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"Two channel" photocatalytic hydrogen peroxide production using g-C₃N₄ coated CuO nanorods heterojunction catalysts prepared via a novel molten salt-assisted microwave process

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Photocatalytic H_2O_2 production has received increasing attention as a sustainable and eco-friendly method to replace conventional anthraquinone-based and electrochemical production processes. In this work, we report a novel molten salt-assisted microwave process to synthesize g-C₃N₄ coated CuO

10 nanorods heterojunction photocatalyst with outstanding H₂O₂ production ability. XRD, UV-Vis, N₂ adsorption, SEM, TEM, XPS, EIS and PL were used to characterize the obtained catalysts. CN@CuO(4) with the largest area of heterojunction displays the highest photocatalytic H_2O_2 production ability of 6.9 mmol·L⁻¹, which is 7.4 and 16.4 times higher than that of individual g-C₃N₄ and CuO. "Two channel pathway" is proposed for this reaction system which causes the remarkably promoted H₂O₂ production

15 ability. In addition, compared with traditional polycondensation method, the catalyst prepared via molten salt-assisted microwave process exhibits larger area of heterojunction and more effective separation rate, causing the higher photocatalytic H₂O₂ production ability and stability.

Introduction

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Hydrogen peroxide (H₂O₂), as a highly efficient and green 20 oxidant, has been widely used in bleaching and disinfectant applications, such as textile, paper pulp and medical industry. H_2O_2 has the highest content of active oxygen (47% w/w) and only H₂O as the by-product.^{1,2} Besides that, H₂O₂ is also an ideal energy carrier alternative to hydrogen with the low volumetric 25 energy.^{3,4} The output potential of H₂O₂ fuel cell is 1.09 V theoretically, which is comparable with that of hydrogen fuel cell (1.23 V).⁵⁻⁷ Industrially, H₂O₂ is produced by the anthraquinone method, in which energy consumption is high because of the multistep hydrogenation and oxidation reactions. Thus this 30 method is unsuitable for the current new concept of "green, energy saving and environmentally friendly" in the chemical industry. Recently, the direct synthesis of H2O2 from H2 and O2 gases has been widely studied using noble metals as catalysts.⁸⁻¹⁰

It is considered to be an alternative and green chemistry process. 35 However, this method presents a potential explosion risk from H₂/O₂ mixtures. In contrast, photocatalytic H₂O₂ production requires only water, oxygen and visible light through twoelectron reduction from the conduction band (Reaction (1)). However, the H_2O_2 can be decomposed by reduction with e_1 ,

⁴⁰ which has caused the H₂O₂ production rate of this photocatalytic reduction method to be unsatisfactory to date (Reaction (2)).

$$O_2 + 2 H^+ + 2 e^- \longrightarrow H_2O_2$$
(1)
$$H_2O_2 + e^- \longrightarrow \bullet OH + OH^-$$
(2)

Graphitic carbon nitride (g-C₃N₄) has attracted a great deal of interest in photocatalytic applications in recent years. The

heptazine ring structure and high condensation degree make it 45 possess many advantages, such as good chemical stability, appropriate band gap energy and unique electronic structure. Since its conduction band potential (-1.3 V) is more negative than the reduction potential of O2/H2O2 (0.695 V), g-C3N4 could reduce O₂ to H₂O₂ under visible light thermodynamically.¹¹ All of 50 these make $g-C_3N_4$ to be the best candidate for photocatalytic H₂O₂ production.

In order to promote the electron utilization to reduce more O_2 molecules, the hole scavenger is usually used. However, some previous reports indicate that some photocatalysts can oxidize 55 OH⁻ to •OH by photogenerated holes.^{12,13} These •OH can combine with each other to form additional H₂O₂, thus changing the H₂O₂ generation pathway from single-channel to twochannel.^{14,15} However, the VB positions is approximately +1.6 V for g-C₃N₄. The VB holes in g-C₃N₄ are not positive enough to ⁶⁰ generate •OH.^{16,17} It is known that, for heterojunction catalyst, electrons and holes will accumulate on two components respectively by crossing the heterojunction interface. Accordingly, the oxidation ability of VB holes may be promoted.

