Supporting Information

Ultra Small Gold Nanoparticles-Graphitic Carbon Nitride Composite: An efficient catalyst for ultrafast reduction of 4-nitrophenol and removal of organic dyes from water

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Material

Formamide (HCONH$_2$, HPLC grade), hydrogen tetrachloroaurate(III) (HAuCl$_4$.x H2O, 99.999%) and 4-nitrophenol(4-NP, >95%), rhodamine-B (>95 %) and methyl red (>95%), methylene blue (>95 %) was bought from Sigma-Aldrich. Sulfuric acid (H$_2$SO$_4$, 98%) was purchased from Merck and sodium borohydride (NaBH$_4$) was taken from Spectrochem. These all chemicals were used as they received without further purification. Mili-Q water was obtained from ultra filtration system (Mili-Q, Milipore) with the measured conductivity 35 mho cm^{-1} at 25^{0}C.

Characterizations

For microwave synthesis of g-C$_3$N$_4$ MAS-II microwave synthesizer from SINEO Microwave Chemistry Technology Company (Shanghai, China) was used. Ultrasound was performed by SINEO UWave-1000 (Shanghai, China) with 28 kHz frequency. The surface morphology was investigated by Transmission Electron Microscopy (TEM, FEI, Technai G2 2010, operated at 200 kV). TEM samples were prepared by drop casting a drop and dried at air around 45^{0}C. For TEM 30 μl of 2x10^{-5} mg/l solution was drop casted in a TEM grid. The powder x-ray diffraction pattern (pXRD) experiment was performed by Bruker DAVINCI D8 ADVANCE diffractometer equipped with Cu Ka radiation (λ 0.15406 nm). Fluorescence study was done by spectrofluorimeter from Perkin Elmer (Model is LS 55). XPS measurements were done using VG Microtech where monochromatic Mg K$_\alpha$ X-ray was the source. Zeta potential of samples in solutions was measured at 25^0 C by using the Malvern Zetasizer Nano series instrument. UV-Vis spectra were recorded in Perkin-Elmer (model: Lamda-750) UV-Vis spectrometer. The UV light was exposed in the dye degradation experiment from Luzchem (Canada) at 250 nm wavelength 84 watt. Dye degradation in visible light was carried out by using 135 watt xenon lamp (ARC lamp, Newport, Oriel Product line) at a distance 25 cm with a cut of filter ≥ 420 nm. Mass spectra were recorded on a Brukermicro TOF-Q II, ESI TOF mass

spectrometer. Thermo gravimetric analysis (TGA) was carried out by TA Instrument (model SDT Q600)
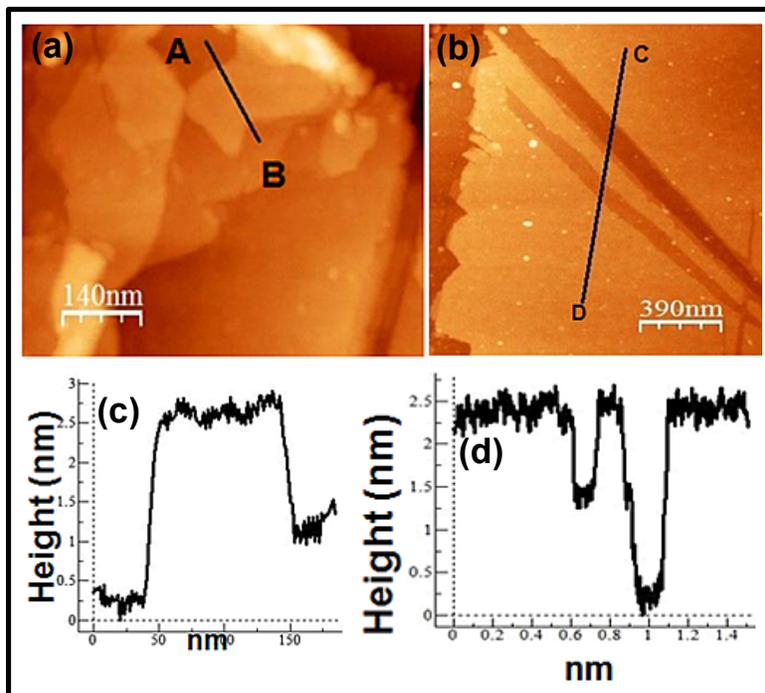
Figure S1 AFM images of thin CN_x sheets and its height profile shows thickness 2.0 to 2.5 nm.

