Clay Supported Au Nanoparticles Deposited N,S doped TiO_2 for Enhanced Photocatalytic Degradation, Esterification Reactions

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Supporting Information

1. Agitation effect:

To study the effect of different agitations to clay suspension for loading of NPs the DLS size measurement of Kaolinite clay were performed right after the agitation. The samples were studied 20 min after stirring, 5 min sonication followed by stirring and 5 min sonication followed by homogenization. The corresponding D_{avg} of the samples are shown in fig. S1 and it was observed that clay flakes which generally stay stacked get considerably exfoliated when agitated at 10,000 rpm after sonication providing higher surface area for NPs loading.

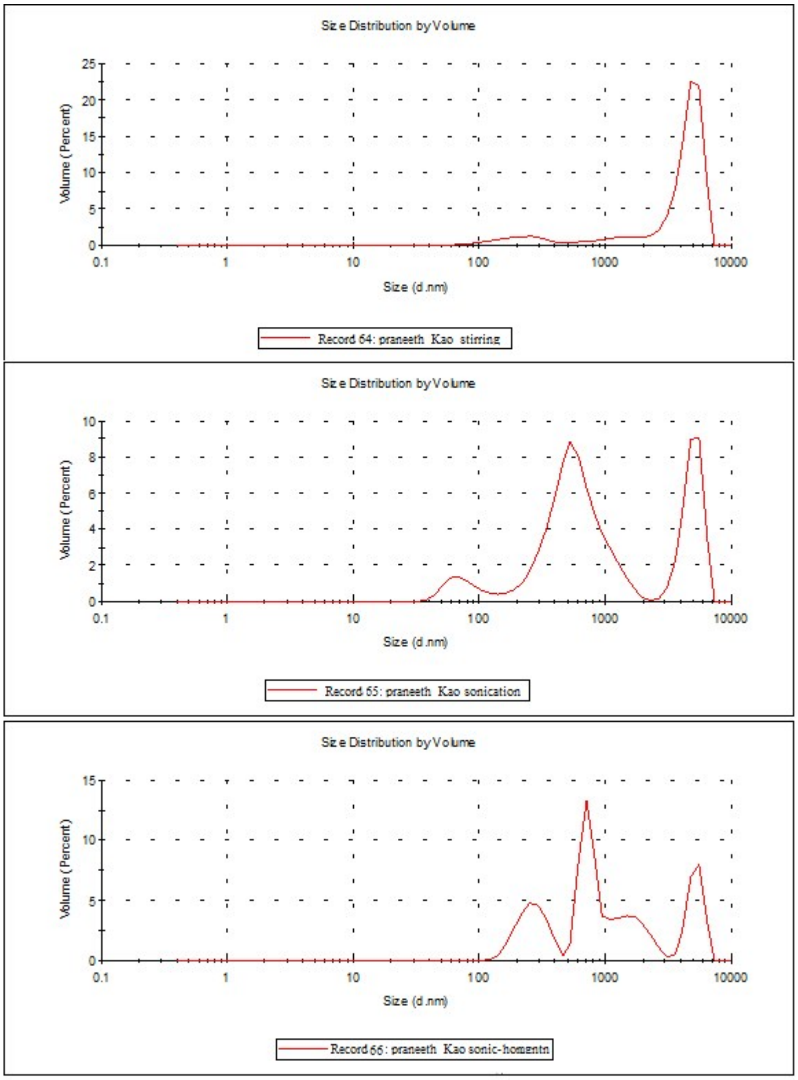
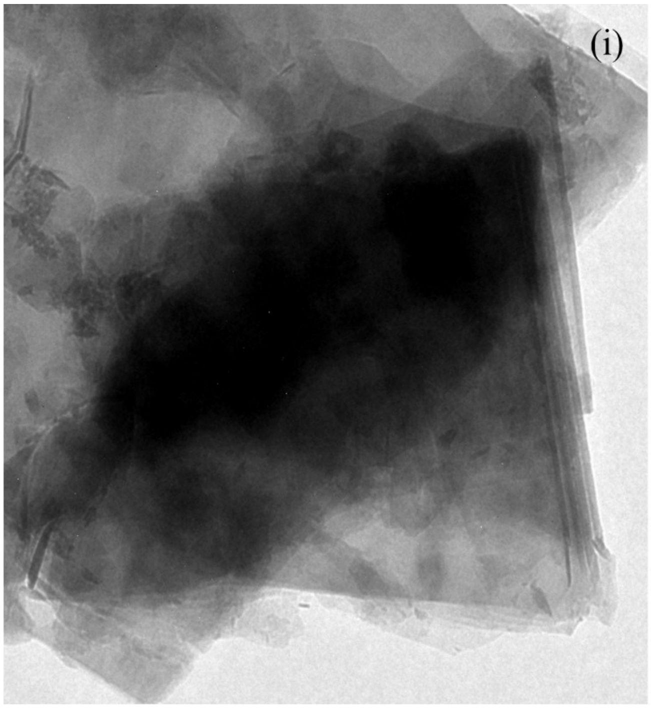
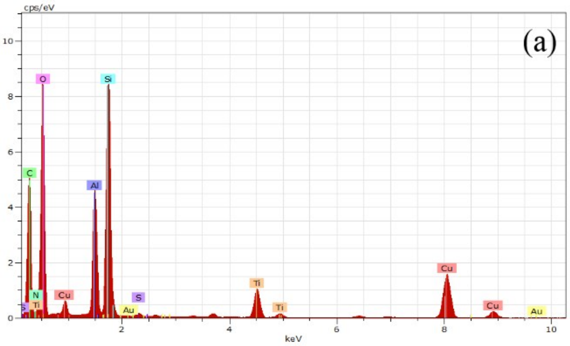


Figure S1. DLS size distribution by volume of clay samples after corresponding agitations.

2. Au NPs loading on Kaolinite clay:

Since it is difficult to anchor deposition of NPs equally on clay surface we have taken 10 individually seen clay particles on TEM as sample for the loading amount study and checked the wt% percentage of NPs on it using EDS as shown in fig S2 and taken an average for the elements in contention.





