TiO_2 -Au nanocomposite materials embedded in polymer matrices and their application in the photocatalytic reduction of nitrite to ammonia

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Electronic Supplementary Information

Fig. S1:



Fig. S1. Diffuse reflectance spectra of MTMOS/ $(TiO_2-Au)_{nps}$ (A) and Nf/ $(TiO_2-Au)_{nps}$ (B) film coated on glass plate. The molar ratios of TiO₂:Au are: 100:1 (a), 100:2 (b), 100:3 (c), 100:4 (d) and 100:5 (e).

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Fig. S2:





Fig. S2. Lattice resolved TEM images of TiO₂ nanoparticle alone (A), TiO₂ (B), Au (C) nanoparticles present in the $(TiO_2-Au)_{nps}$ nanocomposite material (Ti:Au = 33:1) and selected area electron diffraction (SAED) pattern of $(TiO_2-Au)_{nps}$ nanocomposite material (Ti:Au = 33:1) (D).

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Fig. S3:



Fig. S3. Schematic representation for photocatalytic reduction of nitrite by $(TiO_2-Au)_{nps}$.

Table S1: Liquid uptake percentage of the polymer film.

Polymer film	Liquid uptake percentage (%)*
MTMOS	18
MTMOS/TiO ₂	10
$\frac{\text{MTMOS}/(\text{TiO}_2\text{-}\text{Au})_{\text{nps}}}{(\text{Molar ratio of TiO}_2\text{:}\text{Au} = 33\text{:}1)}$	16
Nf	23
Nf/TiO ₂	19
$Nf/(TiO_2-Au)_{nps}$ (Molar ratio of TiO_2:Au = 33:1)	22

Foot note: Liquid uptake percentage of film was calculated by immersing the film in n-butanol for 12 h (Area of the film was 1 cm^2). The film was coated on a glass pate.

* The liquid uptake percentage of polymer film was determined by weight increase method as $(W_2 - W_1) \times 100/W_1$, where W_1 and W_2 were the weights of polymer films before and after the absorption of the n-butanol, respectively.

	Without Matrix		In MTMOS		In Nafion	
Photocatalyst	E _{bg} (eV)	λ (nm)	E _{bg} (eV)	λ (nm)	E _{bg} (eV)	λ (nm)
TiO ₂	3.35	370	3.39	366	3.36	369
TiO ₂ -Au (100:1)	3.26	380	3.31	375	3.27	379
TiO ₂ -Au (50:1)	3.15	394	3.24	383	3.18	390
TiO ₂ -Au (33:1)	3.02	411	3.13	396	3.08	403
TiO ₂ -Au (25:1)	2.94	422	3.03	409	2.98	416
TiO ₂ -Au (20:1)	2.86	434	2.96	419	2.89	429

Table S2: The band–gap energy and their corresponding wavelength for $(TiO_2-Au)_{nps}$, MTMOS/ $(TiO_2-Au)_{nps}$ and Nf/ $(TiO_2-Au)_{nps}$.

Table S3. Amounts of NH_4OH produced in the absence and presence of $[Ni(teta)]^{2+}$ at the MTMOS/ $(TiO_2-Au)_{nps}$ and $Nf/(TiO_2-Au)_{nps}$ films when dipped in a mixture containing 1 mM NaNO₂ and 5 mM oxalic acid in 20 mL. The irradiation time was 1 hr.

	Amount of NH ₄ OH (μM)				
Photocatalyst	Absence of [[Ni(teta)] ²⁺	Presence of [Ni(teta)] ²⁺		
	MTMOS	Nafion	MTMOS	Nafion	
TiO ₂	51.5	126	80.5	200.5	
TiO ₂ -Au (100:1)	92.5	159	144.9	240.5	
TiO ₂ -Au (50:1)	107	180	152.5	281	
TiO ₂ -Au (33:1)	159	196	216	318	
TiO ₂ -Au (25:1)	138.5	195.5	197	308	
TiO ₂ -Au (20:1)	137.5	194	191.5	302.5	

Table S4. Photocataltyic reduction of nitrite to ammonia with various photocatalysts in colloidal systems

and films.

Photocatalyst	Nature of the Catalyst	Irradiation Time	Sacrificial Electron Donors	Amount of ammonia produced (μ mol in 20 mL)	References
$\frac{\text{MTMOS}/(\text{TiO}_2\text{-}\text{Au})_{\text{nps}}/[\text{Ni}(\text{teta})]^{2+}}{(\text{TiO}_2\text{-}\text{Au} \text{ molar ratio was } 33:1)}$	Film	1 h	OA	4.32	Present
$Nf/(TiO_2Au)_{nps}/[Ni(teta)]^{2+}$ (TiO_2Au molar ratio was 33:1)	Film	1 h	OA	6.36	Present work
Nf/FePc	Film	1 h	TEA	3.0	34
$Nf/[Ni(teta)]^{2+}/[Ru(bpy)_3]^{2+}$	Film	1 h	TEA	1.1	33
0.04 wt. % Fe/TiO ₂ (Doping)	Colloids	2 h	Water	0.67	30
0.23 wt. % Cr/TiO ₂ (Doping)	Colloids	2 h	Water	0.25	30
0.25 wt. % Co/TiO ₂ (Doping)	Colloids	2 h	Water	0.37	30
1.41 wt. % Mg/TiO ₂ (Doping)	Colloids	2 h	Water	0.55	30
Sol-gel TiO ₂	Colloids	2 h	Water	6.47	32