Element	Weight%
C K	24.38
N K	29.02
O K	6.35
Au M	40.25
Totals	100.00
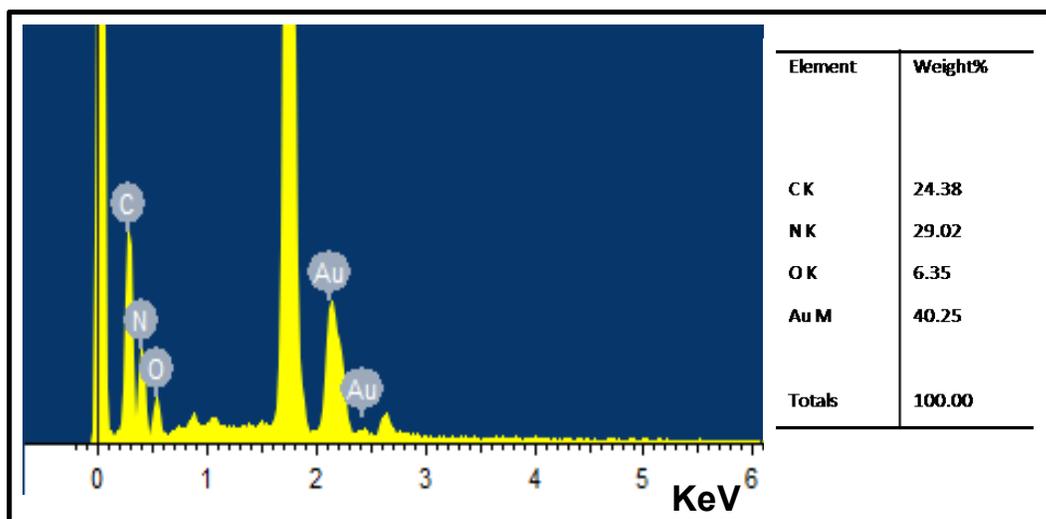
Figure S2. EDS spectra $AuCN_x$ composite prepared on silicon wafer.
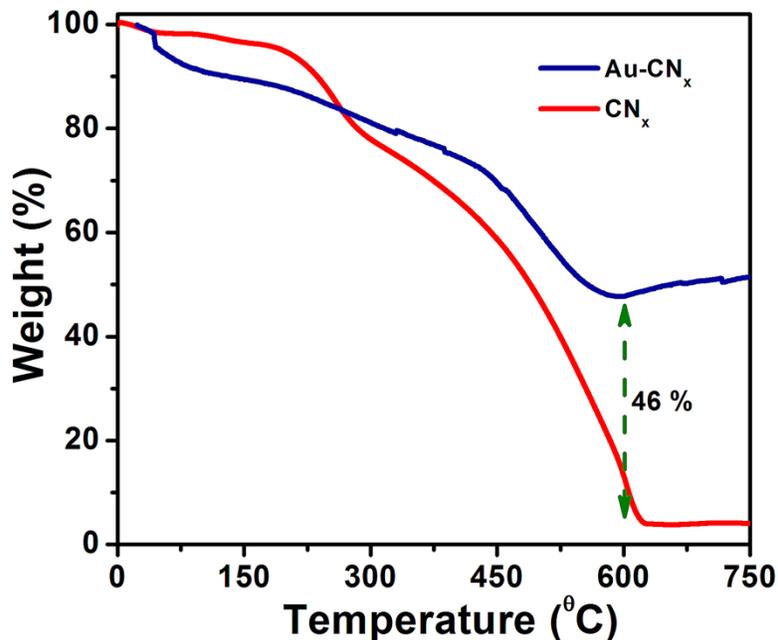
Figure S3. TGA spectra of Au-CNx (blue line) and CNx (red line) at N_2 atmosphere