Molten salt method is widely used in the materials synthesis 65 field in recent years because it can accelerate diffusion of constituent ions, control crystal growth and easily separate from the solid product by dissolving in water.¹⁸⁻²⁰ In general, molten salt can serve as a reaction medium for reactant dissolution and precipitation, as soft template for tailoring micro and 70 mesoporosity of the materials, and as structure-directing agent in the polycondensation and deamination reaction to obtain graphitic materials. The features of this synthesis method are related to the surface and interface energies between the

constituents and the salt, resulting in a tendency to minimize the energies by forming a specific morphology. Though the electric-resistance heating molten-salt method can be used to synthesize $g-C_3N_4$ photocatalysts, the problems of long time consuming and s high energy consumption in synthesis, large emission of harmful gas and low catalyst yield are still difficult to overcome.²¹

Recently, microwave-assisted heating synthesis has also been widely used to prepare nanomaterials.²²⁻²⁴ The microwave treatment can transfer energy from microwave to the microwave-10 absorber material which induces strong heating in minutes. When the microwave energy is absorbed by the raw material, the molecules are orderly arrangement in the electromagnetic field of the microwave. Then the high frequency reciprocating motion occurs inside the molecules of raw materials, causes the frequent 15 collisions between molecules, leading to the generation of a lot of frictional heat. Under this heating method, the raw material is rapidly heated without the presence of temperature gradient. It is reported that g-C₃N₄ can be synthesized by the microwaveassisted heating method in a few minutes, suggesting this is a 20 potential way in rapid synthesis of carbon nitride based materials.²⁵ Besides that, the catalyst yield is high and the emission of harmful gas is also low with this method. It is known that the solid-state reaction system needs a uniform reaction medium to achieve a stable and reliable condition. The molten-25 salt process can offer a unique liquid condition that is stable and

is salt process can offer a unique liquid condition that is stable and convenient for the solid-state reaction system. Thus, we hypothesize that combination two methods mentioned above should be an effective strategy to synthesize $g-C_3N_4$ based materials with high performance.

³⁰ In this work, g-C₃N₄ coated CuO nanorods heterojunction catalyst with outstanding photocatalytic H₂O₂ production ability was synthesized via a novel molten salt-assisted microwave process. Under "Z-scheme" mechanism, CuO/g-C₃N₄ heterojunction catalyst can change photocatalytic H₂O₂ sproduction pathway from "single channel" to "two channel". The possible reaction mechanism is proposed.

Experimental

Preparation and characterization

- CuO nanorods were prepared according to previous work.²⁶ In a ⁴⁰ typical process, eutectic mixture of KCl-LiCl (1:1 weight ratio) was selected as a solvent. The mixture of melamine and CuO (with a weight ratio melamine/CuO = 2, 4 and 8) were added into 100 g of eutectic salts and finely ground in a mortar, then transferred to an alumina crucible and treated by microwave for
- ⁴⁵ 30 min in a normal microwave oven (G70D20CN1P-D2, Galanz). The obtained catalyst was denoted as CN@CuO(x), where x stands for the weight ratio of melamine to CuO. Neat g-C₃N₄ was prepared following the same procedure mentioned above in the absence of CuO, and denoted as GCN. For comparison, CuO/g-
- $_{50}$ C₃N₄ heterojunction catalyst was also prepared by polycondensation method. 10g of melamine and CuO with a weight ratio of 4:1 were added into 30 mL of deionized water. The suspension was stirred for 20 min and was heated to 100 $^{\circ}\mathrm{C}$ under stirring to remove the water. The solid product was dry at
- ⁵⁵ 80 °C in oven, followed by milling and annealing at 520 °C for 2 h (at a rate of 5 °C·min⁻¹). The prepared catalyst was denoted as

CN/CuO.

