Supporting Information

Enhanced visible-light-driven photocatalytic activity of Au@Ag core-shell bimetallic nanoparticles immobilized on electrospun TiO_2 nanofibers for degradation of organic compounds

Mrinmoy Misra,[a‖] Narendra Singh,[a,b‖] and Raju Kumar Gupta*[a,b]

[a] Department of Chemical Engineering, Indian Institute of Technology Kanpur, Kanpur-208016, UP, India

[b] Center for Nanosciences and Center for Environmental Science and Engineering, Indian Institute of Technology Kanpur, Kanpur-208016, UP, India

*Corresponding author. Tel: +91-5122596972; Fax: +91-5122590104.
E-mail address: guptark@iitk.ac.in
[‖] Contributed equally.

Synthesis of Ag NPs

In this synthesis method, 100 mL of 5 mM sodium citrate and 0.025 mM tannic acid, aqueous solution was refluxed at 115 °C. After 10 min, 1 mL of 25 mM silver nitrate aqueous solution was added in the mixed solution under the same conditions. The colour of the solution turned to yellow from colourless, indicating the formation of Ag NPs. The refluxing was continued for another 2 min and then the solution was cooled down at room temperature. To remove the unreacted chemicals, the colloidal solution was centrifuged and redispersed into DI water for further use.

Synthesis of Ag@TNF

50 mg of previously prepared MPA functionalized TNF (S2) was dispersed in 10 mL of DI water. To immobilize the Ag NPs on the surface of TNF, 5 mL of the Ag NPs solution was mixed with the MPA functionalized TNF. The prepared Ag@TNF was washed with DI water *via* centrifugation, and the sample was dried in hot air oven at 60 °C overnight. The prepared sample was named as Ag@TNF.

Synthesis of physically mixed Ag, Au@TNF

50 mg of previously prepared MPA functionalized TNF (S2) was dispersed in 10 mL of DI water. 2.5 mL of Ag NPs and 2.5 mL of Au NPs solutions were mixed with MPA functionalized TNF. The prepared sample was washed with DI water *via* centrifugation to remove unreacted chemical, and the sample was dried in hot air oven at 60 °C overnight. The prepared sample was named as Au+Ag@TNF.

Table S1 Absorption peaks of all the samples

Sample name/material	SPR absorption of Au (nm)	SPR absorption of Ag (nm)	Absorption of TNF (nm)	Combined absorption of Ag and TNF (nm)
Au NPs (S1)	522	-	-	-
TNF (S2)		-	327	-
Au@TNF (S3)	~540	329		
Au@Ag NPs (S11)	519	~371	-	-
Au@Ag NPs (S12)	518	~376	-	-
Au@Ag NPs (S13)	514	~390	-	-
Au@Ag@TNF (S4)	~542		-	~330
Au@Ag@TNF (S5)	~542		-	~332
Au@Ag@TNF (S6)	~542		-	~333