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Spectrum: 1 spc raw.xls

El AN  Series   unn. C norm. C Atom. C Error (1 Sigma)
                [wt.%]  [wt.%]  [at.%]           [wt.%]
-----------------------------------------------------
O   8  K-series  47.08   47.08   64.26             1.43
Si 14  K-series  30.32   30.32   20.37             0.12
Al 13  K-series  13.20   13.20    9.19             0.50
Ti 22  K-series   8.17    8.17    5.75             0.22
Au 79  L-series   0.76    0.76    0.12             0.05
S  16  K-series   0.47    0.47    0.31             0.04
Cu 29  K-series   0.00    0.00    0.00             0.00
C   6  K-series   0.00    0.00    0.00             0.00
N   7  K-series   0.00    0.00    0.00             0.00
-----------------------------------------------------
         Total: 100.00  100.00  100.00
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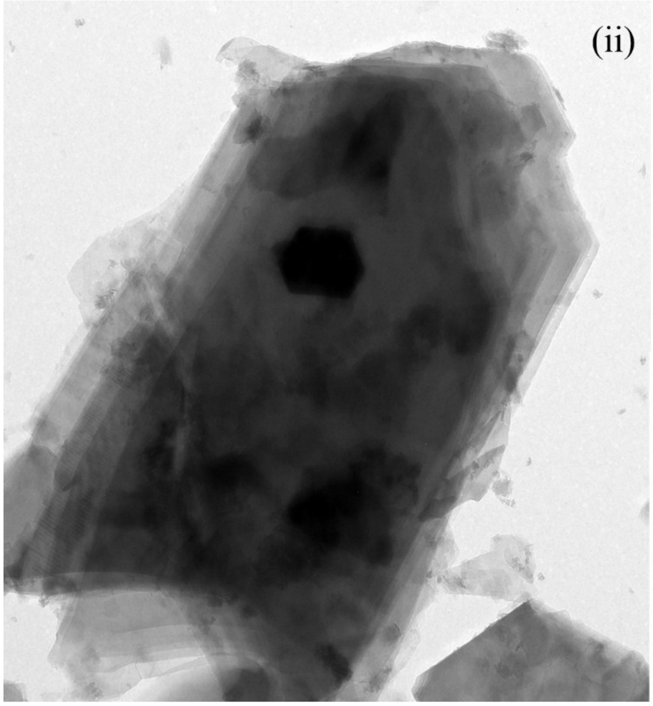

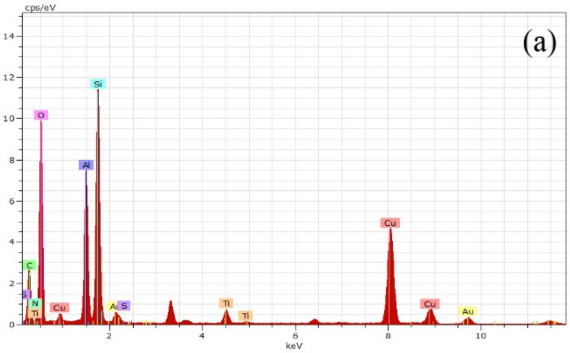

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                [wt.%]  [wt.%]  [at.%]           [wt.%]
-----------------------------------------------------
O   8  K-series  48.35   48.35   58.41             1.13
Si 14  K-series  30.19   30.19   23.37             0.12
Al 13  K-series  11.42   11.42   10.11             0.30
Ti 22  K-series   9.34    9.34    7.81             0.12
S  16  K-series   0.41    0.41    0.31             0.09
Au 79  L-series   0.29    0.29    0.09             0.05
Cu 29  K-series   0.00    0.00    0.00             0.00
C   6  K-series   0.00    0.00    0.00             0.00
N   7  K-series   0.00    0.00    0.00             0.00
-----------------------------------------------------
         Total: 100.00  100.00  100.00
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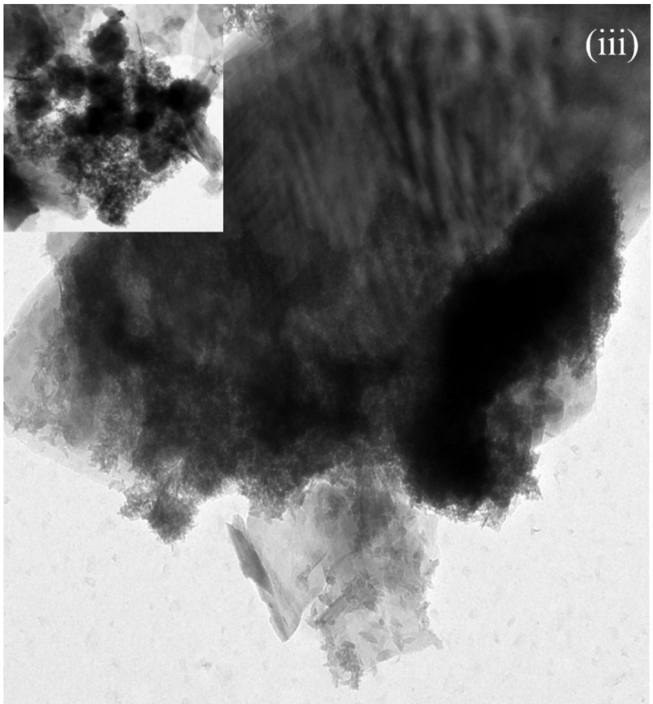

