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Controlled oxygen doping in highly dispersed Ni-loaded g-C₃N₄ nanotubes for efficient photocatalytic H₂O₂ production

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Abstract

Hydrogen peroxide (H₂O₂) is both a key component in several industrial processes and a promising liquid fuel. H₂O₂ can be produced by solar photocatalysis as a suitable strategy to convert and store solar energy into chemical energy. Here we report an oxygen-doped tubular g-C₃N₄ with uniformly dispersed nickel nanoparticles for efficient photocatalytic H₂O₂ generation. The hollow structure of the tubular g-C₃N₄ provides a large surface with a high density of reactive sites and efficient visible light absorption during photocatalytic reaction. The oxygen doping and Ni loading enable a fast separation of photogenerated charge carriers and a high selectivity toward the two-electron process during the oxygen reduction reaction (ORR). The optimized composition, Ni₄%/O₀.₂tCN, displays an H₂O₂ production rate of 2464 μmol g⁻¹·h⁻¹, which is eightfold higher than that of bulk g-C₃N₄ under visible light irradiation (λ > 420 nm), and achieves an apparent quantum yield (AQY) of 28.2% at 380 nm and 14.9% at 420 nm.
**Keywords:** carbon nitride; nanotubes; nickel nanoparticles; photocatalysis, H$_2$O$_2$

1. Introduction

Hydrogen peroxide is an important industrial raw material used among others as an eco-friendly oxidant for industrial synthesis, pulp bleaching and wastewater treatment, with a global annual demand of over 4 million tons.\[1-4\] Besides, H$_2$O$_2$ is also a promising liquid fuel that is safer and easier to store than compressed hydrogen.\[5,6\] At present, H$_2$O$_2$ is industrially produced mainly through the anthraquinone method, which is an energy-intensive process requiring large amounts of organic solvent.\[7\] Therefore, the development of cost-effective and environmentally friendly strategies for the large scale production of H$_2$O$_2$ is a worthwhile endeavour. In this scenario, the production of H$_2$O$_2$ using solar photocatalysis has received increased attention in recent years.\[8,9\]

Several photocatalysts have been applied for H$_2$O$_2$ generation, including titanium dioxide\[10,11\], graphitic carbon nitride (g-C$_3$N$_4$)\[12,13\] and bismuth vanadate\[14\], to cite a few. Among them, g-C$_3$N$_4$ is particularly interesting as a metal-free, non-toxic and chemically stable material that has shown excellent potential not only for H$_2$O$_2$ generation but also for hydrogen generation and wastewater treatment, among others. However, the low surface area, moderate light absorption, rapid recombination of the photogenerated electron-hole pairs and low photocatalytic reaction selectivity towards H$_2$O$_2$ generation limits the cost-effective use of g-C$_3$N$_4$ for photocatalytic H$_2$O$_2$ production. To overcome these limitations, several strategies have been developed, including tuning the g-C$_3$N$_4$ morphology, extrinsically doping it, and forming heterojunctions through the loading of a co-catalyst.\[15-19\]

It is well known that the morphology and nanostructure of g-C$_3$N$_4$ largely affect its photocatalytic performance. To date, several g-C$_3$N$_4$ morphologies, such as nanosheets,\[20\] nanospheres,\[21\] nanorods,\[22\] nanofibers\[23\] and nanotubes\[24\] have been prepared. Among them, nanotubes with a one-dimensional hollow structure offer particularly large surface areas, high light absorption and fast electron transport to optimize photocatalytic performance.

Beyond controlling its morphology, the proper doping of g-C$_3$N$_4$ is critical to adjust its band structure and charge carrier concentration towards enhancing light absorption and promoting charge injection.\[25,26\] Dopants such as oxygen and phosphorus can not only adjust the valence band
structure of the catalyst and improve the separation efficiency of photogenerated electrons and holes, but also improve the selectivity of the OER toward the two-electron pathway.[27,28]

The introduction of a co-catalyst on the surface of g-C$_3$N$_4$ is an effective strategy to improve photocatalytic performance by increasing the charge separation ability. Various noble metal co-catalyst, such as Pt, Pd, Au, have been demonstrated to promote hydrogen evolution performance.[29–33] Nevertheless, the high cost of noble metals and the moderate H$_2$O$_2$ production rates reached limit the cost-effectiveness of the process. Thus, the development of co-catalysts based on abundant and low-cost elements, such as MoS$_2$, Ni, NiP or CoP, [34–37] that provide an efficient and high rate photocatalytic H$_2$O$_2$ production is highly desirable.

In this study, we detail the synthesis of hollow tubular g-C$_3$N$_4$ (tCN), demonstrate their controlled oxygen doping (OtCN), and describe their surface modification with highly dispersed nickel nanoparticles (Ni/OtCN) through a photoreduction process. Nitrogen adsorption-desorption isotherms, UV–vis absorption and photoluminescence spectroscopy, and photochemical test are used to investigate charge separation and transfer abilities. Besides, rotating ring disk electrode analysis, active species capture experiments and the DFT calculations are used to analyze the mechanism for H$_2$O$_2$ generation. With the unique 1-D hollow structure, high charge separation efficiency and excellent reaction selectivity during ORR process Ni/OtCN achieved outstanding H$_2$O$_2$ photocatalytic generation performance.