The XRD patterns of the prepared samples were recorded on a Rigaku D/max-2400 instrument using Cu-K α radiation ($\lambda = 1.54$ 60 Å). The scan rate, step size, voltage and current were 0.05 °/min, 0.01°, 40 kV and 30 mA, respectively. UV-Vis spectroscopy was carried out on a JASCO V-550 model UV-Vis spectrophotometer using BaSO₄ as the reflectance sample. The morphologies of prepared catalyst were observed by using a scanning electron 65 microscope (SEM, JSM 5600LV, JEOL Ltd.). TEM images were taken on a Philips Tecnai G220 model microscope. Nitrogen adsorption was measured at -196 °C on a Micromeritics 2010 analyser. All the samples were degassed at 393 K prior to the measurement. The BET surface area (S_{BET}) was calculated based 70 on the adsorption isotherm. ICP was performed on a Perkin-Elmer Optima 3300DV apparatus. The photoluminescence (PL) spectra were measured with a fluorospectrophotometer (FP-6300) using Xe lamp as the excitation source. The electrochemical impedance spectra (EIS) were recorded using an EIS 75 spectrometer (EC-Lab SP-150, BioLogic Science Instruments) in a three electrode cell by applying a 10 mV alternative signal versus the reference electrode (SCE) over a frequency range of 1 MHz to 100 mHz. The cyclic voltammograms were measured in 0.1 Μ KCl solution containing 2.5 mM а $_{80}$ K₃[Fe(CN)₆]/K₄[Fe(CN)₆] (1:1) as a redox probe at a scanning rate of 20 mV s⁻¹ in the same three electrode cell as the EIS measurement.

Photocatalytic Reaction

The photocatalytic H₂O₂ production ability of the samples were ⁸⁵ evaluated. For these experiments, 0.2 g of photocatalyst was added to 200 mL deionized water. The suspension was dispersed using an ultrasonicator for 10 min. During the photoreaction under visible light irradiation, the suspension was exposed to a 250 W high-pressure sodium lamp with main emission in the ⁹⁰ range of 400 to 800 nm, and O₂ was bubbled at 80 mL/min through the solution. The UV light portion of the sodium lamp was filtered by a 0.5 M NaNO₂ solution. All runs were conducted at ambient pressure and 30 °C. At given time intervals, 5 mL aliquots of the suspension were collected and immediately ⁹⁵ centrifuged to separate the liquid samples from the solid catalyst. The concentration of H₂O₂ was analyzed by normal iodometric method.^{27,28}

Results and discussion

In this work, g-C₃N₄ coated CuO nanorods heterojunction ¹⁰⁰ catalyst (CN@CuO) was synthesized via a novel molten saltassisted microwave process. Compared with traditional polycondensation method, CN@CuO exhibits larger area of heterojunction and more effective separation rate. According to "Z-scheme" mechanism, not only the CB electrons of CN@CuO ¹⁰⁵ reduce O₂ to form H₂O₂, but the VB holes can oxidize OH⁻ to form •OH, which subsequently react with each other to form H₂O₂. Such "two channel pathway" causes the remarkably promoted H₂O₂ production ability.