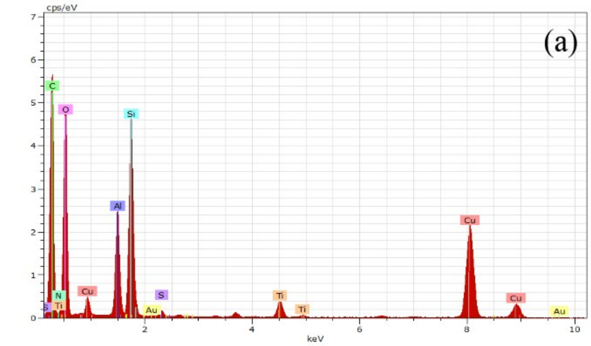

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El AN  Series  unn. C norm. C Atom. C Error (1 Sigma)
               [wt.%]  [wt.%]  [at.%]          [wt.%]
-----------------------------------------------------
O   8  K-series  40.86   40.86   54.16           2.03
Si 14  K-series  32.93   32.93   25.31           0.22
Al 13  K-series  13.76   13.76   10.19           0.60
Ti 22  K-series  11.17   11.17    9.73           0.27
Au 79  L-series   0.91    0.91    0.52           0.05
S  16  K-series   0.37    0.37    0.09           0.44
Cu 29  K-series   0.00    0.00    0.00           0.00
C   6  K-series   0.00    0.00    0.00           0.00
N   7  K-series   0.00    0.00    0.00           0.00
-----------------------------------------------------
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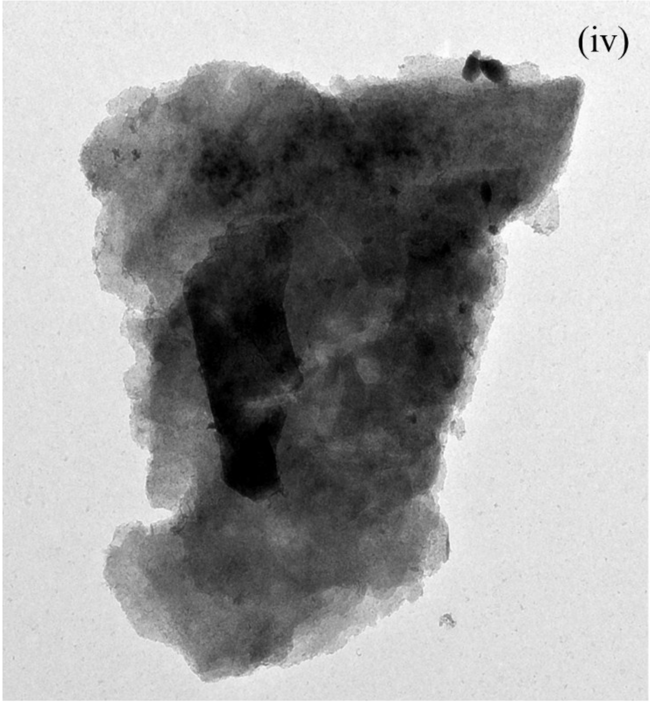

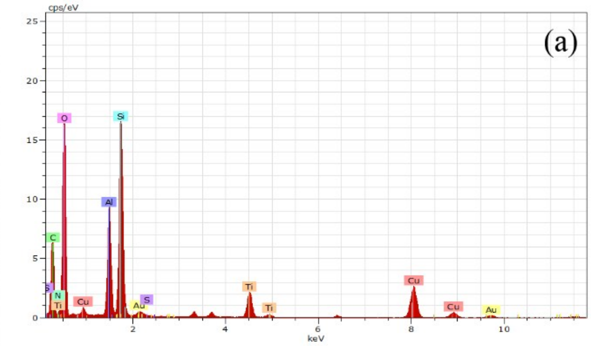

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El AN  Series  unn. C norm. C Atom. C Error (1 Sigma)
               [wt.%]  [wt.%]  [at.%]          [wt.%]
-----------------------------------------------------
O   8  K-series  44.35   44.35   58.36           1.23
Si 14  K-series  27.11   27.11   21.37           0.16
Al 13  K-series  15.32   15.32   12.19           0.50
Ti 22  K-series  12.24   12.24    7.75           0.27
S  16  K-series   0.53    0.53    0.31           0.07
Au 79  L-series   0.45    0.45    0.02           0.01
Cu 29  K-series   0.00    0.00    0.00           0.00
C   6  K-series   0.00    0.00    0.00           0.00
N   7  K-series   0.00    0.00    0.00           0.00
-----------------------------------------------------
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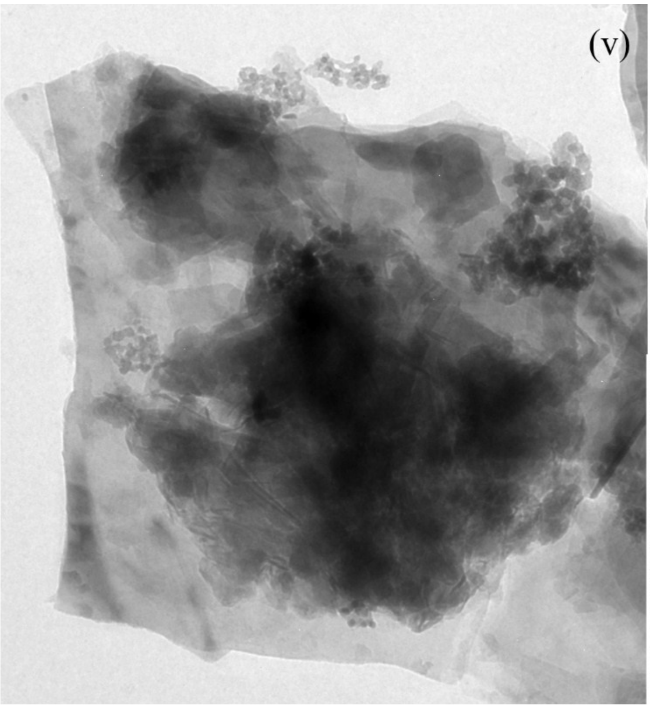