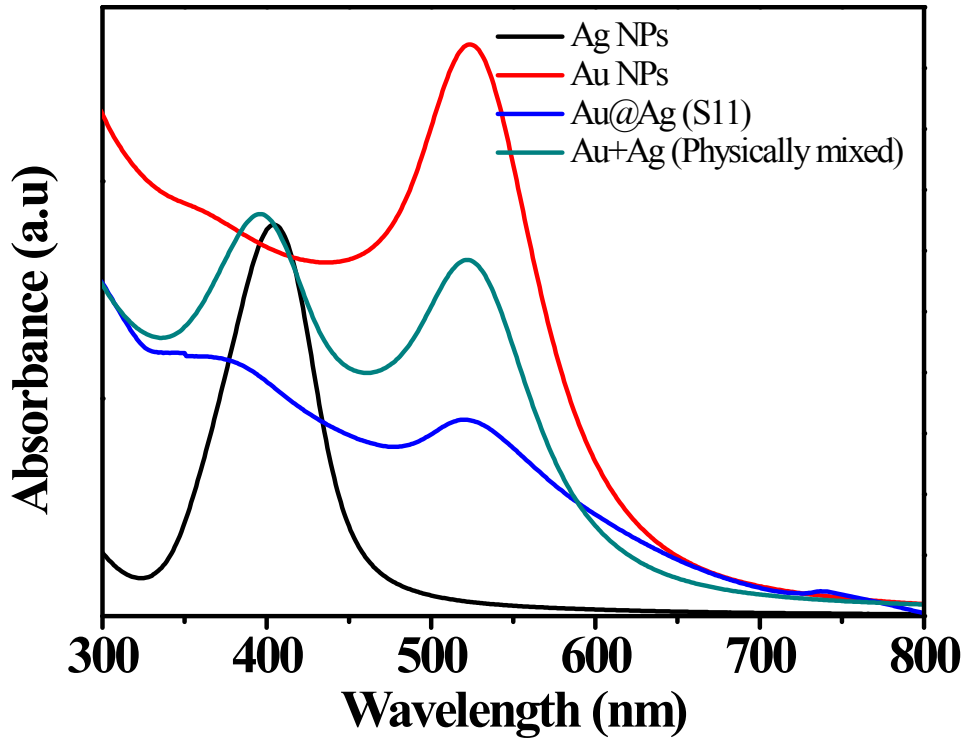

Fig. S1 Optical absorption spectra of Au, Ag, Au@Ag core-shell, Au+Ag (physically mixed) nanostructures.

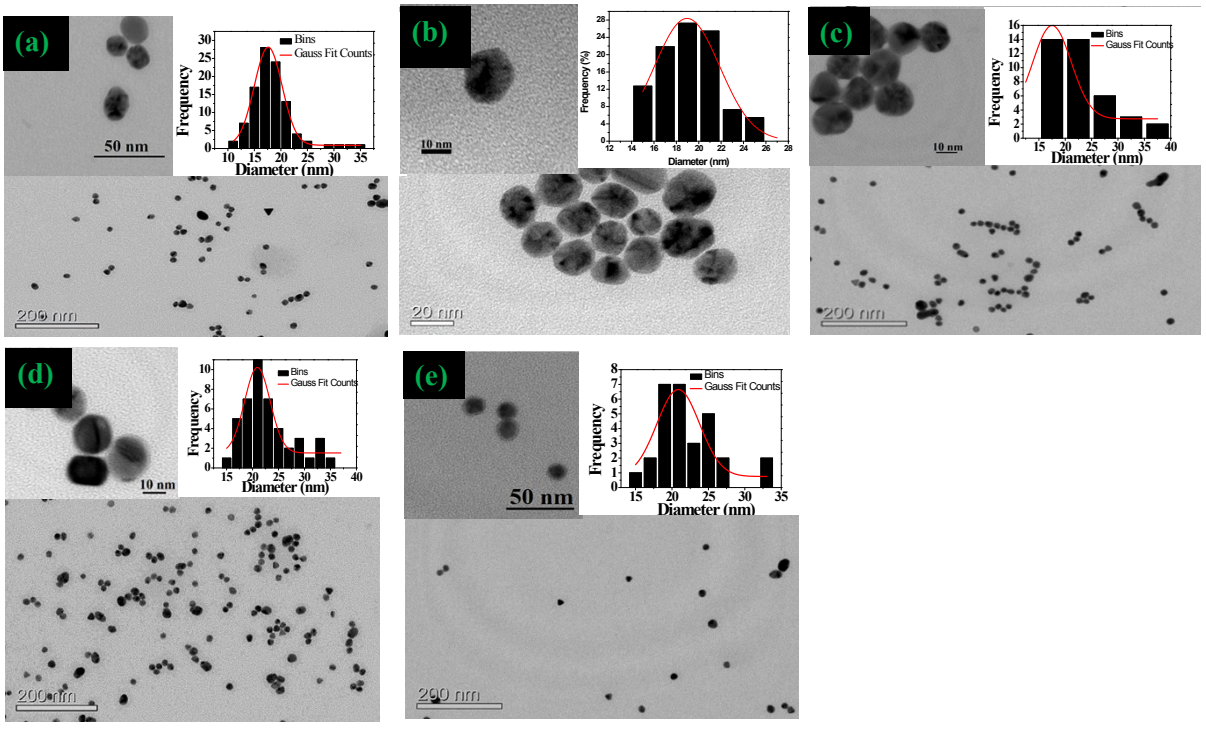

Fig. S2 (a) TEM image of Au NPs (S1), (b) TEM image of Ag NPs, (c) TEM image of Au@Ag (S11), (d) TEM image of Au@Ag (S12) and (e) TEM image of Au@Ag (S13); Inset shows high magnification image and corresponding size distribution of NPs in the sample.