Table T1. Comparison of activity of different catalyst on 4-NP reduction

Catalyst	Amt. Of catalyst (mg)	Amt. Of 4-NP (mmol)	Amt.Of NaBH$_4$ (mmol)	Conv. Time (Sec)	Ref.
Au-CN$_x$	5	3×10^{-4}	3×10^{-1}	15	This Work
Porous Au	0.5	5×10^{-4}	2×10^{-1}	80	1
Porous Au-PdNPs	0.5	5×10^{-4}	2×10^{-1}	12	1
RGO@Pd@C	5	3×10^{-4}	3×10^{-2}	30	2
Pd–rGO-CNT	5	3×10^{-4}	3×10^{-2}	20	3
Au-mpg C$_3$N$_4$	5	3×10^{-4}	3×10^{-1}	300	4

Table T2. Parameters of different isotherm model of MB dye.

MB dye	Isotherm models		
Parameter	Freundlich	Langmuir	sips
K(mg/gm)	20.63	-	-
n	2.72	-	1.30
q_{max}(mg/gm)	-	200	235
b	-	0.01	0.02
R^2	0.985	0.993	0.994
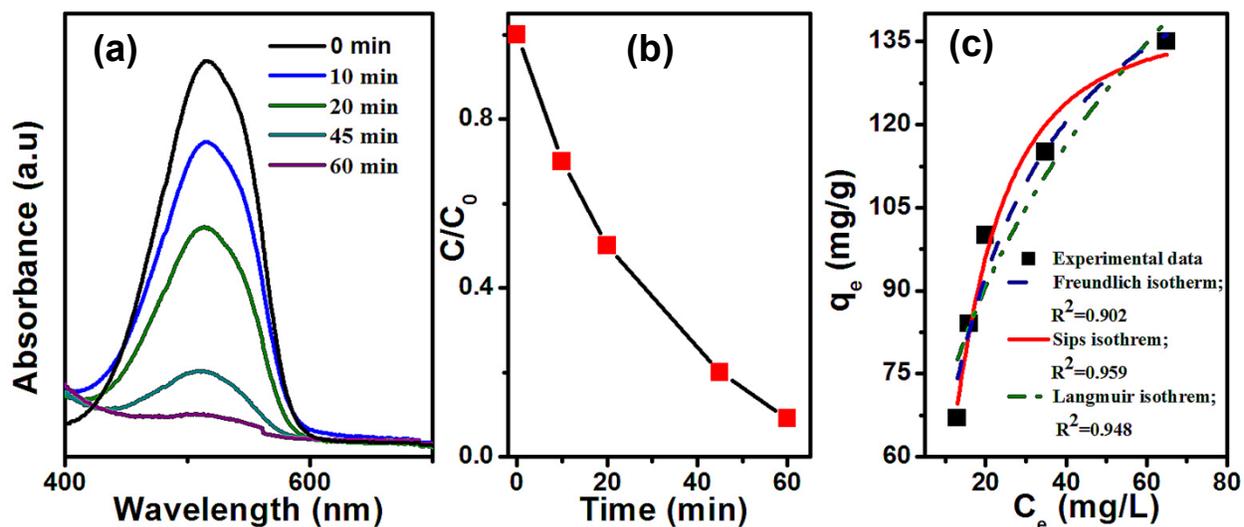
Figure S4. (a) UV-Visible absorption spectra of aqueous solution of MR at different time interval in presence of Au-CNx catalyst. (b) Plot of C/C_0 *vs* time for MR dyes respectively where C_0 is initial concentration of dyes (20 ppm) and C is the concentration at different time interval. (c) Fitting of different isotherm model with adsorption of MR on Au-CNx surfaces. All the experiment was done with 1 ml of 20 ppm dyes with 1 mg Au-CNx catalyst

Table T3. Parameters of different isotherm model of MR dye.