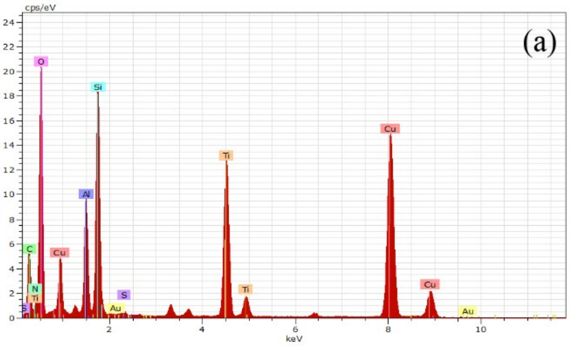

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El AN  Series   unn. C norm. C Atom. C Error (1 Sigma)
                [wt.%]  [wt.%]  [at.%]          [wt.%]
-------------------------------------------------------
O  8  K-series  50.20   50.20   66.36            1.67
Si 14 K-series  26.41   26.41   19.31            0.35
Ti 22 K-series  14.12   14.12    9.29            0.62
Al 13 K-series   8.46    8.46    4.75            0.09
Au 79 L-series   0.42    0.42    0.08            0.01
S  16 K-series   0.39    0.39    0.21            0.04
Cu 29 K-series   0.00    0.00    0.00            0.00
C  6  K-series   0.00    0.00    0.00            0.00
N  7  K-series   0.00    0.00    0.00            0.00
-------------------------------------------------------
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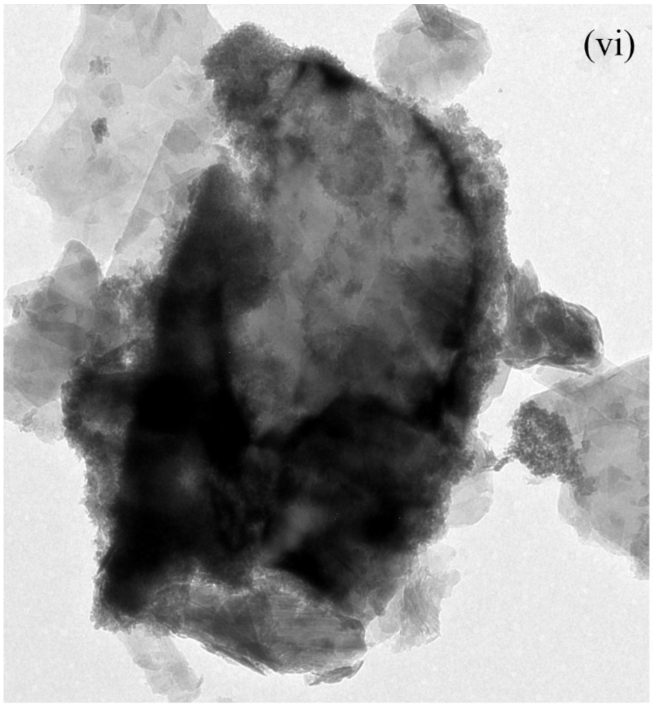

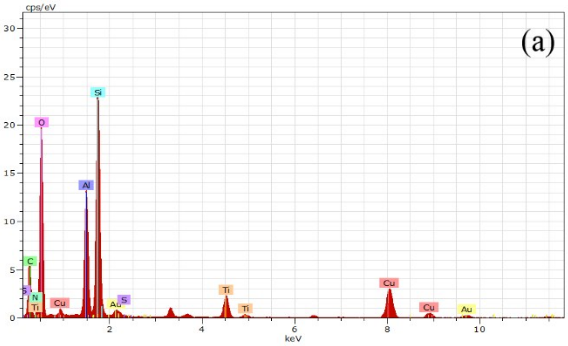

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Spectrum: 6 spc raw.xls

El AN  Series   unn. C norm. C Atom. C Error (1 Sigma)
                [wt.%]  [wt.%]  [at.%]          [wt.%]
-------------------------------------------------------
O  8  K-series  60.22   60.22   73.76            1.20
Si 14 K-series  20.28   20.28   13.37            0.32
Al 13 K-series   9.82    9.82    6.19            0.50
Ti 22 K-series   8.42    8.42    6.05            0.26
Au 79 L-series   0.65    0.65    0.23            0.13
S  16 K-series   0.61    0.61    0.40            0.11
Cu 29 K-series   0.00    0.00    0.00            0.00
C  6  K-series   0.00    0.00    0.00            0.00
N  7  K-series   0.00    0.00    0.00            0.00
-------------------------------------------------------
        Total: 100.00  100.00  100.00
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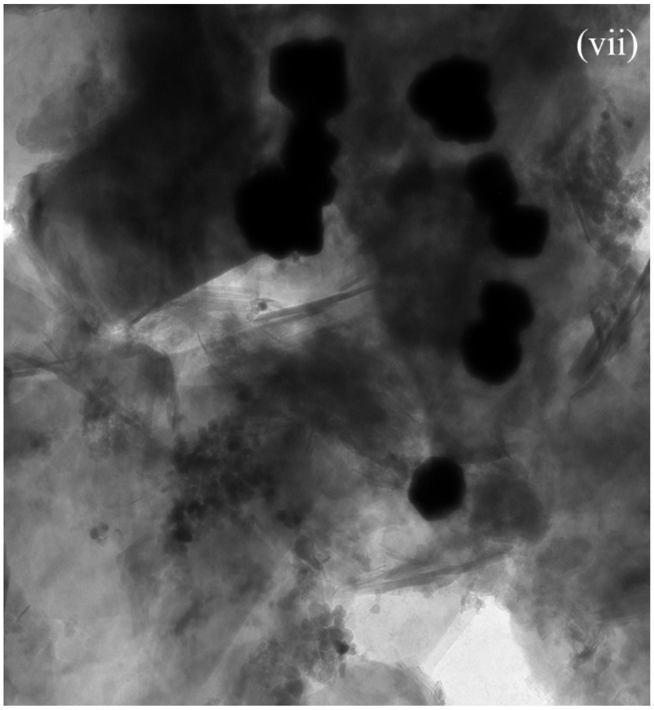