Figure 1a shows the XRD patterns of as-prepared catalysts. ¹¹⁰ CuO matches well with standard diffraction data (JCPDS file no. 05-0661).^{29,30} GCN has two characteristic peaks, which are located at $2\theta = 13.1^{\circ}$ and 27.5° , respectively. The diffraction peak

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at 27.5° is the characteristic peak of the interlayer stacking of the aromatic segments with a Miller index of (002). The diffraction peak at 13.1° is assigned to the melon-like structure with a Miller index of (100). These two characteristic peaks are in agreement s with that reported in previous literature.¹⁶ In the case of composite materials, the crystal phase of CuO and g-C₃N₄ does not change. The diffraction peak intensities of CuO in CuO/g-C₃N₄ composite materials become weaker when increasing the mass percentage of g-C₃N₄. In addition, no other impurity peak ¹⁰ exits in the XRD patterns, indicating that CuO and g-C₃N₄ are the only two components in the composites. The CuO contents of asprepared catalysts, measured by ICP, are 52.5, 32.8 and 18.7 wt.% for CN@CuO(2), CN@CuO(4) and CN@CuO(8), respectively. The specific surface area of catalyst is an important 15 factor that determines the photocatalytic performance. To characterize the specific surface area of as-prepared catalysts, the nitrogen adsorption and desorption isotherms of GCN, CuO and heterojunction photocatalysts were measured (Figure 1b). The isotherms of all the samples are of classical type IV. The BET

 $_{20}$ specific surface areas (S_{BET}) of GCN, CuO, CN@CuO(2), CN@CuO(4) and CN@CuO(8) are calculated to be 9.5, 20.1, 17.9, 17.2 and 13.8 $m^2 \cdot g^{-1}$.



⁴⁰ Figure 1. XRD (a), N₂ adsorption (b) and UV-Vis spectra (c) of as-prepared catalysts.

The UV-Vis spectra of the as-prepared photocatalysts are shown in Figure 1c. GCN displays an absorption edge at ⁴⁵ approximately 460 nm. The band gap energy, which is calculated according to the method of Oregan and Gratzel, is 2.7 eV.³¹ CuO shows obviously improved visible light absorption ability compared with GCN. Its absorption edge is observed at 718 nm, and the corresponding band gap is estimated to be 1.72 eV. For

⁵⁰ the as-prepared heterojunction photocatalysts, benefitting from the addition of CuO, the as-prepared composite catalysts display enhanced absorption in the visible light region. The higher CuO content, the stronger light absorption.

The morphologies of the representative samples were ⁵⁵ examined by using SEM analysis. Figure 2a indicates that asprepared GCN is composed of a large number of irregular particles. Those particles exhibit layer structure that is similar to analogue graphite. In Figure 2b, the nanorod-like CuO with 1~2 µm long is observed. Besides that, it is noted that the surface of ⁶⁰ CuO is smooth. For CN@CuO(4) (Figure 2c), it can be seen that the nanorod-like CuO is coated by the GCN. The CuO surface is not as smooth as shown in Figure 2b but very rough, confirming the GCN coating. High-resolution transmission electron microscopy (HRTEM) analysis was performed to get information ⁶⁵ on the microstructure of as-prepared CN@CuO(4) (Figure 2d). The observed lattice fringe spacing of 0.324 nm corresponds to the (002) crystal plane of g-C₃N₄ (JCPDS 87-1526). The lattice fringe of 0.252 nm in the HRTEM image should be assigned to the (111) plane of CuO.³² Smooth and intimate interface is clearly ⁷⁰ observed between GCN and CuO in Figure 2d, which confirms the formation of g-C₃N₄/CuO heterojunction. Such strong interaction can result in the higher interfacial charge transfer rate and H₂O₂ production ability.



Figure 2. SEM images of GCN (a), CuO (b), CN@CuO(4) (c) and HRTEM of CN@CuO(4) (d).