2. Experimental

2.1. Preparation of tubular g-C$_3$N$_4$ precursor (C-M)

g-C$_3$N$_4$ nanotubes were prepared by a self-assembly method using melamine (99%, Acros Organics) and cyanuric acid (99%, Acros Organics). Typically, 1 g melamine and 1 g cyanuric acid were separately added into 300 ml deionized water under stirring at 80 °C for about 10 minutes until completely dissolved. Then the melamine solution was slowly added to the cyanuric acid solution under homogeneous stirring, and let it self-assemble at 80 °C for 1.5 hours. The product was centrifuged and washed twice with 80 °C deionized water to remove the unassembled melamine and cyanuric acid. The filtered product was re-dispersed in deionized water and then settled at room temperature for 12 hours. Then the supernatant was removed to obtain a flocculent precipitate. The
precipitate was then freeze-dried for 48 hours to obtain the g-C$_3$N$_4$ precursor that we will refer to as C-M.

2.2. Preparation of O-doped tubular g-C$_3$N$_4$ (OtCN) and bulk g-C$_3$N$_4$ (bCN)

The OtCN was prepared by a two-step heating process. In detail, 2 g C-M was introduced into a lidded porcelain crucible and calcined at 520 °C for 2h with a temperature increase rate of 2 °C·min$^{-1}$ under Ar atmosphere. Then the product was mixed with the proper amount (0 g, 200 mg, 400 mg, 600 mg, or 800 mg) of ammonium persulfate (98%, Sigma) and calcined again at 520 °C for 2h with a temperature ramp of 5 °C·min$^{-1}$. The products were named O$_x$tCN, with $x$=0, 0.1, 0.2, 0.3, or 0.4 for the different amounts of ammonium persulfate introduced. The bulk g-C$_3$N$_4$ (bCN) was prepared through a similar method but replacing the C-M with melamine and adding no ammonium persulfate.

2.3. Preparation of Ni/OtCN, Au/OtCN and Pt/OtCN

100 mg of OtCN was added into 100 ml deionized water containing 10 ml triethanolamine (99%, Acros Organics), 8.5 mg nickel acetate tetrahydrate (99%, Acros Organics), and 500 mg sodium hypophosphite (99%, Sigma), and the solution was sonicated for 30 min. Afterwards, argon was bubbled into the solution for 30 min to displace the oxygen. Then the solution was irradiated with UV-vis light (300 W Xe lamp) under continuous stirring and argon bubbling for 30 min. The product was centrifuged and washed 3 times with water and ethanol (90%, Acros Organics) and finally dried under vacuum for 6h. The sample was named Ni$_{2x}$/OtCN. Samples with higher Ni concentration, Ni$_x$/OtCN ($x$=4%, 6% and 8%), were prepared using the same procedure but adding the proper higher amount of nickel acetate. Au/OtCN and Pt/OtCN samples were also prepared by this photo-deposition method using H$_2$PtCl$_6$·6H$_2$O (99%, Acros Organics) and HAuCl$_4$·4H$_2$O (99%, Acros Organics) precursors and irradiating the samples with UV light for 1 h.

3. Results and discussions

3.1. Structural and chemical properties of oxygen-doped tubular g-C$_3$N$_4$ and the Ni-loaded composite

Oxygen-doped tubular carbon nitride samples loaded with Ni nanocrystals (Ni/OtCN) were obtained through a 4-step process involving the synthesis of the carbon nitride precursor from the
combination of melamine and cyanuric acid in water, annealing under argon at 520 °C, oxygen
doping using ammonium persulfate, and photo-deposition of Ni (Figure 1).

![Figure 1. Schematic illustration on the synthesis of Ni/OtCN samples.](image)

Because the water solubility of melamine and cyanuric acid is very low at room temperature, the two
components were dissolved at 80 °C to ensure their full and uniform dispersion before self-assembly.
The assembly is driven by the hydrogen bond formation between the amino group on melamine and
the hydroxyl group on cyanuric acid. To determine the optimum precursor composition, materials
with different melamine and cyanuric acid molar ratios (1:2, 1:1 and 2:1) were prepared for
comparison. SEM analysis of the obtained precursors (Figures 2a and S1) showed the 1:1 ratio to
provide the best-defined nanorod structures, with a diameter in the range 300-600 nm and lengths
of 15-30 µm. This result is consistent with the equal number of functional groups of both molecules,
thus assembling at a 1:1 molar ratio. While the 1:2 and 2:1 ratios also resulted in nanorod-like
structures, they showed poor uniformity and presented a large amount of unassembled precursor on
their surfaces.

