Outstanding visible light photocatalysis by nano-TiO$_2$ hybrids with nitrogen-doped carbon quantum dots and/or reduced graphene oxide

1. Figures:

Figure S1. The optical properties of the solar simulator lights showing: (a) the irradiance spectrum of the quartz tungsten halogen lamp (Osram 1 kW R7s 22000 lm) (b) the light composition between 200-800 nm and (c) the ultraviolet radiation composition of the quartz tungsten halogen lamp (Osram 1 kW R7s 22000 lm linear halogen lamp); (d) The optical properties of the Minisol$^{\text{TM}}$ LED solar simulator with wavelength in the range of 400-800 nm. The light intensity was varied from 1-0.25 sun setting and irradiance was recorded using Ocean Optics spectrophotometer. The distance of the lamp from the photocatalytic reactor was kept constant (27 cm).
Supplementary Information

Figure S2: The XPS elemental composition of TiO$_2$ and its carbonaceous nanocomposites.

Figure S3: Photo-response activities of the catalyst, showing photodecomposition of methylene blue under visible light ($\lambda_{irradiation} \geq 400$ nm (0.5 sun); (a) first order rate constants and (b) the final % conversation (C = final concentration to C$_0$ = initial concentration, C/C$_0 \times 100$) for each photocatalyst during the total solar light exposure period. In both graphs, control = methylene blue.
Supplementary Information

Light intensity studies

**Figure S4:** Photo-response activities of the best performing catalyst, TiO$_2$-NCQDs-rGO, showing photodecomposition of methylene blue under different light intensities (1-0.25 sun) in visible light region only ($\lambda_{\text{irradiation}} \geq 400$ nm); (a) first order rate constants and (b) the final % conversation ($C = \text{final concentration, } C/C_0 \times 100$) for each photocatalyst during the total solar light exposure period. In both graphs, control = methylene blue.
Supplementary Information

2. Tables:

**Table S1:** Adsorption coefficients \( q_t \), TEM particle size and size distribution (nm), and \( S_{\text{BET}} \) values \( \text{m}^2 \text{g}^{-1} \) for each corresponding photocatalysts.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>( q_t )</th>
<th>TEM (nm)</th>
<th></th>
<th>( S_{\text{BET}} ) (m(^2) g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>mean particle size</td>
<td>particle size distribution</td>
<td></td>
</tr>
<tr>
<td>TiO(_2)</td>
<td>4.4</td>
<td>5.4 ± 1.2</td>
<td>3.22 - 8.22</td>
<td>232</td>
</tr>
<tr>
<td>TiO(_2)-rGO</td>
<td>14.2</td>
<td>5.3 ± 1.7</td>
<td>2.13 - 11.56</td>
<td>254</td>
</tr>
<tr>
<td>TiO(_2)-NCQDs</td>
<td>5.5</td>
<td>4.5 ± 0.9</td>
<td>2.92 - 6.34</td>
<td>238</td>
</tr>
<tr>
<td>TiO(_2)-NCQDs-rGO</td>
<td>11.2</td>
<td>4.5 ± 1.0</td>
<td>2.74 - 7.1</td>
<td>253</td>
</tr>
</tbody>
</table>

**Table S2:** Calculated Apparent Quantum Efficiency (AQE) values using different light sources.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>UV-Vis solar simulator</th>
<th>Visible solar simulator</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Quartz tungsten halogen lamp (Osram 1 kW R7s 22000, ( \lambda_{\text{irradiation}} = 200-1000 \text{ nm} ))</td>
<td>Minisol(^\text{TM}) LED solar simulator (LSH-7320, MKS Newport) ( \lambda_{\text{irradiation}} = 400-1000 \text{ nm} ))</td>
</tr>
<tr>
<td>TiO(_2)</td>
<td>0.9</td>
<td>0.6</td>
</tr>
<tr>
<td>TiO(_2)-NCQDs</td>
<td>1.3</td>
<td>1.0</td>
</tr>
<tr>
<td>TiO(_2)-rGO</td>
<td>2.1</td>
<td>1.0</td>
</tr>
<tr>
<td>TiO(_2)-NCQDs-rGO</td>
<td>2.1</td>
<td>1.6</td>
</tr>
</tbody>
</table>

**Table S3:** Light intensity variations for the best performing catalyst, TiO\(_2\)-NCQDs-rGO, and the calculated AQE values.

<table>
<thead>
<tr>
<th>Minisol(^\text{TM}) LED solar simulator (LSH-7320, MKS Newport)</th>
<th>Light intensity</th>
<th>AQE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 sun</td>
<td>0.9%</td>
</tr>
<tr>
<td></td>
<td>0.5 sun</td>
<td>1.6%</td>
</tr>
<tr>
<td></td>
<td>0.25 sun</td>
<td>4.6%</td>
</tr>
</tbody>
</table>
3. Equations:

1. Adsorption coefficients were also determined using Langmuir-Hinshelwood model (Table S1).¹

\[ q_t = \frac{\Delta C \cdot 1000 \cdot M \cdot V}{m} \]  
(Eq. S1)

Where:
- \( \Delta C = C_0 - C_t \) (\( C_0 \): initial concentration and \( C_t \): equilibrium concentration) [mol/L]
- \( M \) is the molecular mass of methylene blue [g/mol]
- \( V \) is the reaction mixture volume [L]
- \( m \) is the mass of the photocatalyst [g]

2. Apparent Quantum Efficiency²

\[ N_p = \frac{I}{E_p} = \frac{\int_{1000}^{200} I \, d\lambda \times 10^{-9}}{h \times c} \]  
(Eq. S2)

\[ N_p = \frac{I}{E_p} = \frac{\int_{400}^{1000} I \, d\lambda \times 10^{-9}}{h \times c} \]  
(Eq. S3)

Where:
- \( N_p \) = number of photons
- \( I \) = power density
- \( E_p \) = energy of photon
- \( h \) = Plank constant
- \( c \) = speed of light

\[ N_{p \, Total} = N_p \times t_{irradiation} \times S_{reactor} \]  
(Eq. S4)

Where:
- \( N_{p \, Total} \) = total number of photons generated by the simulator during the photocatalytic process
- \( N_p \) = number of photons
- \( t_{irradiation} \) = the irradiation time of the photocatalytic process [s]
- \( S_{reactor} \) = reactor irradiation surface [m²]

\[ AQE(\%) = \frac{N_{PM_{MB}}}{N_{p \, Total}} \times 100 \]  
(Eq. S5)

Where:
- AQE = Apparent Quantum Efficiency [%]
- \( N_{PM_{MB}} \) = number of photodegraded molecules of methylene blue
- \( N_{p \, Total} \) = total number of photons generated by the simulator during the photocatalytic process


4. Additional References

**XPS analysis:** As stated in the main text: “It is prudent at this point to state that all calibration of the spectra have been made to the Ti(2p$_{3/2}$) peak taken to be 459.3 eV in line with that of Diebold and Madey [1]. Whilst, for example, the NIST database [2] has a mean value of ca. 458.5 eV, there is significant deviation (approx. 1.5 eV)[3].”


**Theoretical calculations:** Plane-wave DFT as implemented in the VASP code was used [1,2].