110 Figure 3. XPS spectra of as-prepared catalysts in the region of C 1s (a), N 1s (b), Cu 2p (c) and VB XPS (d).

XP spectra are used to investigate the structure of the asprepared catalysts. In Figure 3a, the spectra of both two catalysts ¹¹⁵ in C 1s region can be fitted with two contributions which located at 284.6 and 288.6 eV. The sharp peak around 284.6 eV is

attributed to the pure graphitic species in the CN matrix. The peak with binding energy of 288.6 eV indicates the presence of sp^2 C atoms bonded to aliphatic amine (-NH₂ or -NH-) in the aromatic rings.^{33,34} In Figure 3b, the main N 1s peak of GCN 5 located at 398.2 eV can be assigned to sp²-hybridized nitrogen (C=N-C), thus confirming the presence of sp²-bonded graphitic carbon nitride. The peak at a higher binding energy of 399.9 eV is attributed to tertiary nitrogen (N-(C)₃) groups.^{35,36} For GCN@CuO(4), a 0.3 eV shift to higher binding energy is 10 observed, indicating the decreased electron density of nitrogen atoms. In Cu 2p region (Figure 3c), the CN/CuO shows the main binding energy of 934 eV, which is assigned to the Cu²⁺ of $CuO.^{37}$ In the case of CN@CuO(4), the binding energy in Cu 2p region shifts to 933.7 eV, hinting the increased electron density of 15 Cu atoms. Combined with the binding energy shift in N 1s region, it is deduced that the strong electronic interaction between the g-C₃N₄ and CuO exists in CN@CuO(4). The electron-rich g-C₃N₄ transfer of partial electrons to CuO, leading to the change of electron densities in N 1s and Cu 2p regions. Figure 3d shows the $_{\rm 20}$ VB XPS of GCN and CuO. The $E_{\rm VB}$ is +1.45 and +2.36 V for GCN and CuO, respectively. Combine with the UV-Vis result, it is deduced that the E_{CB} for GCN and CuO is -1.25 and +0.64 V.



These results are close to the previous report.^{3,38}

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Figure 4. PL (a) and EIS (b) spectra of as-prepared catalysts.

- PL and EIS were used to characterize charge-carrier migration and confirm the interfacial charge transfer effect of the asprepared heterojunction catalysts. Figure 4a shows the PL spectra of as-prepared catalysts using excitation at 255 nm. For GCN, broad PL band around 460 nm is observed with the energy of 40 light approximately equal to the band gap of g-C₃N₄. CuO exhibits emission peak which intensity is lower than that of GCN. In the case of as-prepared heterojunction catalysts, the PL spectra show the similar shape to that of GCN, whereas the intensities are obviously decreased. CN@CuO(4) shows the lowest PL intensity,
- ⁴⁵ hinting its most effective separation rate of electrons and holes. This is reasonable because, with this g-C₃N₄/CuO mass ratio, g-C₃N₄ and CuO have the approximate S_{BET} (9.5 and 20.1 m²·g⁻¹ for GCN and CuO, and the yield of GCN is approximately 50% by this microwave process). They can contact with each other as
- ⁵⁰ much as possible, leading to the formation of the maximum area of the heterojunction. As shown in Figure 4b, the as-prepared heterojunction catalysts exhibit a decreased arc radius compared to that of GCN and CuO. In general, the radius of the arc in the EIS spectra reflects the reaction rate on the surface of the
- ⁵⁵ electrode.³⁹ The reduced arc radius indicates a diminished resistance of the working electrodes, suggesting a decrease in the solid-state interface layer resistance and the charge transfer resistance across the solid-liquid junction on the surface between

g-C₃N₄ and CuO.^{40,41} CN@CuO(4) displays the smallest arc ⁶⁰ radius, confirming that a more effective separation of photogenerated electron-hole pairs and a faster interfacial charge transfer occur on the CN@CuO(4) surface.