Once the self-assembly process was completed, the material was washed with hot water to remove
the residual not-assembled precursors. To prevent agglomerating during the drying process, samples
were freeze-dried, which yielded dried materials with high porosity, as observed in Figure S2. The
freeze-drying step was demonstrated as particularly important because an extensive agglomeration
of the nanorods results in a high sintering and very notable loss of porosity during the posterior
annealing step at 520 °C.
To minimize the damage to the nanostructure during the thermal polymerization of the C-M precursor, the annealing and oxygen doping of the material was divided into two steps. The first annealing step at 520 °C used a relatively low heating rate of 2 °C·min⁻¹. After this step, samples were combined with a proper amount of ammonium persulfate and the mixture was annealed again at 520 °C for two additional hours using a temperature ramp of 5 °C·min⁻¹. This second annealing step completed the polymerization process. Besides, during the annealing process, the ammonium persulfate releases ammonia, sulfur dioxide, and oxygen, which partially react with the polymerizing carbon nitride thus regulating its surface oxygen content. After the two-step thermal polymerization at 520 °C, the nanorod precursor was turned into g-C₃N₄ nanotubes that maintained approximately the same size as the precursor nanorods (Figure 2b).

The annealed and oxygen-doped samples, OtCN, were dispersed in a solution containing nickel acetate tetrahydrate to be loaded with nickel nanoparticles through a photodeposition process. As a result, as observed in Figure 2c, uniformly and highly dispersed Ni nanoparticles were grown on the surface of the OtCN. Figure S3 provides results from the EDX analysis of Ni₄%O₀.2tCN showing the weight percentage of O and Ni to be 2.1 % and 3.2 %, respectively.

TEM analysis of OtCN samples confirmed the tubular structure of the products and further showed the nanotube walls to have a porous structure (Figure 2d). The tubular structure of OtCN was thus significantly different from that of bulk g-C₃N₄ (bCN) produced from directly annealing the melamine (Figure S5a). TEM images of the Ni/OtCN samples also confirmed the homogeneous distribution of Ni nanoparticles and showed their size to be in the range 20-60 nm (Figure 2e). HRTEM micrographs revealed that the selected nanoparticles had a crystal phase matching the Ni cubic phase (space group=FM3-M) with a=b=c=3.5241 Å. (Figure 2f). EELS chemical composition maps obtained on the Ni/OtCN nanotubes displayed a uniform distribution of O, N and C and the presence of Ni-rich regions corresponding to the Ni nanoparticles.
Figure 2. (a) SEM image of the C-M precursor. (b) SEM image of OtCN. (c) SEM image of Ni/OtCN. (d) TEM image of OtCN. (e) TEM image of Ni/OtCN. (f) HRTEM micrograph obtained on a representative region of the Ni/OtCN nanostructures. On the top right, we show a magnified detail (top right) of the orange squared region in the HRTEM image and its corresponding indexed power spectrum (bottom right) which reveals that this nanoparticle has a crystal phase in agreement with the Ni cubic phase (space group=FM3-M) with \(a=b=c=3.5241\ \text{Å}\), visualized along its [011] zone axis. (g) HAADF STEM general detail of the Ni/OtCN catalyst, showing the presence of Ni nanoparticles as bright spots. EELS chemical composition maps were obtained on the red squared area of the STEM micrograph. Individual composition maps were obtained by using: (h) Individual Ni \(L_{2,3}\)-edges at 855 eV (pink), (i) C K-edges at 284 eV (blue), (j) N K-edges at 401 eV (red) and (k) O K-edges at 532 eV (green), as well as their composites for C-N-O and Ni-C-N-O.

Figure 3a displays the XRD patterns of \(\text{O}_{0.2}\text{tCN}, \text{Ni}_x/\text{O}_{0.2}\text{tCN}\) and a reference bCN. The main diffraction peaks at about 13.1° and 27.4° observed from all the samples are assigned to the (100) and (002) family planes of g-C\(_3\)N\(_4\), respectively. Compared with bCN, the (002) peak of OtCN samples shows a slight shift from 27.4° to 27.2° which is a signature of an increase of the interplanar distance associated with the presence of oxygen.\(^{38,39}\) Besides, the (002) diffraction peak of OtCN is broader and weaker than that of bCN, which is attributed to the tubular structure of OtCN. The samples
containing Ni show no alteration of the g-C$_3$N$_4$ diffraction peaks compared with OtCN, which indicates that the loading of Ni has no effect on the OtCN structure. Meanwhile, Ni/OtCN samples display two additional XRD peaks at 44.3° and 51.5° that are assigned to the (111) and (200) family planes of cubic nickel. The intensity of these peaks correlates with the amount of Ni introduced, proving the successful loading of controlled amounts of nickel.

