Supporting Information

Carbon nitride polymer sensitized TiO$_2$ nanotube arrays with enhanced visible light photoelectrochemical and photocatalytic performance

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**Photoelectrodes Fabrication.** The highly ordered TiO$_2$ nanotube array film was prepared by anodic oxidation in a NH$_4$F organic electrolyte, similarly to that described by Paulose et al.$^1$ First, metal Ti foil was cleaned with ethanol and de-ionized water prior to anodization. Then the Ti foil was immersed in a mixed ethylene glycol solution of 0.05% NH$_4$F, and subjected to a constant 60 V anodic potential for 12 h at room temperature in a two-electrode electrochemical cell connected to a DC power supply. After anodic oxidation, the sample was rinsed with de-ionized water, and dried in a N$_2$ stream. The resulting amorphous titania nanotube array film was annealed at 450 ºC for 4h with heating and cooling rates of 10 ºC/min in an O$_2$ atmosphere to crystallize the tube walls and improve its stoichiometry.

Carbon nitride polymer was deposited into the crystallized TiO$_2$ nanotubes by electrodeposition. The preparation of method is similar to that reported in literature.$^2$ The experimental setup used to synthesize the composite film is like that described in literature.$^3,^4$ Typically, the crystallized TiO$_2$ nanotube array film was used as positive electrode and iron silk was used as negative electrode. The interelectrode separation in all the cases was 2 mm. Analytically pure methanol ($\geq 99.5\%$) and acetonitrile mixtures were used as solvent and 0.1 M dicyandiamide was used as electrolyte. The typical sample was deposited under an applied potential of 120 V at room temperature.

**The amounts of CN polymer deposited.** It is very difficult to measure the amount of CN polymer deposited. Herein, the amount of C-N polymer deposited was calculated.

\[
\text{Charge: } Q = I \cdot t \quad (1-1)
\]

\[
\text{Number of electrons: } N = \frac{Q}{e} = \frac{It}{e} \quad (1-2)
\]
n = N/N₀  

C₂H₈N₂ + 12e⁻ → C₃N₄ + CH₄ + 6H₂  

Using formula (1-1), (1-2), (1-3) and equation (1-4), we can calculate the amount of C-N polymer with different deposited time according to the below formula:

\[ m_{(C₃N₄)} = M_{(C₃N₄)} I/12eN₀ \]  

Here, \( I = 0.001 \) A; \( e = 1.6 \times 10^{-19} \) C; \( N₀ = 6.02 \times 10^{23} \) mol⁻¹; \( M_{(C₃N₄)} = 92.06 \) g/mol

**Table S1** The amount of C-N polymer deposited with different deposited time

<table>
<thead>
<tr>
<th>Deposited time, ( t ) (min)</th>
<th>2.5</th>
<th>5.0</th>
<th>10.0</th>
<th>30.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount of C₃N₄, ( m ) (mg)</td>
<td>0.012</td>
<td>0.024</td>
<td>0.048</td>
<td>0.143</td>
</tr>
<tr>
<td>Unit amount of C₃N₄, ( m/S^* ) (mg/m²)</td>
<td>24</td>
<td>48</td>
<td>96</td>
<td>287</td>
</tr>
</tbody>
</table>

*TNT array electrode area: \( 2.5 \times 10^{-2} \) m × \( 2.0 \times 10^{-2} \) m = \( 5.0 \times 10^{-4} \) m²

**Photocatalytic activity test.** The photocatalytic activity was measured in a XPAII reactor (Nanjing Xujiang Machineelectronic Plant). The sample film (8×20 mm) was immersed in 10-ml quartz test tube containing 4 ml Acid Orange II (OII) (10 mg/ L) in the dark for 1 h to achieve adsorption equilibrium before irradiation. After that, a 1000 W Xe lamp (the UV light was cut off by 2.0 M sodium nitrite) was used as the visible light source to conduct the photocatalytic experiment at 40 °C. The remaining dye concentration in the reaction solution was determined using the U3010 spectrophotometer. The whole decomposing process was conducted in air without sparging oxygen gas.

**X-ray photoelectron spectroscopy (XPS).** The chemical bonds of the sample were detected by the XPS analysis, as shown in Figure S1. The C 1s and N 1s spectra were deconvoluted into various peaks (Figure S1a and S1b). The C 1s peak at 284.6 eV is assigned
to the C–C bond in the turbostratic CN structure,\textsuperscript{5} and the peak at 286.3 eV is attributed to the
sp\textsuperscript{2} C atoms bonded to N inside the aromatic structure. We assign the peak at 288.4 eV to the
sp\textsuperscript{3} C–N bond of the sp\textsuperscript{3} bonded composition.\textsuperscript{5,6} The N 1s peak is comprised of two
components centered at 398.7 eV and 400.1 eV, which are identified as the C–N–C groups\textsuperscript{5} and the nitrogen surrounded by an amorphous N–(C\textsubscript{3}) network,\textsuperscript{7} respectively. The result
shows that the turbostratic CN structure is nearly to the mesoporous carbon nitride reported
by Vinu's\textsuperscript{8} and the one in bulk by Gao's group\textsuperscript{6}, who used the same kind of carbon nitride
precursor. The O 1s core level peak at 530.0 eV comes from Ti-O-Ti linkages in TiO\textsubscript{2} (Figure
S1c), which is consistent with that of the reports.\textsuperscript{9,10} The pair of peaks of Ti 2\textit{p}\textsubscript{3/2} and 2\textit{p}\textsubscript{1/2}
appeared at 458.7 and 464.4 eV, respectively, which can be assigned to Ti\textsuperscript{4+} 2\textit{p} peaks of
TiO\textsubscript{2}\textsuperscript{9,10} (Figure S1d).
Figure S1. XPS spectra of CN deposited TiO$_2$ nanotube array: (a) C 1s; (b) N 1s; (c) O 1s; (d) Ti 2p.
**Fig. S2.** The FT-IR of the CN deposited TiO$_2$ nanotube array (deposition time is five minutes).

**Figure S3** DRS spectrum of the CN polymer / TNT array (a) and the plain TNT array (b) (deposition time is five minutes).
**Supplementary References.**


