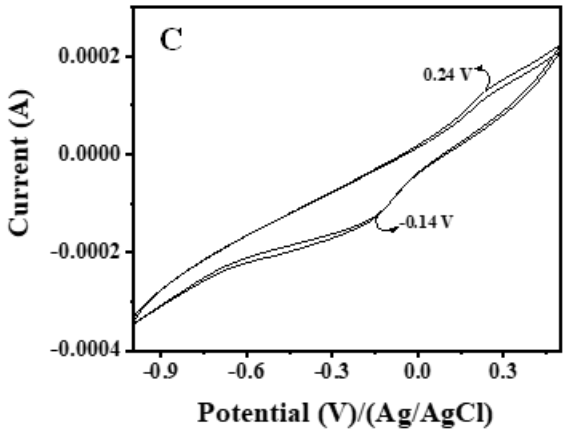


Fig S10.A- $Ag_3PO_4@SiO_2$ in the absence of light under same conditions. **B**-Voltammogram of $Ag_3PO_4@SiO_2$ between potential -0.1 V and +1 V. **C**- Voltammogram of $Ag_3PO_4@SiO_2$ between potential between -1 V to +0.5 V.

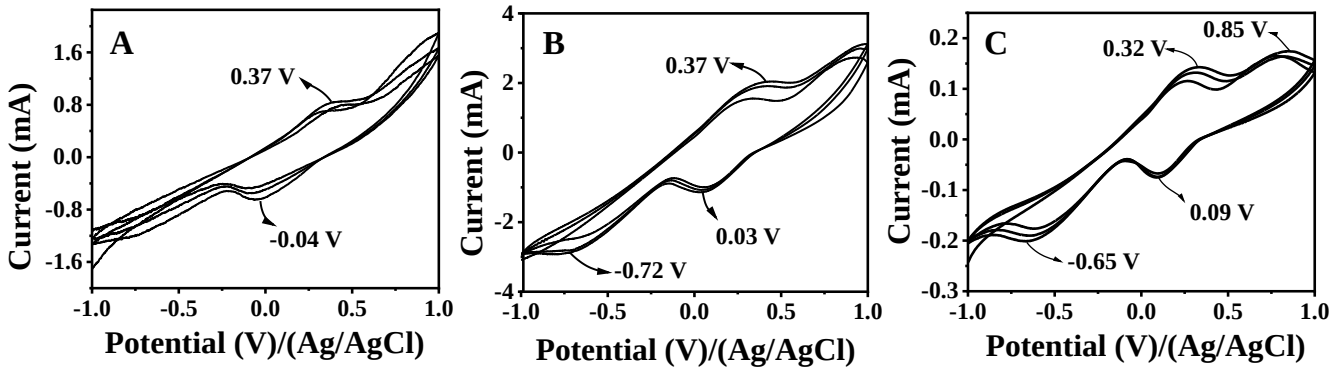


Fig S11. Voltammogram of $Ag_3PO_4@SiO_2$ in the presence of light and water at a scan rate of 0.1 V/sec**A)** 0 min **B)**15 min **C)**30 min

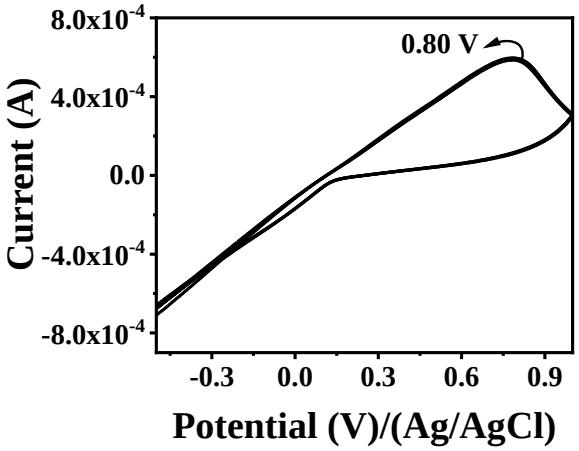


Fig S12. Voltammogram of bare Ag_3PO_4 in presence of light and water at a scan rate of 0.1 V/sec

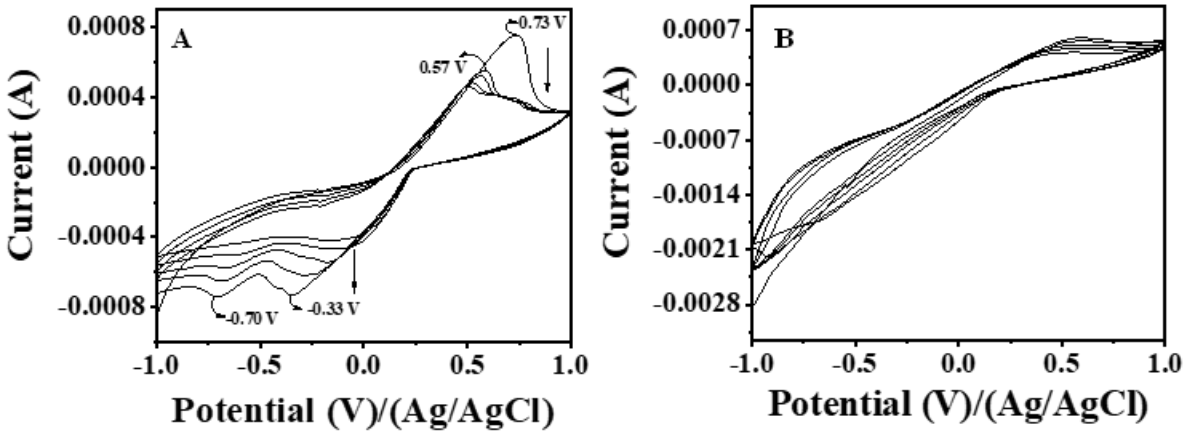


Fig S13. **A-** Addition of 1mM $AgNO_3$ to the electrolyte in the presence of light and water. **B-**Addition of 1mM $AgNO_3$ to the electrolyte in the Absence of light and water.