FTIR spectroscopy was used to gain further insight into the structure of the material. As shown in Figure 3b, all OtCN materials displayed the fingerprints of g-C$_3$N$_4$, including the absorption peak at 812 cm$^{-1}$ that corresponds to the out-of-plane bending of the triazine units, and the range of peak at 1200–1600 cm$^{-1}$ that are related to the stretching modes of C-N in the aromatic heterocyclic rings. Besides, OtCN samples displayed FTIR peaks at 1235 and 1075 cm$^{-1}$, which intensity increased with the amount of ammonium persulfate used during the synthesis. These peaks are associated with the stretching mode of C-O-C group.$^{[27,40]}$

Figure 3c displays the UV–vis diffuse reflectance spectra of the different samples. The absorption edge of OtCN samples presented an obvious red-shift compared with bCN. This redshift was accentuated with the increase of the oxygen content. As shown in Figure 3d, the band gaps of bCN and OtCN samples, calculated according to Kubelk-Munk function, shifted from 2.73 eV for bCN, to 2.56 eV for O$_{0.4}$tCN. Besides, the presence of oxygen resulted in a notable enhancement of the Urbach tail, which is associated with the presence of defects as a result of oxygen doping.$^{[27,39]}$ As expected from the metallic character of the introduced Ni nanoparticles, the Ni/OtCN composites presented a strong absorption in the visible range of the spectra, which was enhanced with the increasing contents of Ni, from 2 to 8%. On the other hand, the presence of Ni did not result in a shift of the OtCN absorption edge.

Mott-Schottky analysis was used to further investigate the band structure of the samples (Figure S4). The flat band potentials of bCN and OtCN were obtained from the fitting of the Mott-Schottky plots and were used to estimate the position of the conduction band minimum (assuming it is ca. 0.1 eV above the flat band)$^{[41][42]}$ and valence band maximum (considering $E_g = E_{vb} - E_{cb}$).$^{[43]}$ Figure 3e displays the schematized band structure experimentally determined from bCN and OtCN samples.

Figure 3f displays the nitrogen adsorption-desorption isotherms of bCN and O$_{0.2}$tCN nanotubes. Both samples exhibit type IV isotherms with H3 hysteresis loops, indicating the presence of a mesoporous
structure. As shown in Table S1, the specific surface area (SSA) of O$_{0.2}$tCN nanotubes was 124 m$^2$·g$^{-1}$, which is over six-fold larger than that of bCN (18.7 m$^2$·g$^{-1}$). The calculated pore size distribution of the two samples is shown in Figure S5b. As expected from SEM images, the pore volume of OtCN, 0.97 cm$^3$·g$^{-1}$, was significantly larger than that of bCN, 0.19 cm$^3$·g$^{-1}$.

![Figure 3](image)

**Figure 3.** (a) XRD pattern of bCN, O$_{0.2}$tCN and Ni$_x$/O$_{0.2}$tCN (x=2%, 4%, 6% and 8%). (b) FTIR spectra of bCN and O$_{0.2}$tCN. (c) UV–Vis absorption spectra of bCN, O$_{0.2}$tCN and Ni$_4$/O$_{0.2}$tCN. (d) plot of the band energy spectra and (e) band structure alignments for the bCN and O$_{0.2}$tCN samples. (f) N$_2$ adsorption-desorption isotherms of bCN and O$_{0.2}$tCN.

Figure 4 displays the XPS spectra of bCN, O$_{0.2}$tCN, and Ni$_4$/O$_{0.2}$tCN samples. The high-resolution C 1s XPS spectra showed three main contributions at 288.2 eV, 286.5 eV, and 284.8 eV, which were assigned to C-(N$_3$), C–NH$_x$ and C–C=C, respectively.$^{[40]}$ Besides, the OtCN samples displayed a fourth C 1s peak 288.5 eV corresponding to C-O obtained from the replacement of N atoms by O in the CN heterocycles. All samples displayed the presence of oxygen at their surface, including the bCN. The high-resolution O 1s XPS spectrum of bCN was fitted with two peaks at 531.7 eV and 533.1 eV, which were associated with adsorbed oxygen-containing species such as water, O$_2$, OH$^-$ groups and even CO$_2$. $^{[38]}$ Besides, samples O$_{0.2}$tCN and Ni/O$_{0.2}$tCN displayed an additional contribution at 530.7 eV which is assigned to the C-O bond. Additionally, a peak at 529.7 eV was identified in the XPS spectrum of Ni/O$_{0.2}$tCN, and it was assigned to oxygen within a nickel oxide chemical environment created by the
surface oxidation of the Ni nanoparticles. The high-resolution N 1s XPS spectra of bCN, O$_{0.2}$tCN and Ni$_{4\%}$/O$_{0.2}$tCN was fitted with three peaks at binding energies of 398.1 eV, 499.4 eV, and 400.5 eV, which were assigned to N-(C$_2$), N-(C$_3$) and N-H, groups of the heptazine framework, respectively. Finally, the high-resolution Ni 2p XPS spectrum of Ni/OtCN was fitted with three doublets, corresponding to metallic Ni (2p$_{3/2}$ at 851.6 eV), Ni $^{2+}$ (2p$_{3/2}$ at 855.8 eV) and a Ni $^{2+}$ shake-up satellite (2p$_{3/2}$ at 860.4 eV).[44]

The EPR spectra of bCN and OtCN samples are displayed in Figure 4f. The Lorentzian absorption line at $g = 2.0027$ is a fingerprint of the unpaired electrons of the sp$^2$ hybridized C atoms in the aromatic rings.[27,38] The EPR signal of the OtCN sample is significantly less intense than that of bCN, which is consistent with the partial replacement N by O atoms, thus decreasing the number of lone pair electrons. Overall, the above experimental results confirmed the presence of O within OtCN replacing N atoms.