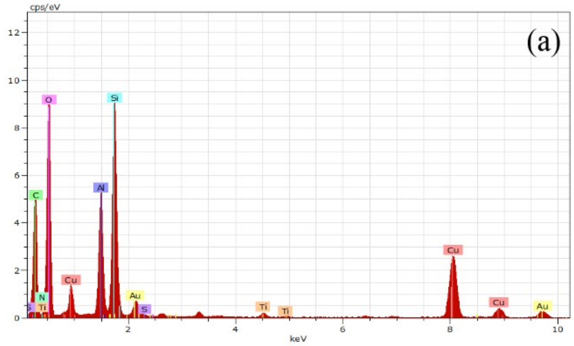

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Spectrum: 7 spc raw.xls

El AN  Series   unn. C norm. C Atom. C Error (1 Sigma)
                [wt.%]  [wt.%]  [at.%]           [wt.%]
-----------------------------------------------------
O  8  K-series  42.73   42.73   56.36             2.03
Si 14 K-series  30.04   30.04   23.37             0.32
Al 13 K-series  13.17   13.17    9.18             0.54
Ti 22 K-series  12.26   12.26   10.05             0.27
Au 79 L-series   1.27    1.27    0.71             0.09
S  16 K-series   0.53    0.53    0.33             0.13
Cu 29 K-series   0.00    0.00    0.00             0.00
C  6  K-series   0.00    0.00    0.00             0.00
N  7  K-series   0.00    0.00    0.00             0.00
-----------------------------------------------------
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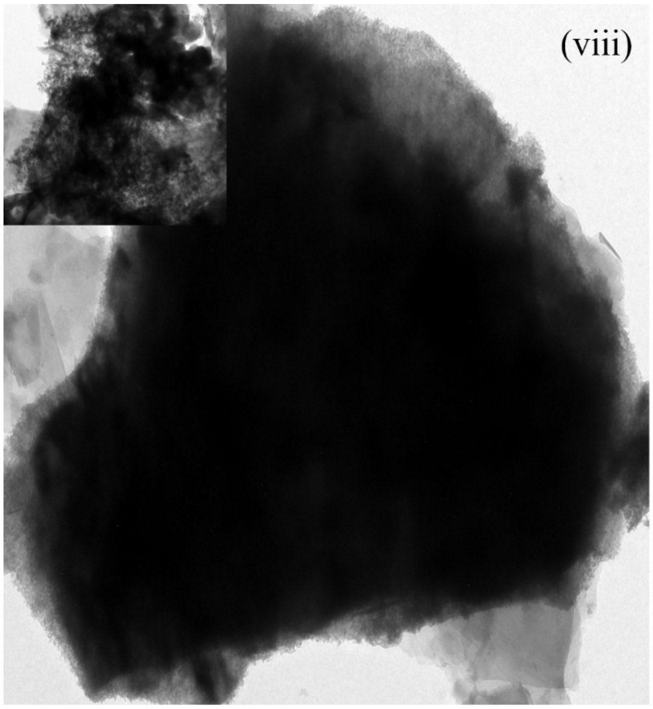

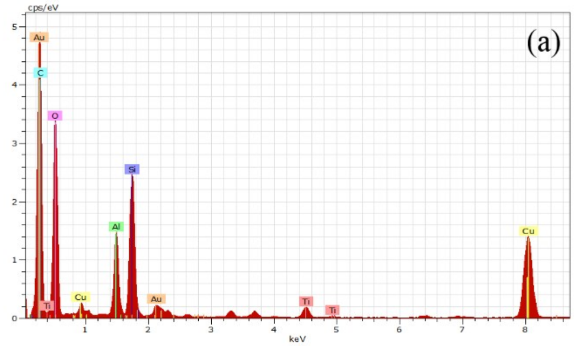

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El AN  Series   unn. C norm. C Atom. C Error (1 Sigma)
                [wt.%]  [wt.%]  [at.%]           [wt.%]
-----------------------------------------------------
O  8  K-series  42.32   42.32   55.87             1.53
Si 14 K-series  29.08   29.08   21.37             0.42
Al 13 K-series  14.53   14.53   10.63             0.61
Ti 22 K-series  12.14   12.14   10.96             1.03
Au 79 L-series   1.21    1.21    0.74             0.12
S  16 K-series   0.72    0.72    0.43             0.07
Cu 29 K-series   0.00    0.00    0.00             0.00
C  6  K-series   0.00    0.00    0.00             0.00
N  7  K-series   0.00    0.00    0.00             0.00
-----------------------------------------------------
       Total: 100.00  100.00  100.00
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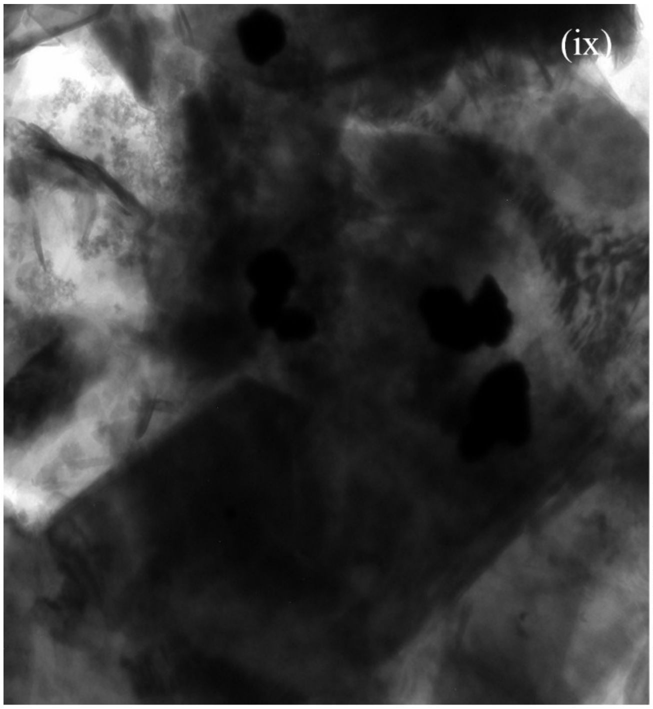