Figure 5a displays the photocatalytic H₂O₂ production ability over as-prepared catalysts. It is clearly seen that the H₂O₂ 65 concentration of as-prepared catalyst increases with time for about 4 h when it reaches a constant level. This level corresponds to the steady-state where the rate of H₂O₂ production is equal to the rate of decomposition.^{42,43} GCN and CuO display low H₂O₂ concentration, 0.93 and 0.42 mmol·L⁻¹. In the case of as-prepared 70 heterojunction catalyst, the H₂O₂ production ability promotes obviously. CN@CuO(4) shows the highest H_2O_2 equilibrium concentration of 6.9 mmol·L⁻¹, which is 7.4 and 16.4 times higher than that of GCN and CuO. Figure 5b shows the H₂O₂ production ability of CN@CuO(4) under different reaction conditions. The 75 addition of AgNO₃ (10 mmol·L⁻¹) as an electron scavenger should suppress the H₂O₂ production ability. However, interestingly, the H2O2 production ability of CN@CuO(4) increases to 7.7 mmol· L⁻¹ when AgNO₃ is added. Still 3.2 mmol· L^{-1} H₂O₂ is obtained in the absence of O₂. These results indicate 80 that H₂O₂ is not only produced by O₂ reduction over CN@CuO(4). The detailed explanation is given below. The H₂O₂ concentration is trivial in the absence of photocatalyst, indicating that H_2O_2 is produced via a photocatalytic process. No H_2O_2 is generated when using dimethylformamide (DMF, aprotic solvent) 85 instead of water, confirming that H₂O is necessary as the proton source for H₂O₂ production.



Figure 5. The photocatalytic H_2O_2 production ability over asprepared catalysts (a) and H_2O_2 production ability of CN@CuO(4) under different reaction conditions (b).



Figure 6. The influence of various scavengers on the H_2O_2 production ability over as-prepared catalysts (a) and the sketch map of double charge transfer mechanism and Z-scheme ¹¹⁰ mechanism over heterojunction catalyst (b).

Besides the O_2 reduction to form H_2O_2 , another channel to produce H_2O_2 is reported by Dong et al.¹⁵ It is reported that photogenerated holes can oxidize OH^- to •OH ¹¹⁵ thermodynamically, as shown in Reaction (3). Two •OH can form H_2O_2 though combination with each other, as shown in Reaction (4). In order to investigate the reaction mechanism of as-prepared heterojunction catalyst, the influence of various scavengers on the H_2O_2 production ability is carried out and shown in Figure 6a. AgNO₃ and EDTA-2Na are used as the electrons (e⁻) and hole ⁵ (h⁺) scavenger, respectively.⁴⁴ When AgNO₃ is added to trap the electrons, H_2O_2 is still formed with the concentration of 0.3 mmol·L⁻¹ over CuO. It is known that the redox potential for •OH/OH⁻ is +1.99 V.⁴⁵ Whereas the VB of CuO is +2.36 V. The

- VB holes in CuO is positive enough to generate •OH. Therefore, ¹⁰ H₂O₂ should be produced by Reaction (4). When EDTA-2Na is added to trap the holes, although the utilization rate of electrons is promoted, the H₂O₂ equilibrium concentration over CuO decreases to 0.12 mmol·L⁻¹. This is probably due to the close position between reduction potential of O₂/H₂O₂ (+0.695 V) and ¹⁵ CB of CuO (+0.64 V), leading to the poor driving force. In the case of GCN, the CB and VB positions are -1.25 V and +1.45 V, respectively. Thus, when AgNO₃ is added, no H₂O₂ is produced due to that the VB holes in g-C₃N₄ are not positive enough to generate •OH. Without any doubt, the H₂O₂ production ability of ²⁰ g-C₃N₄ is obviously promoted by adding EDTA-2Na to trap the
 - $h^+ + OH^- \longrightarrow \bullet OH$ (3)

holes

•OH + •OH \longrightarrow H₂O₂ (4)