Figure 4. (a) XPS survey spectra. (b-d) High-resolution XPS spectra of (b) C 1s, (c) O 1s and (d) N 1s obtained from bCN, O$_{0.2}$tCN and Ni$_{4\%}$/O$_{0.2}$tCN samples. (e) Ni 2p XPS spectrum of Ni$_{4\%}$/O$_{0.2}$tCN. (f) EPR spectra of bCN and O$_{0.2}$tCN.

3.2. Photocatalytic $\text{H}_2\text{O}_2$ evolution

Figure 5a displays the photocatalytic $\text{H}_2\text{O}_2$ generation from bCN, O$_{0.2}$tCN, and Ni$_{4\%}$/O$_{0.2}$tCN irradiated
during 2h with visible light (λ > 420 nm). The H₂O₂ production rate of OₐtCN was fourfold higher than that of bCN (Figure 5b). Besides, when loading the OₐtCN with Ni, the H₂O₂ evolution rate further increased to reach nearly an order of magnitude higher values than bCN. Besides the Ni/OtCN sample displayed higher H₂O₂ evolution rates than noble metal co-catalyst: Au/OtCN and Pt/OtCN. The presence of Au showed an obvious improvement over OtCN, but the presence of Pt had no positive impact on the H₂O₂ generation, which is associated with a low two-electron reaction selectivity and a high H₂O₂ decomposition rate during the oxygen reduction reaction.

To find the optimal amount of oxygen doping, OₓtCN samples produced using different amounts of ammonium persulfate were tested (Figure S7a-b). OₓtCN samples containing relatively small amounts of oxygen (0 < x < 0.4) exhibited a significant enhancement of the H₂O₂ generation rate over tCN, but too high oxygen substitutions resulted in a lower H₂O₂ evolution rate. Among all the OₓtCN samples, O₀.₂tCN displayed the best H₂O₂ generation performance, 58.1 μmol·h⁻¹.

The amount of Ni was optimized by measuring the photocatalytic hydrogen peroxide generation on Niₓ/O₀.₂tCN containing different Ni concentrations (Figure S7c-d). The loading of O₀.₂tCN with a moderate amount of Ni nanoparticles largely enhanced the photocatalytic performance toward H₂O₂ generation. At a Ni loading of 2% and 4%, the H₂O₂ generation rate was improved to 88.2 μmol·h⁻¹ and 123.2 μmol·h⁻¹, which is 1.5 and 2.1 times higher than that of O₀.₂tCN, respectively. When further increasing the Ni loading to 6% and 8% the H₂O₂ production rate decreased to 101 μmol·h⁻¹ and 75 μmol·h⁻¹, respectively. This decrease of the H₂O₂ production rate at high Ni loads may be related to the aggregation of small Ni particles and the blocking of the visible light absorption of the C₃N₄ caused by an excess of Ni.

As displayed in Figure 5c, control experiments demonstrated that the presence of O₂ and light irradiation were required for the H₂O₂ generation, but the Ni₄%/O₀.₂tCN sample was able to achieve a notable photocatalytic H₂O₂ generation rate even in the absence of ethanol as a sacrificial agent. Besides, as shown in Fig. S8, Ni₄%/O₀.₂tCN also shows a prominent photocatalytic hydrogen peroxide generation performance of about 5012 μmol g⁻¹·h⁻¹ under simulated solar light, using an AM1.5 filter.

The apparent quantum yield (AQY) of the process was evaluated under 380 nm (0.53 mW·cm⁻²), 420 nm (9.91 mW·cm⁻²) and 600 nm (17.66 mW·cm⁻²) irradiation (Figures 5d and S8, and Table S2, see details in the SI). For Ni₄%/O₀.₂tCN, the AQY at 380 nm and 420 nm was estimated at 28.2% and
14.9%, respectively. Even under 600 nm light irradiation, an AQY of 0.7% was achieved for Ni$_{0.4}$/O$_{0.2}$tCN, which is consistent with UV-vis spectroscopy results (Figure 5d).

Figure 5. (a) Photocatalytic hydrogen peroxide generation on bCN, O$_{0.2}$tCN and Ni$_{4\%}$/O$_{0.2}$tCN during two hours under visible light illumination ($\lambda > 420$ nm). (b) Photocatalytic hydrogen peroxide generation rate of bCN, O$_{0.2}$tCN, Ni$_{4\%}$/O$_{0.2}$tCN, Au$_{4\%}$/O$_{0.2}$tCN and Pt$_{4\%}$/O$_{0.2}$tCN (c) H$_2$O$_2$ production on Ni$_{4\%}$/O$_{0.2}$tCN under different conditions including the use of N$_2$ instead of O$_2$, no irradiation, no ethanol and no photocatalyst. (d) Wavelength-dependent AQY of Ni$_{4\%}$/O$_{0.2}$tCN.