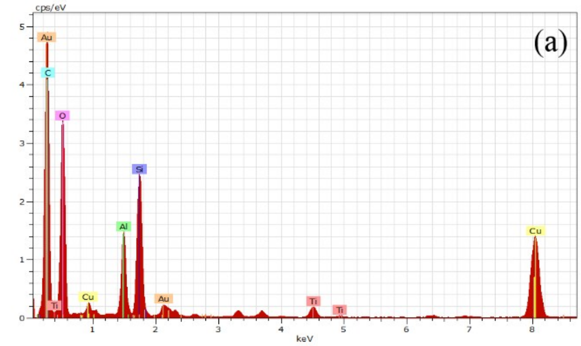

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Spectrum: 9 spc raw.xls

El AN  Series   unn. C norm. C Atom. C Error (1 Sigma)
                [wt.%]  [wt.%]  [at.%]           [wt.%]
-----------------------------------------------------
O   8  K-series  42.57   42.57   56.16             1.93
Si 14  K-series  31.23   31.23   23.92             0.72
Al 13  K-series  12.91   12.91    9.93             0.56
Ti 22  K-series  11.63   11.63    9.35             0.22
Au 79  L-series   1.09    1.09    0.43             0.22
S  16  K-series   0.57    0.57    0.21             0.04
Cu 29  K-series   0.00    0.00    0.00             0.00
C   6  K-series   0.00    0.00    0.00             0.00
N   7  K-series   0.00    0.00    0.00             0.00
-----------------------------------------------------
        Total: 100.00  100.00  100.00
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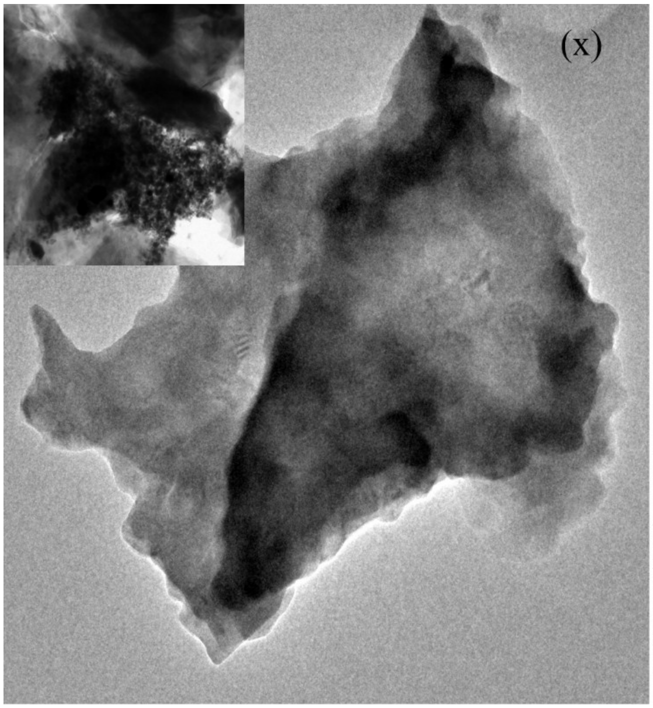

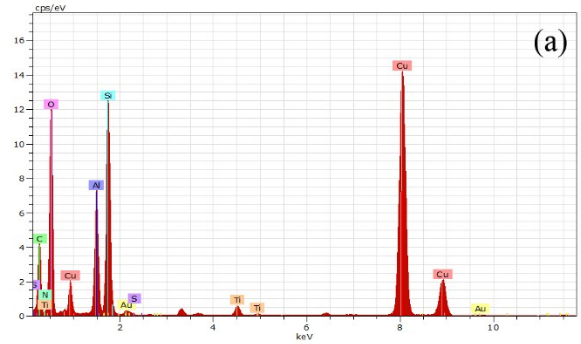

(b)

