Supporting information

Green synthesis of porous Au-Nx-TiO2 nanospheres for solar light induced photocatalytic degradation of diazo, triazo dyes and their eco-toxic effects

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Fig. S1. The molecular structures for the model pollutants (diazo (RR120) and triazo dyes (DB71)).
Fig. S2. SEM images of porous TiO$_2$ NSPs (a,b) and N$_x$-TiO$_2$ NSPs (c,d).
Fig. S3. EDAX spectra of porous TiO$_2$ NSPs (a) and N$_x$-TiO$_2$ NSPs (b).
**Fig. S4.** TEM images (a), HRTEM image (b), EDAX spectrum (c) of porous Au-TiO$_2$ NSPs.

Inset (c): Corresponding SAED pattern.
Fig. S5. XPS survey spectra of prepared photocatalysts.

- $\text{Au}_x\text{-N}_x\text{-TiO}_2$
- $\text{N}_x\text{-TiO}_2$
- $\text{Au-TiO}_2$
- $\text{TiO}_2$
Fig. S6. UV-visible spectra of RR120 (a), DB71 (b) at different irradiation periods in the presence of porous Au-Nx-TiO2 NSPs. [Dyes] = 4 × 10^{-5} M and [Au-Nx-TiO2 NSPs] = 0.2 g L^{-1}. Plot of (C/C_0) vs. time for the photocatalytic degradation of RR120 (c) and DB71 (d) at various concentration of porous Au-Nx-TiO2 NSPs [Dye] = 4 × 10^{-5} M. Inset: corresponding rate constant plot. Error bars are the standard deviations of triplicate experiments.
Fig. S7. PL spectra of 2-hydroxy terephthalic acid (standard) at various concentrations (a), fluorescence calibration curves as a function of 2-hydroxy terephthalic acid concentration (b,c), PL spectra of terephthalic acid at various irradiation times in the presence of porous Au-N₃-TiO₂ NSPs (d). [Catalysts] = 0.2 g L⁻¹; [TA] = 5 × 10⁻⁴ M.
Table S8. Summary of the results obtained for the amount of photocatalytic degradation of azo dyes and formation of HO• radical in the presence of various catalysts. *(The reaction parameters are identical in the dye degradation and HO• radical quantification)*

<table>
<thead>
<tr>
<th>Irradiation</th>
<th>Catalyst</th>
<th>Amount of HO• radical formation (10⁻⁵ M)</th>
<th>Amount of degradation (10⁻⁵ M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct Solar light</td>
<td>TiO₂ (Degussa P25)</td>
<td>0.33 ± 0.04</td>
<td>1.80 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>Porous TiO₂ NSPs</td>
<td>0.47 ± 0.03</td>
<td>1.95 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>Porous Nₓ-TiO₂ NSPs</td>
<td>0.89 ± 0.05</td>
<td>2.79 ± 0.13</td>
</tr>
<tr>
<td></td>
<td>Porous Au-TiO₂ NSPs</td>
<td>1.21 ± 0.03</td>
<td>3.36 ± 0.09</td>
</tr>
<tr>
<td></td>
<td>Porous Au-Nₓ-TiO₂ NSPs</td>
<td>1.79 ± 0.05</td>
<td>3.90 ± 0.08</td>
</tr>
<tr>
<td>Solar (visible) light</td>
<td>TiO₂ (Degussa P25)</td>
<td>0.05 ± 0.01</td>
<td>0.40 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>Porous TiO₂ NSPs</td>
<td>0.07 ± 0.01</td>
<td>0.44 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>Porous Nₓ-TiO₂ NSPs</td>
<td>0.44 ± 0.02</td>
<td>1.04 ± 0.06</td>
</tr>
<tr>
<td></td>
<td>Porous Au-TiO₂ NSPs</td>
<td>0.66 ± 0.02</td>
<td>1.30 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>Porous Au-Nₓ-TiO₂ NSPs</td>
<td>1.32 ± 0.01</td>
<td>3.32 ± 0.05</td>
</tr>
<tr>
<td>Solar (λ &gt; 395 nm)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
S9: The principle involved in the photocatalytic degradation is the formation of $\text{HO}^\cdot$ radicals by the utilization of the photocatalytically generated excitons. In this context, the photocatalytically generated $\text{HO}^\cdot$ radicals in the presence of Au-N$_x$-TiO$_2$ NSPs on the direct solar light irradiation is identified and quantified through the photoluminescence (PL) technique. Terephthalic acid (TA) was used as the probe molecule and a change in the PL intensity of the photocatalytically formed 2-hydroxyterephthalic acid is directly proportional to the amount of the $\text{HO}^\cdot$ produced during the photocatalytic reaction. The qualitative identification of the $\text{HO}^\cdot$ radicals during the photocatalytic degradation reaction has been reported elsewhere $^1$-$^4$. It is important to quantify the photocatalytically generated $\text{HO}^\cdot$ radicals. The experiments are carried out carefully to make a calibration curve using 2-hydroxyterephthalic acid as shown in Fig. S7a-c. The linear regression ($R^2 = 0.9998$) of the calibration curve clearly indicated that the PL intensity of the 2-hydroxy terephthalic acid is increased with respect to its concentration upto $0.25 \times 10^{-5}$ M (Fig. S7b) but the linear regression ($R^2 = 0.9936$) slightly deviates at high concentration of 2-hydroxy terephthalic acid (Fig. S7c) which may be caused by 2-hydroxy terephthalic acid absorption and/or fluorescence quenching $^5$. Fig. S7d reveals that there is no remarkable change in the PL intensity ($\lambda_{\text{max}} = 425$ nm) of aqueous TA in the presence of the catalyst under dark as well as light irradiation in the absence of the porous Au-N$_x$-TiO$_2$ NSPs. Whereas, the PL intensity of TA is increased in the presence of both solar light irradiation and porous Au-N$_x$-TiO$_2$ NSPs in the photocatalytic system due to the formation of 2-hydroxy terephthalic acid through the reaction between TA and the photocatalytically generated hydroxyl radicals ($\text{HO}^\cdot$).
Fig. S10. Histograms showing the percentage degradation of dyes in the presence of Au-Nₓ-TiO₂ NSPs under direct solar light irradiation. The experiments carried out in the both Milli-Q and tap water and concentrations are maintained as follows: [Catalyst] = 0.2 g L⁻¹; [dye] = 4 × 10⁻⁵ M.
Fig. S11. Histograms showing the comparison of the photocatalytic degradation rate constant (a, b) and mineralization (c,d) of RR120 and DB71 in the presence of oxidants with and without porous Au-Nx-TiO2 NSPs under direct solar light irradiation. Inset (a,b): maximized area of corresponding plots. The experiments carried out in the both Milli-Q and tap water and concentrations are maintained as follows: [Catalyst] = 0.2 g L\(^{-1}\); [dye] = 4 \times 10^{-5} M and [Oxidants] = 2.5 \times 10^{-4} M.
**Fig. S12.** Photocatalytic degradation of DB71 using recycled porous Au-N_x-TiO_2 NSPs (a). Initial concentrations: [Catalyst] = 0.2 g L^{-1}; [dye] = 4 \times 10^{-5} M. DRS of porous Au-N_x-TiO_2 NSPs before and recycled (b).
References