3.3. Charge carrier dynamics

The electrochemical characterization of the samples allowed further study of their charge transfer and transport properties. As observed in Figure 6a, bCN, O$_{0.2}$tCN and Ni$_{4\%}$/O$_{0.2}$tCN electrodes showed positive photocurrents under visible-light irradiation. Among them, O$_{0.2}$tCN showed a slightly higher photocurrent density than bCN, but the highest photocurrents were obtained with the Ni$_{4\%}$/O$_{0.2}$tCN electrode, reaching about 7.2 and 4 times higher current densities than with bCN and O$_{0.2}$tCN, respectively. These results demonstrate that O$_{0.2}$tCN and especially the presence of Ni nanoparticles significantly increase the charge separation and transfer efficiency, which is in good agreement with the photocatalysis results. [46]
Charge transfer and transport properties were further evaluated by electrochemical impedance spectroscopy (EIS). Figure 6b displays the Nyquist plot of the impedance spectra for the different materials. The larger arc associated with the transfer resistance of photo-generated charges has a significantly smaller diameter for O\textsubscript{0.2}tCN than bCN, indicating a faster charge transfer efficiency in the former. Besides, the sample containing Ni, Ni\textsubscript{4%}/O\textsubscript{0.2}tCN, presents a much smaller arc radius than the other two samples, confirming the much lower charge transfer resistance in the presence of Ni.

The photoluminescence (PL) spectra of the different samples under 300 nm light excitation is displayed in Figure 6c. The bCN sample displayed a broad and intense PL band at ca. 455 nm, which is associated with the radiative band-to-band recombination of photogenerated charge carriers within C\textsubscript{3}N\textsubscript{4}. With oxygen doping, the PL intensity significantly decreases owing to the presence of oxygen-related non-radiative recombination centers. Besides, the presence of Ni introduces additional recombination sites which further quenches the C\textsubscript{3}N\textsubscript{4} PL. As obtained from time-resolved PL (TRPL) spectroscopy (Figure 6d) and consistently with previous results, O\textsubscript{0.2}tCN and Ni\textsubscript{4%}/O\textsubscript{0.2}tCN samples exhibited much shorter average PL lifetimes (4.06 ns and 3.39 ns) than bCN (6.22 ns), demonstrating the strong electronic effect of the substitutional oxygen and nickel nanoparticles.

![Figure 6](image_url)

Figure 6. (a) Photocurrent response curves of bCN, O\textsubscript{0.2}tCN and Ni\textsubscript{4%}/O\textsubscript{0.2}tCN; (b) Electrochemical impedance
spectroscopy (EIS) Nyquist plots of bCN\(, O_{0.2}tCN\) and Ni\(4\% / O_{0.2}tCN\); (c,d) Pls spectra and TRPL decay of bCN\(, O_{0.2}tCN\) and Ni\(4\% / O_{0.2}tCN\).

3.4. Reaction mechanism

The generation of \(H_2O_2\) from the coupling of the oxygen reduction reaction (ORR) with the oxidation of an alcohol takes place through two main pathways. Both paths share the alcohol dehydrogenation reaction as hole-scavenging process and the oxygen adsorption as the initial ORR step:

\[
RCH_2OH + 2h^+ \rightarrow RCHO + 2H^+ \tag{1}
\]

\[
O_2 + * \rightarrow *O_2 \tag{2}
\]

In one possible path, the reduction of the adsorbed oxygen molecule (*\(O_2\)) can take place through a direct two-electron route:

\[
*O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{3}
\]

The second possible ORR pathway is a two-step single-electron process, that can be deglosed as follows:

\[
*O_2 + e^- \rightarrow *O_2^- \tag{3}
\]

\[
*O_2^- + H^+ \rightarrow *HOO \tag{4}
\]

\[
*HOO + e^- \rightarrow HOO^- \tag{5}
\]

\[
HOO^- + H^+ \rightarrow H_2O_2 \tag{6}
\]

Besides, the \(H_2O_2\) evolution reaction competes with the oxygen reduction to \(H_2O\), which overall involves a total of \(4e^-\) (see details in the SI):

\[
O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \tag{7}
\]

To electrochemically determine the selectivity of the catalyst toward the production of \(H_2O_2\) instead of \(H_2O\), one can estimate the electron transfer number (\(n\)) of the ORR reaction. The closer the electron transfer number is to 2, the higher the \(H_2O_2\) generation efficiency. A rotating ring-disk electrode (RRDE) was used to estimate \(n\), and thus assess the ORR pathway and \(H_2O_2\) generation efficiency. Within an RRDE, the peroxide species produced at the disk electrode are detected by the ring electrode. Thus, \(n\) can be determined from the ratio of the ring current (\(J_r\)) and the disk current
(\(I_d\)) using the following equation:

\[
n = 4\frac{I_d}{I_d + I_r/N}
\]  