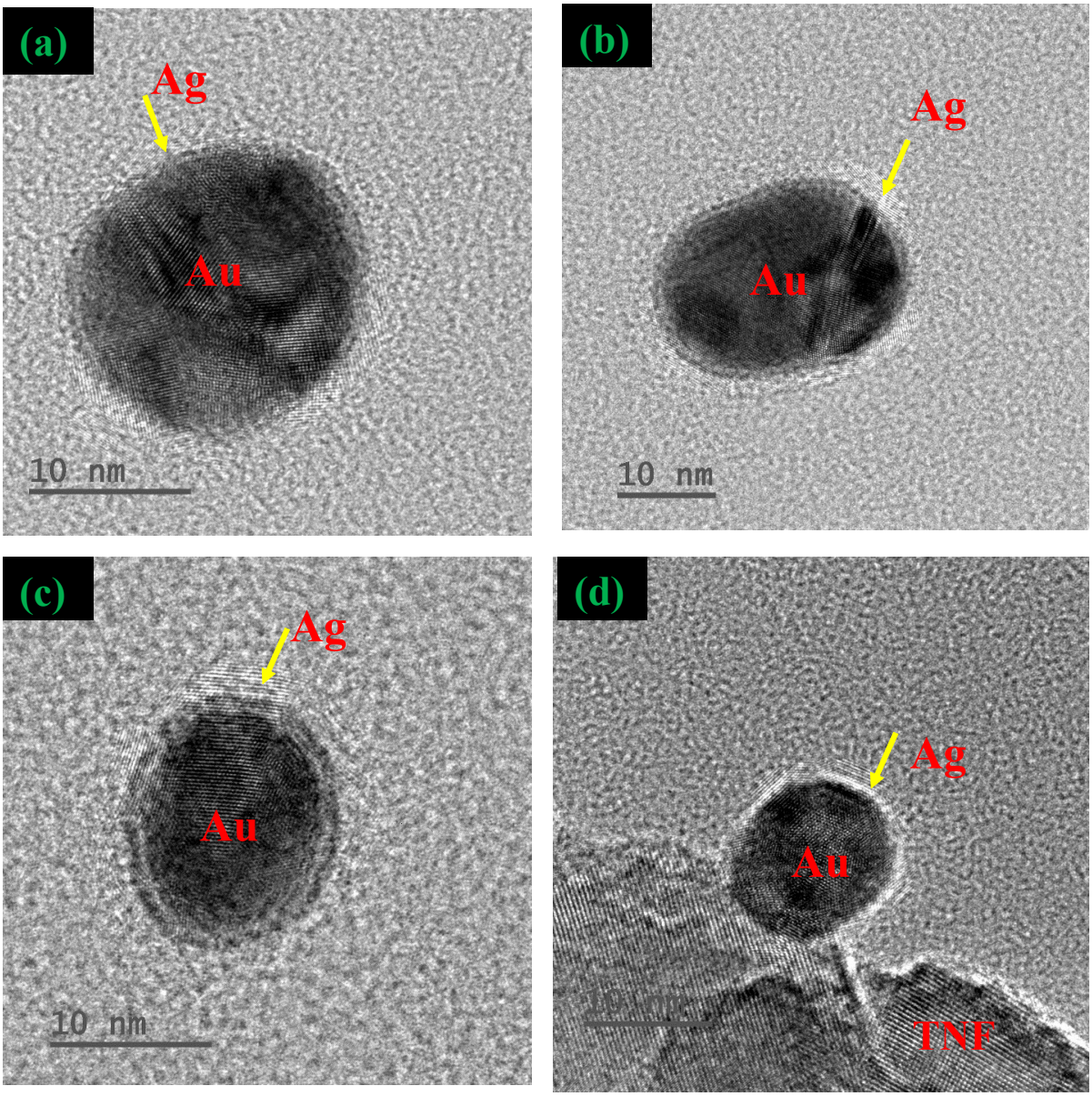

Fig. S3 HRTEM image of (a) Au@Ag (S11), (b) Au@Ag (S12) and (c) Au@Ag (S13), and (d) Au@Ag@TiO_2 (S4).