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Spectrum: 10 spc raw.xls

El AN  Series   unn. C norm. C Atom. C Error (1 Sigma)
                [wt.%]  [wt.%]  [at.%]           [wt.%]
-----------------------------------------------------
O   8  K-series  42.87   42.87   56.76             1.49
Si 14  K-series  28.02   28.02   21.17             0.72
Al 13  K-series  14.61   14.61   10.13             0.56
Ti 22  K-series  12.94   12.94   11.05             0.43
Au 79  L-series   0.89    0.89    0.30             0.04
S  16  K-series   0.67    0.67    0.59             0.07
Cu 29  K-series   0.00    0.00    0.00             0.00
C   6  K-series   0.00    0.00    0.00             0.00
N   7  K-series   0.00    0.00    0.00             0.00
-----------------------------------------------------
        Total: 100.00  100.00  100.00
```

Figure S2. (i-x) TEM images of different clay cluster on a grid at 5600X magnification and (a and b) are its corresponding EDS spectrum and composition mapping.

The EDS analysis shows the presence of TiO_2 and Au to be around 11.24 and 0.79 wt% respectively when TBOT and Au molar concentration were 15 mM and 0.20 mM respectively.

3. Study of adsorption-desorption equilibrium:

The adsorption-desorption equilibrium time was established by studying the adsorption saturation on different catalysts under dark using UV-Vis spectroscopy. The system parameters were same as used for photocatalysis. We observed that the adsorption saturates after 25 minutes of stirring under dark.

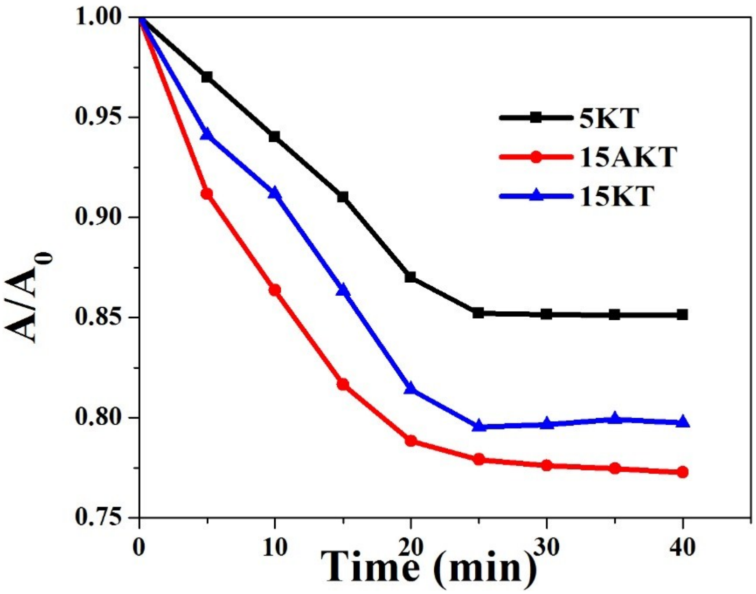

Figure S3. Normalized adsorption of MB on different catalysts in dark under stirring.

4. MB degradation by different Au NPs loading:

The degradation profile of MB dye in the 15AKT$_{N,S}$ at different molar concentrations of $HAuCl_4$ used for loading Au NPs over the clay surface is shown in fig S3. The degradation showed a slight decrease in efficiency with deposition of more Au NPs on surface as they decrease the adsorption of MB dye over clay and photocatalyst TiO_2 resulting in generation of lesser number of ROS. The sample loaded with Au NPs with 0.2 mM concentration of showed 97% degradation while higher concentration of 0.5 mM and 1.0 mM showed a degradation of 84 and 78%, respectively.

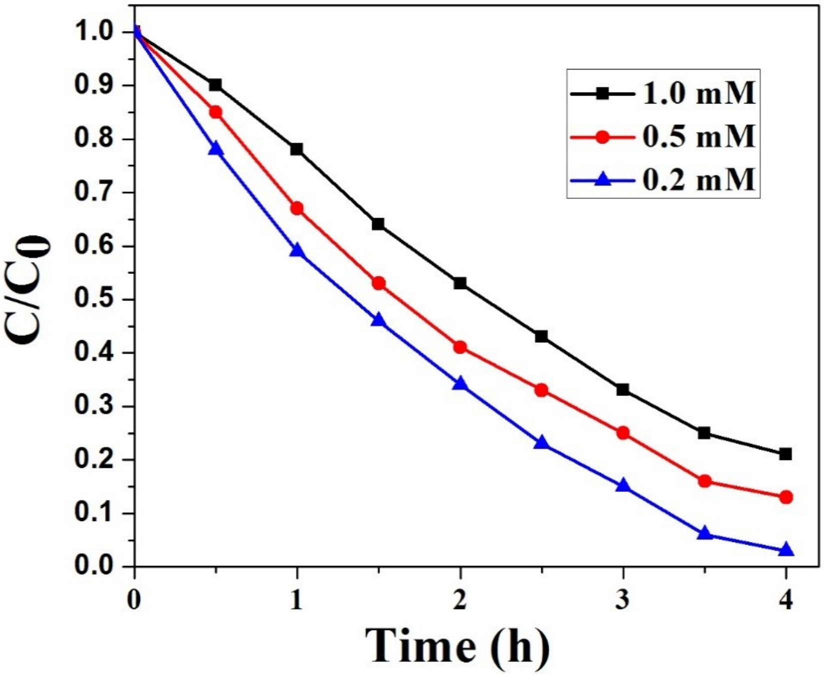

Figure S4. Degradation profile of MB for different concentrations of Au NPs loading on Kaolinite clay. Where, C_0 and C are the concentrations of MB at 0 and *t* times respectively.

5. Detection of Singlet Oxygen

The MB molecules generate SO in an excited state, from the available triplet oxygen in the solution. The generation of SO by MB sensitized on TiO_2 and kaolin was detected by the decrease in UV-vis absorbance of DPBF[1]. DPBF is a known scavenger of SO and converts to DBB (1,2-phelnylenebis (phenylmethanone)), the rate of conversion is proportional to the decrease in absorbance at 410 nm. The rate of DPBF conversion directly corresponds to SO generation. This study was performed with 4.0 mM DPBF in 2 mL ethanol in the presence of 2 mg catalyst under red LED exposure which corresponds to its absorption cross-section. This was done as a control experiment to test the SO generation ability of MB dye. The generation of SO is manifolds higher under Na-X lamp leading a large amount of scavenger usage to study the rate, therefore, the study was scaled down using LED light. Figure S4a shows that the DPBF degradation rate increases in the presence of electrolyte because of higher adsorption capacity of MB on 15KT surface as mentioned before, which in turn enhance the SO generation rate significantly. In case of 15AKT, the EM field because of the surface plasmon effect of Au NPs helps in generation of more SO from the adsorbed dye MB molecules, this phenomenon is called metal enhance SO generation, its degradation spectra are given in Figure S4b.

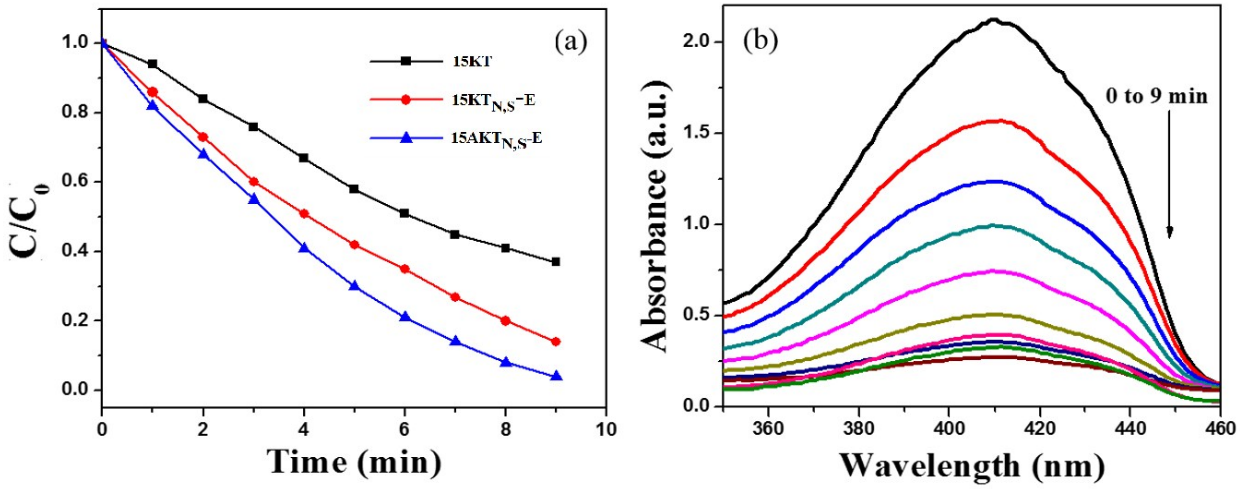

Figure S5. (a) DPBF concentration change profile by 15KT, 15KT$_{N,S}$-E and 15AKT$_{N,S}$-E NC catalyst and (b) the DPBF degradation spectra by 15AKT$_{N,S}$-E catalyst.

6. Effect of scavengers:

The effect of hole and electron scavenger was also analyzed to check which one plays an important role in dye degradation. Benzoquinone and KI were used as an $\cdot O_2^-$ and ·OH scavengers respectively and degradation of MB dye in the presence of these individual scavengers were studied to ascertain that the degradation process involves the formation of these ROS and that there is a synergetic effect of all these ROS in enhancing the photocatalytic activity as we compare 15AKT$_{N,S}$-E, 15KT$_{N,S}$-E and 15KT NCs. The scavenger will inhibit the ROS formed from attacking the dye and the decreased in ROS available for MB degradation will lead to fall in photocatalytic activity which can be seen in Figure S5. It was observed that compared to $\cdot O_2^-$, ·OH generation is greater and is the predominant specie responsible for degradation while the other also plays a significant role albeit little less. In the presence of KI scavenger the degradation efficiency decreased significantly but the difference of efficiency loss was lesser for 15AKT$_{N,S}$-E indicating the generation of more hole and electrons in that NC due to higher charge separation and activity by visible light.

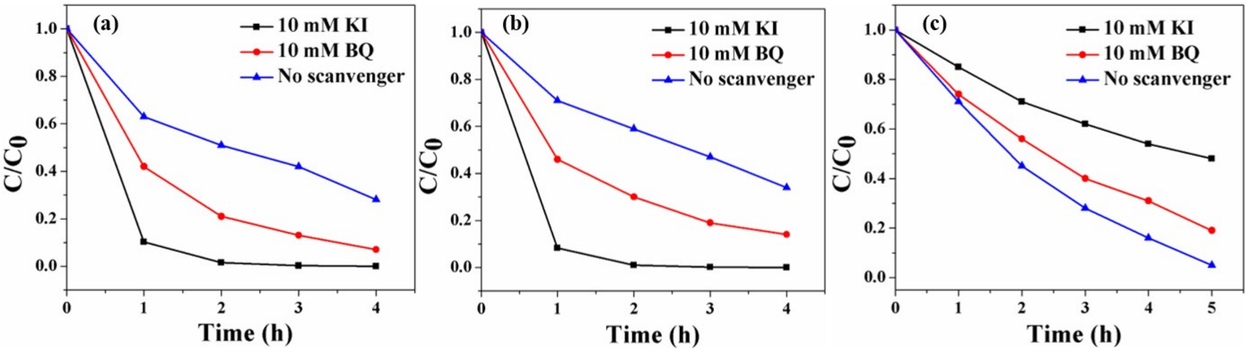

Figure S6. (a-c) Concentration change by degradation in the presence of scavenger for 15AKT$_{N,S}$-E, 15KT$_{N,S}$-E and 15KT NC catalyst.

7. Comparison of performance in literatures:

Table S1: MB and dye Degradation performance of different Clay-TiO$_2$ nanocomposites:

Sample	Parameters	Degradation	Ref.
Montmorillonite- TiO$_2$ (calcined at 400 ºC)	Light source: 250 W high-pressure Hg lamp Reaction volume: 250 mL Catalyst loading: 50 mg Initial Dye Concentration: 30 mg/L	98% in 90 min	[2]
Montmorillonite- TiO$_2$ (in presence of H_2O_2)	Light source: 200 W high-pressure Hg lamp Reaction volume: 200 mL Catalyst loading: 250 mg Initial Dye Concentration: 100 ppm	100% in 60 min	[3]
Cu^{2+}-polygorskite-TiO$_2$	Light source: 125 W high-pressure Hg lamp Reaction volume: 165 mL Catalyst loading: 200 mg Initial Dye Concentration: 12 mg/L	100% in 60 min	[4]
Montmorillonite-Ag/TiO$_2$	Light source: 500 W high-pressure Hg lamp Reaction volume: 100 mL Catalyst loading: 50 mg Initial Dye Concentration: 0.1 mM	100% in 15 min	[5]
Halloycite nanotube-TiO$_2$	Light source: 12 W UV lamp Reaction volume: 50 mL Catalyst loading: 500 mg/L Initial Dye Concentration: 0.1 mM	82% in 4 hours	[6]

Kaolinite-TiO$_2$ (600 ºC calcined)	Light source: 100 W high-pressure Hg lamp Reaction volume: 200 mL Catalyst loading: 600 mg/L Initial Dye Concentration: 32 mg/L	K= 0.031 min^{-1}	[7]
Kaolinite-TiO$_2$ and Bentonite-TiO$_2$	Light source: 100 W high-pressure Hg lamp Reaction volume: 50 mL Catalyst loading: 10 mg Initial Dye Concentration: 0.091 mM	K= 0.031 min^{-1} K= 0.029 min^{-1}	[8]
Zeolite-TiO$_2$ (zeolite made from kaolinite clay and rice husk)	Light source: 300 W Xenon and UV lamp Reaction volume: 100 mL Catalyst loading: 100 mg Initial Dye Concentration: 20 ppm	99.43% removal after 45 min	[9]
Kaolinite nanotube-TiO$_2$-C$_3$N$_4$ nanospheres	Light source: UV-Visible light Reaction volume: 20 mL Catalyst loading: 5 mg Initial Dye Concentration: 10 mg/L	K= 0.07 min^{-1}	[10]
Kaolinite-TiO$_2$ (calcined at 400 ºC for 24 hours)	Light source: 30 W UV lamp Reaction volume: 5 mL Catalyst loading: 50 mg Initial Dye Concentration: 25 mg/L	99% in 1 hours	[11]
Reduced graphene oxide-N,S-co-dopedTiO$_2$	Light source: 500 W Tungsten lamp Reaction volume: 100 mL Catalyst loading: 50 mg Initial Dye Concentration: 0.00312 mM	K= 0.025 min^{-1}	[12]
1. g-C$_3$N$_4$ 2. g-C$_3$N$_4$/TiO$_2$ (P25) 3. g-C$_3$N$_4$/TiO$_2$ (nanotubes) 4. g-C$_3$N$_4$/TiO$_2$ (nanorods) 5. g-C$_3$N$_4$/TiO$_2$ (nanospheres)	Light source: 65 W CFL lamp, Phillips, k > 400 nm and intensity = 125 W/m^2 Reaction volume: 05 mL Catalyst loading: 02 mg Initial Dye Concentration: Rhodamine B, 05 ppm	K (min^{-1}) 1. 0.0173 2. 0.0217 3. 0.0403 4. 0.0359 5. 0.0175	[13]

Our Study Exfoliated Kaolinite-Au-N,S_doped_TiO_2	Light source: 150 W Metal-halide lamp Reaction volume: 50 mL Catalyst loading: 100 mg Initial Dye Concentration: 2.5 mM	K= 0.04 min^{-1}	

References:

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