(8)

where \(N\) is the collection efficiency of the ring electrode, which is estimated at 0.42 [see details in the SI]. Besides, the percentage of \(\text{H}_2\text{O}_2\) produced can be determined from:

\[
\%\text{HOO}^- = 200 \times \frac{I_r/N}{I_d + I_r/N}
\]  

(9)

The disk electrode was scanned cathodically at a scan rate of 10 mV·s\(^{-1}\), while the ring potential was set at 0.5 V vs. Ag/AgCl (Figure 7). The linear sweep voltammetry (LSV) curves of bCN achieved \(I_r = 0.40 \text{ mA·cm}^{-2}\) and \(I_d = -1.91 \text{ mA·cm}^{-2}\) at -1.0 V vs. Ag/AgCl. From these values, a transfer number \(n = 2.71\) and an \(\text{H}_2\text{O}_2\) selectivity of 60.8% was determined. Similarly, a transfer number \(n = 2.32\) and an \(\text{H}_2\text{O}_2\) selectivity of 81.2% was obtained for \(\text{O}_{0.2}\text{tCN}\), and \(n = 2.24\) and an \(\text{H}_2\text{O}_2\) selectivity of 88.9% for \(\text{Ni}_{4\%}/\text{O}_{0.2}\text{tCN}\). Overall, the RRDE measurements indicated that the oxygen doping and the presence of Ni significantly promoted the two-electron pathway for oxygen reduction to \(\text{H}_2\text{O}_2\) over the four-electron \(\text{H}_2\text{O}\) generation.

To differentiate between the one-step two-electron direct ORR (\(\text{O}_2 \rightarrow \text{H}_2\text{O}_2\)) and the sequential two-step single-electron indirect reduction (\(\text{O}_2 \rightarrow *\text{O}_2^- \rightarrow \text{H}_2\text{O}_2\)) routes, [19][18] LSV curves were analyzed in more detail (Figures 7 and S10). Notice that the bCN and \(\text{O}_{0.2}\text{tCN}\) samples exhibit two reduction plateaus at around \(-0.2\) V and \(-0.5\) V, suggesting a two-step pathway for \(\text{H}_2\text{O}_2\) generation. As observed in Figure 7b,c, no obvious \(\text{H}_2\text{O}_2\) current is detected in the ring electrode during the first plateau, in the potential range -0.2 V to -0.4 V. Only when reaching the second plateau a ring current is measured, which indicates the successive two single-electron reduction pathway. On the other hand, after loading the Ni nanoparticles, the first plateau almost disappears and the onset potential of the \(\text{H}_2\text{O}_2\) current at the ring electrode approximately matches that of the disk electrode, pointing at a one-step two-electron direct reduction pathway in \(\text{Ni}_{4\%}/\text{O}_{0.2}\text{tCN}\). Overall, these results indicate that the introduction of nickel transforms the reaction from a two-step single-electron process to a direct two-electron process.
Figure 7. LSV curves of (a) bCN, (b) O\textsubscript{0.2}tCN and (c) Ni\textsubscript{4%}/O\textsubscript{0.2}tCN obtained using an RRDE with a rotating speed of 1600 rpm and a ring biased at 0.5 V.

DFT calculations were carried out to further understand the selectivity of the ORR process on CN, OCN and Ni/OCN. The top view of the intermediates adsorption and the free energy diagram of ORR on the three materials are shown in Figure S12 and Table S4. The bCN sample is characterized by the strongest adsorption strength of ORR intermediates, which may hamper the product formation. The reduction of *OOH and *OH to form the final products, H\textsubscript{2}O\textsubscript{2} or H\textsubscript{2}O, are generally considered as the limiting ORR steps determining the reaction rate and pathway, either 2e\textsuperscript{−} or 4e\textsuperscript{−}.\textsuperscript{[17]} The change of Gibbs free energy (ΔG) for the reduction of *OOH and *OH on CN was calculated to be 1.42 eV and 1.35 eV, respectively (Figure 7d). The similar ΔG for *OOH and *OH reduction on CN points toward the simultaneous occurrence of the two-electron and four-electron pathways. With the oxygen doping, ΔG for the reduction of *OOH and *OH on OCN decreased to 0.72 eV and 0.99 eV, respectively. Besides, with the introduction of Ni, ΔG values further decreased down to 0.35 eV and 0.66 eV, respectively. The lower ΔG values obtained for OCN and particularly for Ni/OCN are consistent with experimental data obtained for OtCN and Ni/OtCN. Besides, notice that the ΔG of the reduction of *OOH is significantly lower than that of *OH reduction in OCN and Ni/OCN samples, involving a higher probability of the 2e\textsuperscript{−} ORR pathway than the 4e\textsuperscript{−}. These DFT calculation results are consistent with the experimental data obtained from the RRDE test, further demonstrating that the oxygen doping and the Ni loading incline the catalyst toward two-electron reactions, which can significantly improve the H\textsubscript{2}O\textsubscript{2} generation efficiency.
Additional experimentally of the ORR pathway were obtained by introducing a $\cdot O_2^-$ trapping agent in the solution, PBQ (1 mM). As shown in Figure S13a-c, after introducing the PBQ, the $H_2O_2$ generation rate strongly decreased for bCN and $O_{0.2}tCN$, by an 88% and 84%, respectively, demonstrating the important role played by $\cdot O_2^-$ as an intermediate during $H_2O_2$ generation process, i.e. pointing at the two-step single-electron process as the main pathway for $H_2O_2$ generation process in bCN and $O_{0.2}tCN$. On the contrary, the Ni$_{4\%}$/O$_{0.2}tCN$ sample showed just a 35% decrease of $H_2O_2$ generation in the presence of PBQ, indicating the predominance of the two-electron process over the two single-electron processes.