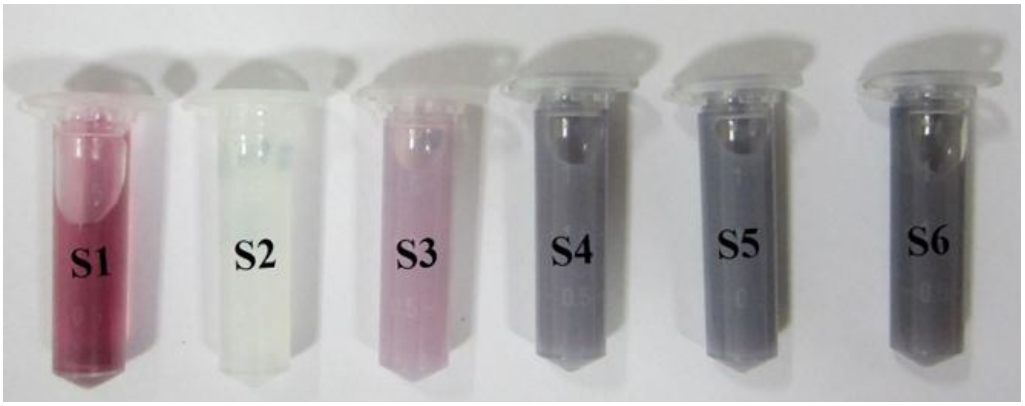

Fig. S4 Photograph of (S1) Au NPs, (S2) TNF, (S3) Au@TNF, (S4) Au@Ag@TNF, (S5) Au@Ag@TNFs and (S6) Au@Ag@TNF solution.

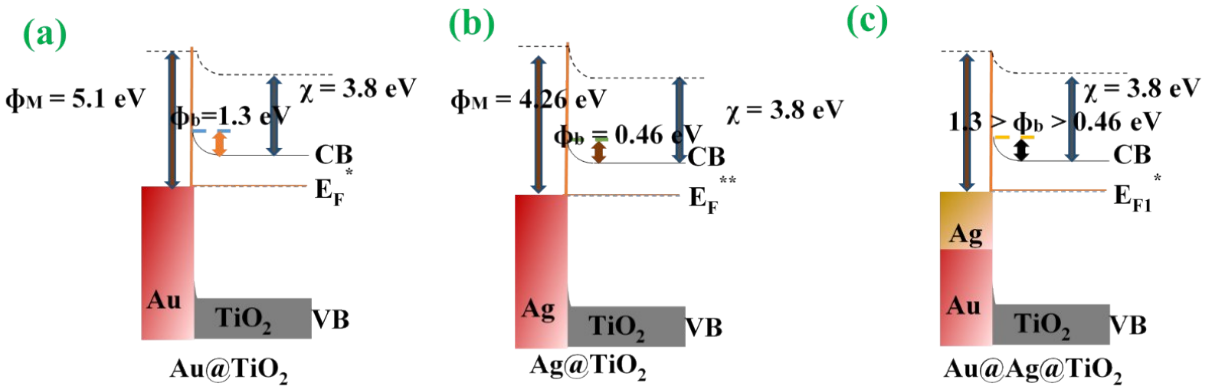

Fig. S5 Schematic energy-band diagrams for (a) Au@TiO_2, (b) Ag@TiO_2, and (c) Au@Ag@TiO_2 nanostructure, where E_{vac}, Φ_M, Φ_b, and χ denote the vacuum level, work function of metal, Schottky barrier height and electron affinity of TiO_2 . Fermi level of TiO_2, Au@TiO_2 and Au@Ag@TiO_2 represent as E_F, E_F^{**} and E_{F1}^{*} respectively (in eV).

