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_4F 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_4F, 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 (≧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.

Charge: $Q=I\cdot t$ (1-1)

Number of electrons: $N=Q/e= It /e$ (1-2)

$$n = N/N_0 \qquad\qquad (1\text{-}3)$$

$$C_2H_8N_2 + 12e^- \rightarrow C_3N_4 + CH_4 + 6H_2 \qquad (1\text{-}4)$$
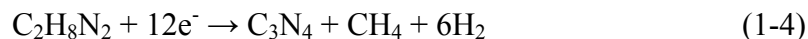
Using formula (1-1), (1-2), (1-3) and equation (1-4), we can calculate the amount of C-N polymer with different deposited time according to the below formula:

$$m_{(C3N4)} = M_{(C3N4)}It/12eN_0 \qquad (1\text{-}5)$$

Here, $I = 0.001$ A; $e = 1.6 \times 10^{-19}$ C; $N_0 = 6.02 \times 10^{23}$ mol^{-1}; $M_{(C3N4)} = 92.06$ g/mol

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

Deposited time, t (min)	2.5	5.0	10.0	30.0
Amount of C_3N_4, m (mg)	0.012	0.024	0.048	0.143
Unit amount of C_3N_4, m/S* (mg/m^2)	24	48	96	287

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

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 . 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,[5] and the peak at 286.3 eV is attributed to the sp^2 C atoms bonded to N inside the aromatic structure. We assign the peak at 288.4 eV to the sp^3 C–N bond of the sp^3 bonded composition.[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[5] and the nitrogen surrounded by an amorphous N–(C)$_3$ network,[7] respectively. The result shows that the turbostratic CN structure is nearly to the mesoporous carbon nitride reported by Vinu's[8] and the one in bulk by Gao's group[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$_2$ (Figure S1c), which is consistent with that of the reports.[9,10] The pair of peaks of Ti 2$p_{3/2}$ and 2$p_{1/2}$ appeared at 458.7 and 464.4 eV, respectively, which can be assigned to Ti^{4+} 2p peaks of TiO$_2$[9,10] (Figure S1d).
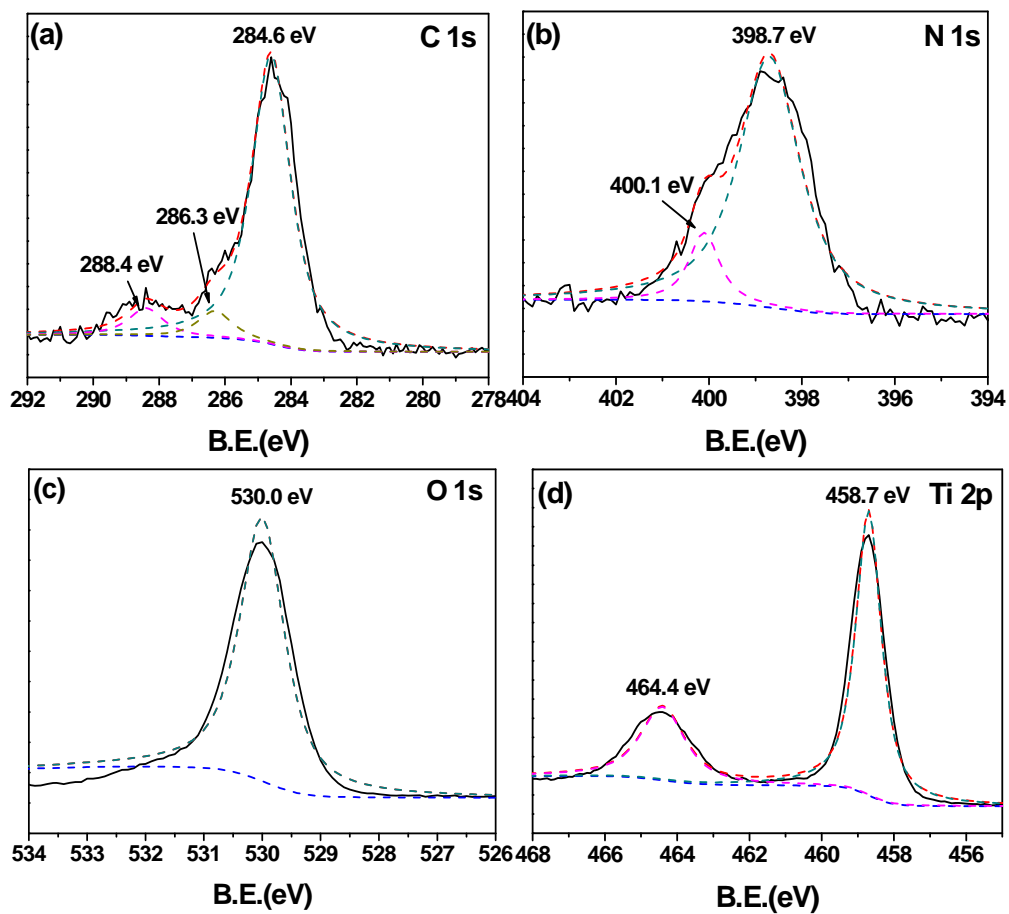
Figure S1. XPS spectra of CN deposited TiO_2 nanotube array: (a) C 1s; (b) N 1s; (c) O 1s; (d)
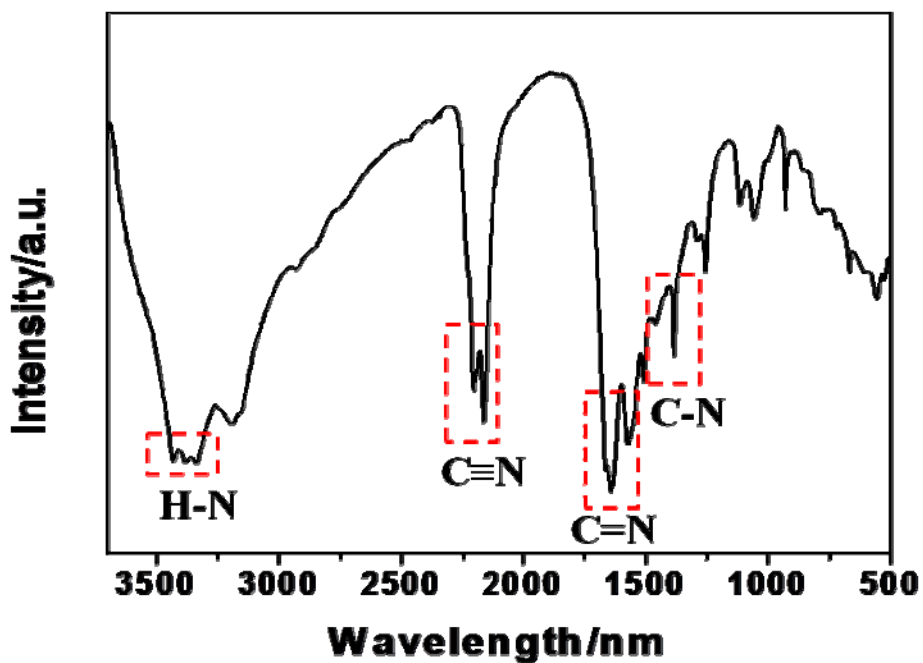
Ti 2p.