To further explore the reaction mechanism and determine the role of superoxide radicals in the reaction process, DMPO spin-trapping EPR spectroscopy was used to determine the presence of $\cdot O_2^-$ in the surface of the photocatalyst. As shown in Figure S13d, after irradiating bCN with visible light for 3 min with DMPO and methanol, four characteristic EPR features were observed. These DMPO-$\cdot O_2^-$ characteristic EPR peaks were much more intense for the $O_{0.2}tCN$ sample under the same conditions, indicating that $O_{0.2}tCN$ can generate larger amounts of $\cdot O_2^-$ during the $H_2O_2$ evolution process, which is consistent with its higher $H_2O_2$ generation rate. On the other hand, while Ni$_{4\%}$/O$_{0.2}tCN$ provided much higher $H_2O_2$ generation rates than $O_{0.2}tCN$, the $\cdot O_2^-$ characteristic EPR signal was less intense, involving significant participation of an alternative path for $H_2O_2$ generation, i.e. the direct two-electron process. This result further confirms that the direct two-electron process...
has a fundamental role in the large H₂O₂ generation rates obtained in the presence of Ni.

Stability cycles of the Ni₄%/O₀.₂tCN for H₂O₂ evolution under visible-light irradiation are displayed in Figure S14a. After 8 hours of reaction, with four two-hour cycles, the catalyst maintained over 86 % photocatalytic H₂O₂ generation activities, i.e. about 106 μmol·h⁻¹, demonstrating excellent stability and reusability. Besides, SEM and XRD analysis of the catalyst after 8 h photocatalytic H₂O₂ reaction demonstrated the morphology and crystallographic structure of the material to be stable under photocatalytic reaction conditions (Figure S14b,c).

**Conclusion**

In summary, we detailed the synthesis of hollow tubular g-C₃N₄ (tCN), and demonstrated their controlled oxygen doping (OtCN), and their surface modification with highly dispersed nickel nanoparticles (Ni/OtCN) through a photoreduction process. OtCN samples displayed a hollow tubular structure with a large specific surface area (124 m²·g⁻¹). With larger SSA and more porous structure OtCN can provide more reactive sites, improve the light absorption by the multiple diffusion and accelerate the diffusion of reactants and products on the surface, thereby significantly improving the photocatalytic performance. OtCN samples displayed a lower bandgap (2.59 eV) associated to the presence of oxygen atoms replacing N within the OtCN structure. Thus, OtCN enabled the capture of a wider range of the solar spectrum. In addition, the addition of Ni can provide additional active reaction sites and significantly promote the separation of photogenerated carriers. Based on the DFT and RRDE results, the doping with oxygen and the presence of Ni nanoparticles greatly reduced the energy barrier for H₂O₂ generation and improved the H₂O₂ selectivity from 60.8% to 88.9%, which enabled a more effective and efficient ORR towards H₂O₂ evolution. Upon absorbing a photon of proper energy, electron-hole pairs are photogenerated in bCN and OtCN. The holes in the valence band rapidly react with the sacrificial agent while electrons in the conduction band will be involved in the ORR. At the bCN surface, only part of the electrons can selectively undergo a two-step single-electron indirect reduction (O₂→*O₂→H₂O₂) two-electron process to generate H₂O₂. As for O₀.₂tCN, the selectivity of the two-electron process is enhanced, but still within a two-step single-electron indirect reduction process. After loading the Ni nanoparticles, the electrons on the conduction band of OtCN are transferred to the surface of Ni which has a lower Femi level and then reducing the
oxygen through a one-step two-electron direct reduction (O\textsubscript{2} $\rightarrow$ H\textsubscript{2}O\textsubscript{2}) route, which is more efficient for H\textsubscript{2}O\textsubscript{2} generation. Thus, the introduction of Ni could transform the reaction from a two-step single-electron process to a direct two-electron process which is more efficient and high yield. Efficient charge separation and high selective formation of H\textsubscript{2}O\textsubscript{2} during ORR process allow Ni\textsubscript{4%}/O\textsubscript{0.2}tCN to achieve an outstanding production rate up to 2464 $\mu$mol g$^{-1}$h$^{-1}$ under visible light and 5021 $\mu$mol g$^{-1}$h$^{-1}$ under simulated solar light and AQY of 28.2% at 420 nm and 14.9% at 420 nm.

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Conflict of Interest
The authors declare no conflict of interest.

Reference


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