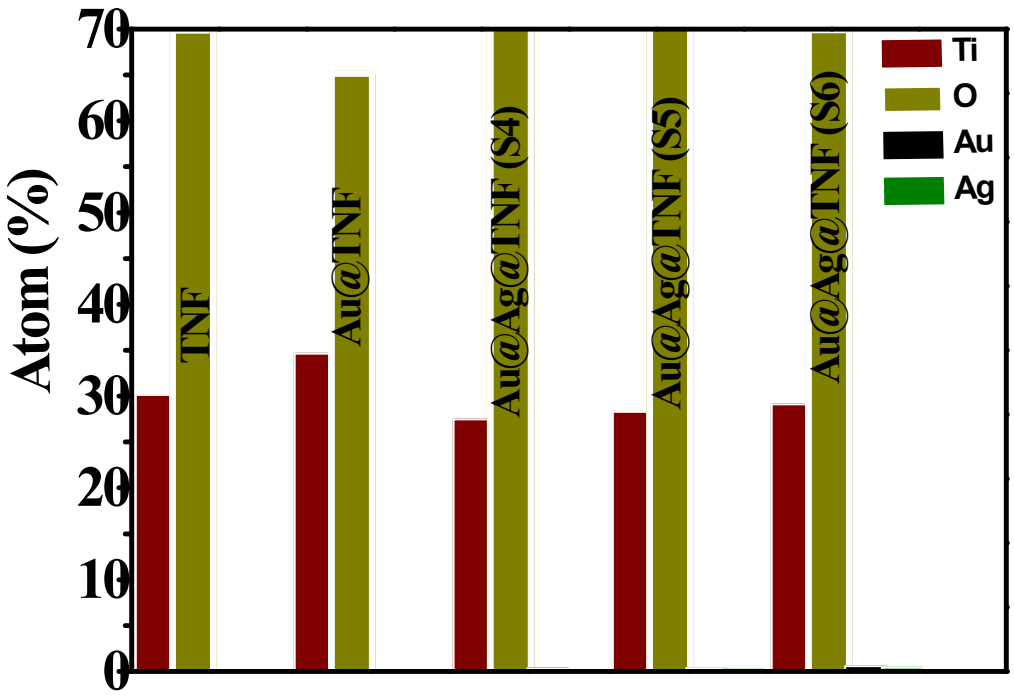

Fig. S6 EDX analysis of different photocatalysts.

Table S2 EDX of TNF, Au@ TNF and Au@Ag@ TNF with different Ag shell thickness on Au core

Sample name	**Ti (Atomic %)**	**O (Atomic %)**	**Au (Atomic %)**	**Ag (Atomic %)**
TNF (S2)	30.11	69.89	-	-
Au@ TNF (S3)	34.64	65.19	0.17	-
Au@Ag@ TNF (S4)	27.46	72.10	0.33	0.10
Au@Ag@ TNF (S5)	28.29	71.14	0.36	0.21
Au@Ag@ TNF (S6)	29.11	69.90	0.57	0.42

Table S3 Photocatalytic rate constants of the MB dye degradation using TNF, Au@ TNF and Au@Ag@ TNF with different Ag shell thickness under UV irradiation.

Sample name	Rate constant (min^{-1})
Au@TNF (S3)	0.0036
Au@Ag@TNF (S4)	0.0047
Au@Ag@TNF (S5)	0.0042
Au@Ag@TNF (S6)	0.0037
TNF(S2)	0.0034

Table S4 Photocatalytic rate constants of the MB dye degradation using TNF, Au@ TNF and Au@Ag@ TNF with different Ag shell thickness under solar light irradiation.

Sample name	Rate constant (min^{-1})
Au@TNF (S3)	0.0130
Au@Ag@TNF (S4)	0.0291
Au@Ag@TNF (S5)	0.0176
Au@Ag@TNF (S6)	0.0129
TNF (S2)	0.0100

Fig. S7 Photographs of MB dye before and after the photocatalytic degradation using Au@Ag@TNF (S4) photocatalyst under solar light irradiation.