MR dye	Isotherm models		
Parameter	**Freundlich**	**Langmuir**	**sips**
K(mg/gm)	30.7	-	-
n	2.7	-	0.54
q_{max}(mg/gm)	-	120	130
b	-	0.05	0.01
R^2	0.89	0.948	0.959

Table T4. Comparison of rate constant for photocatalytic degradation of different dyes.

Catalyst	Dye	Concentration of Dye	Light source	Rate constant	Ref.
Graphene- Gold	RhB	2.5 ppm	Visible light	8.3×10^{-3}	[5]
PD/MW	RhB	2 ppm	Microwave light	1.7×10^{-2}	[6]
RGO-CuNO$_3$	RhB	2.5 ppm	Visible light	1.5×10^{-2}	[7]
Ag-C$_3$N$_4$	RhB	10 ppm	Visible light	2.53×10^{-2}	[8]
Au-CN$_x$	**RhB**	**~30 ppm**	**Visible light**	**2.4×10^{-2}**	**This work**
Ag/AgCl	MB	20 ppm	Visible light	7.0×10^{-3}	[9]
Ag/AgCl/g-C$_3$N$_4$	MB	10 ppm	Visible light	7.8×10^{-2}	[10]
Au^{+3}-TiO$_2$ (0.5%)	MB	12 ppm	Visible light	9.2×10^{-3}	[11]
Au-CN$_x$	**MB**	**~35 ppm**	**Visible light**	**2.4×10^{-2}**	**This work**