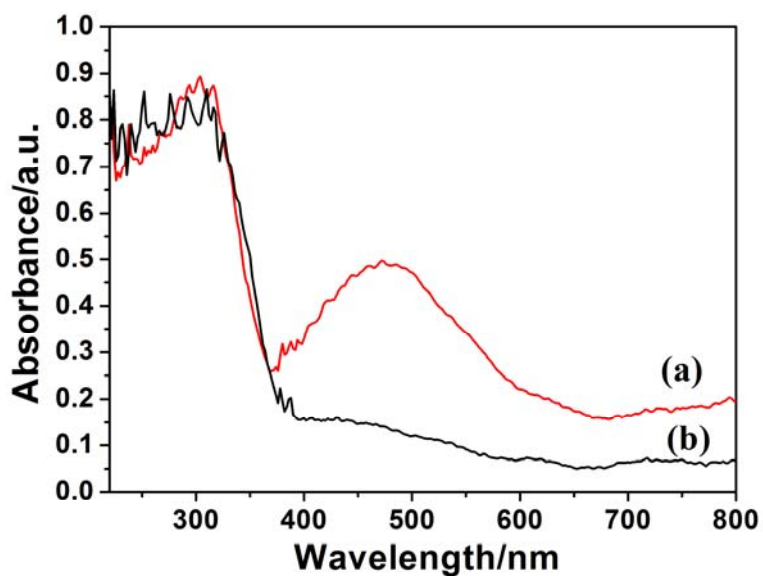**Fig. S2.** The FT-IR of the CN deposited TiO_2 nanotube array (deposition time is five minutes).

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

Supplementary References.

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