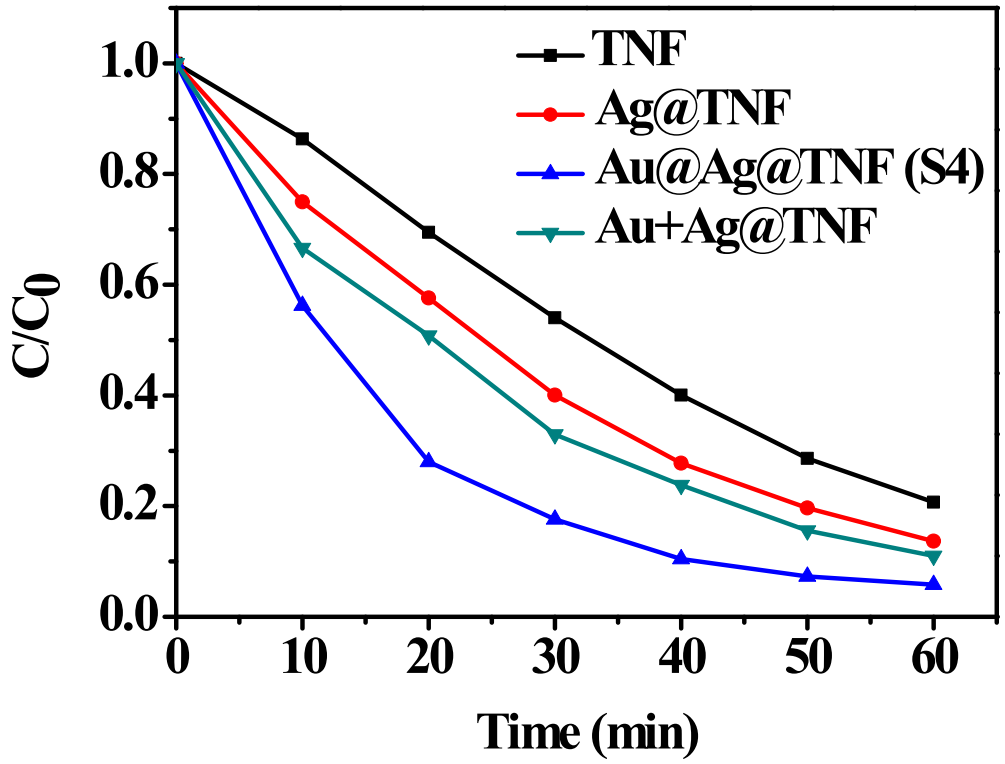

Fig. S8 Kinetics of MB photo-degradation by TNF, Ag@TNF, Au@Ag@TNF (S4) and Au+Ag@TNF under solar light irradiance.

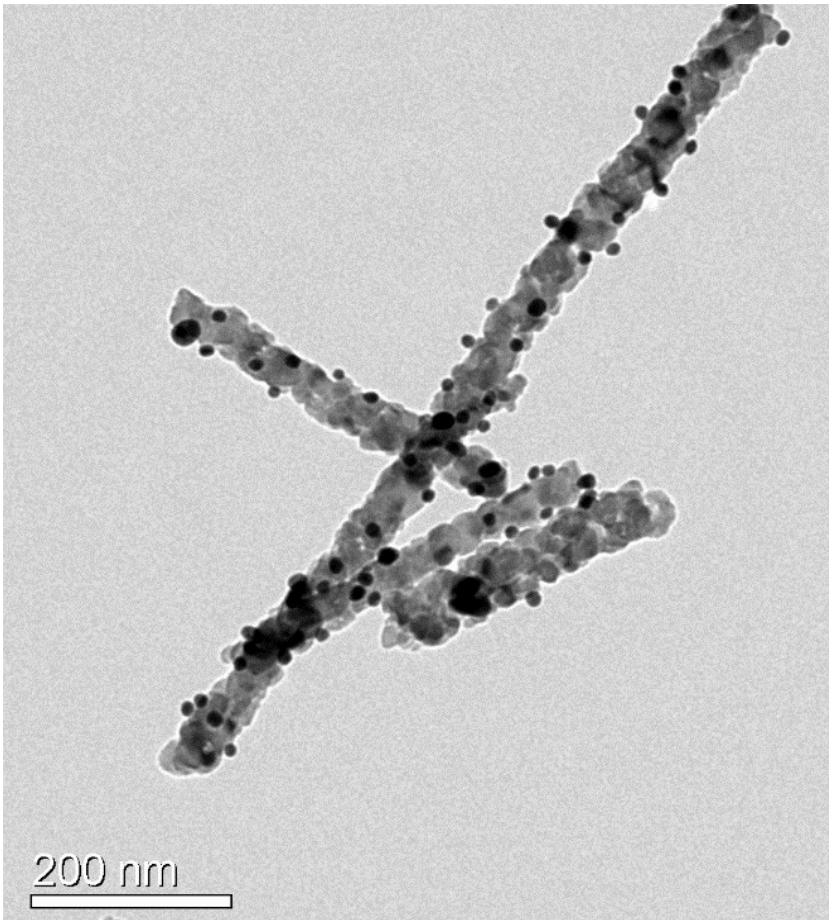

Fig. S9 TEM image of Au@Ag@TNF (S4) photocatalyst after five successive cycles of photocatalytic runs.