TiO$_2$	MR	4 ppm	UV light	1.3×10^{-2}	[12]
Ag$^+$/TiO$_2$	MR	6 ppm	UV light	5.02×10^{-3}	[13]
Au-CN$_x$	**MR**	**~35 ppm**	**Visible light**	**2.0×10^{-2}**	**This work**
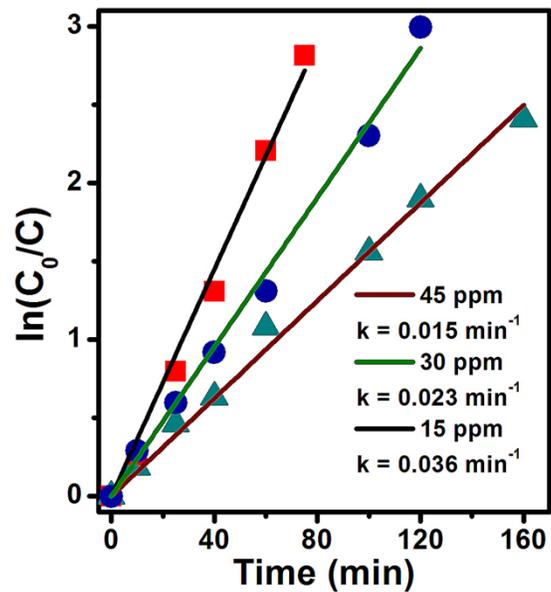
Figure S5. ln (C_0/C) vs time plot of different concentration of RhB under visible light illumination.
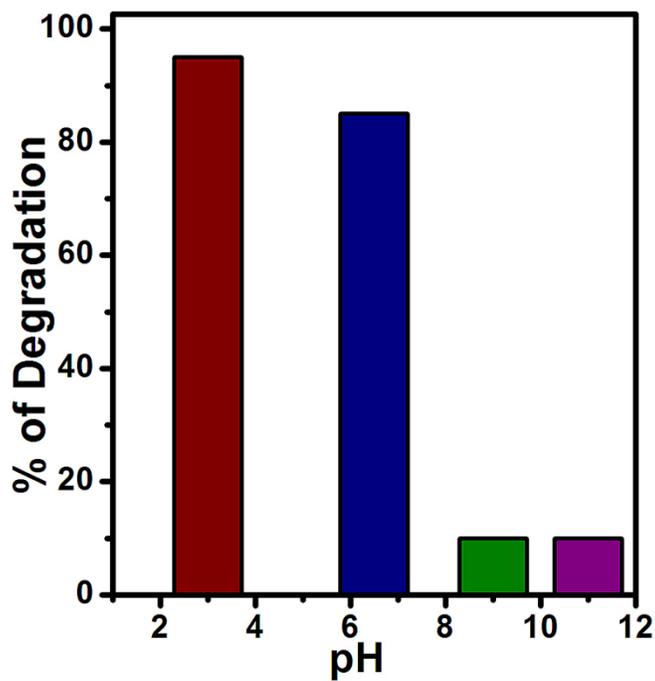
Figure S6. pH dependent degradation efficency of 70 ppm RhB with Au-CN$_x$ catalyst
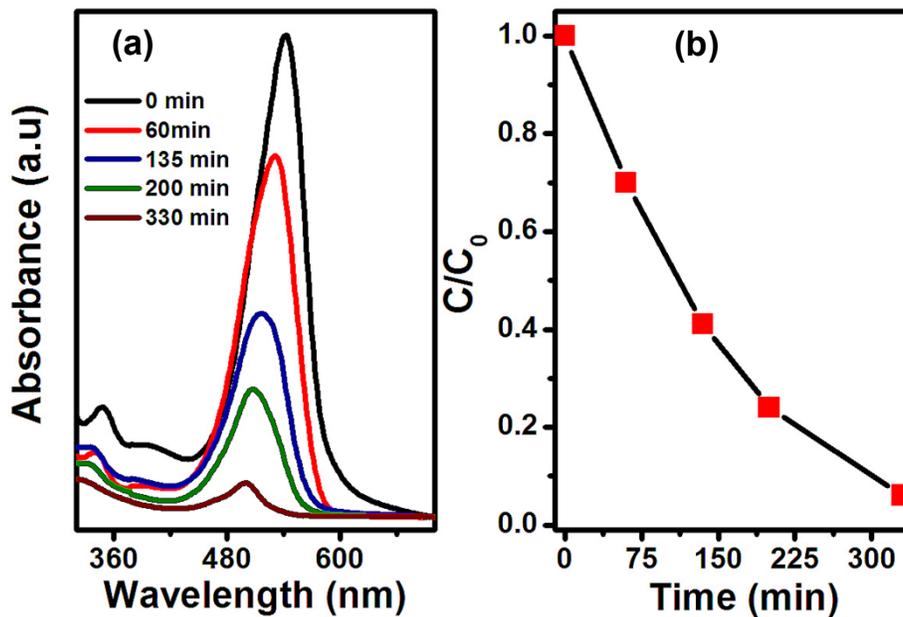
Figure S7. Degradation of 250 ppm RhB dye by Au-CNx under visible light after 10 hour adsorption. (a) The change of UV-Visible Spectra at different time intervals, (b) C/C_0 vs time plot.
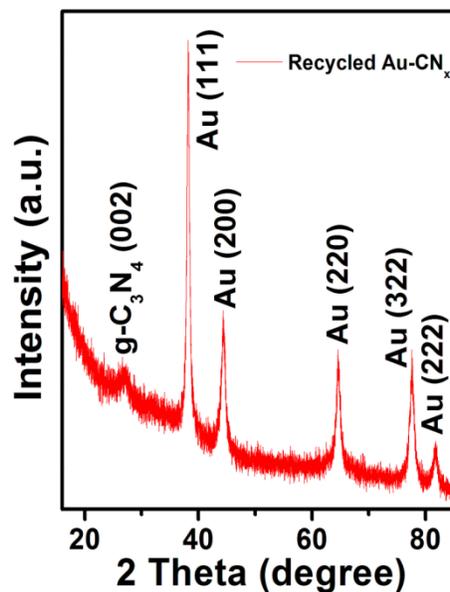
Figure S8. p-XRD of recycled (after 3rd catalytic cycles) catalyst.

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