In general, there are two typical working mechanisms for heterojunction catalyst, double charge transfer mechanism and Zscheme mechanism, as shown in Figure 6b.⁴⁶⁻⁴⁸ If CN@CuO(4) ²⁵ heterojunction catalyst follows the double charge transfer mechanism, holes should be transferred to the VB of g-C₃N₄. When CB electrons is trapped by AgNO₃, VB holes in g-C₃N₄ are not positive enough to generate •OH. Thus H₂O₂ should be not produced. However, the H₂O₂ with the concentration of 7.7 ³⁰ mmol·L⁻¹ is formed over CN@CuO(4) when AgNO₃ is added. Similarly, if CN@CuO(4) heterojunction catalyst follows the double charge transfer mechanism, the electrons should be transferred to the CB of CuO. The H₂O₂ production ability should be low by adding EDTA-2Na to trap the holes because of the ³⁵ poor driving force of CB electrons. Whereas, the H₂O₂

- equilibrium concentration over CN@CuO(4) is promoted to 8.9 mmol·L⁻¹ when EDTA-2Na is added. Based on the above results, it is deduced that not double charge transfer mechanism but Z-scheme mechanism with "two channel pathway" is proposed.
- ⁴⁰ Under visible light irradiation, the photogenerated electron-hole pairs are formed in both components. The electrons in the CB of CuO combine with the holes in the VB of g-C₃N₄ at the interface of the heterojunction. Therefore, the holes tend to stay in the VB of CuO and the electrons accumulate in the CB of g-C₃N₄,
- ⁴⁵ leading to the enhanced separation rate of electron-hole pairs. The CB electrons in g-C₃N₄ can reduce O_2 to form H₂O₂, as well as the VB holes in CuO can oxidize OH⁻ to form •OH, which subsequently react with each other to form H₂O₂. Such "two channel pathway" causes the remarkably promoted H₂O₂
- ⁵⁰ production ability. When AgNO₃ (or EDTA-2Na) is added to trap the electrons (or holes), the separation efficiency of catalyst is promoted, leading to the enhanced H_2O_2 production ability (Figure 6a).

In order to prove the advance of this $g-C_3N_4$ coated CuO $_{55}$ nanorods heterojunction catalyst prepared via molten salt-assisted

microwave process, CN/CuO heterojunction catalyst was also prepared by polycondensation method. Figure 7a clearly displays that the as-prepared CN/CuO is composed of bulk g-C₃N₄ and nanorod-like CuO. CuO nanorods seem to stick to the g-C₃N₄ ⁶⁰ surface. This interaction between two components is poor. Figure 7b compares the PL spectra of CN/CuO and CN@CuO(4). It can be seen that the PL intensity of CN/CuO is remarkably stronger than that of CN@CuO(4), hinting its much lower separation rate of electrons-holes. This should be due to that the cladding ⁶⁵ structure of CN@CuO(4) can form the maximum area of heterojunction, which results in an increase in the migration efficiency.



Figure 7. SEM image of CN/CuO (a), PL spectra of CN/CuO and CN@CuO(4) (b), photocatalytic H₂O₂ production ability of ⁸⁵ CN/CuO and CN@CuO(4) (c) and XPS spectra of reused CN/CuO and CN@CuO(4) in Cu 2p region (d).

Figure 7c compares the photocatalytic H₂O₂ production ability of CN/CuO and CN@CuO(4). CN/CuO shows the H2O2 90 concentration of 1.8 mmol·L⁻¹, much lower than that of CN@CuO(4) (6.9 mmol·L⁻¹). In addition, the H₂O₂ production ability for CN@CuO(4) keeps stable after 48 h reaction. Whereas, the activity for CN/CuO decreases obviously with increasing the reaction time, hinting its poor photocatalytic 95 stability. Figure 7d compares the XPS spectra of reused CN/CuO and CN@CuO(4) in Cu 2p region. The binding energies locate at 933.9 and 933.6 eV for reused CN/CuO and CN@CuO(4). Such difference in binding energy confirms that the strong electronic interaction between g-C₃N₄ and CuO in CN@CuO(4) still exist 100 after reaction. All of these results confirm that, compared with traditional polycondensation method, the g-C₃N₄ coated CuO nanorods heterojunction catalyst prepared via molten salt-assisted microwave process exhibits larger area of heterojunction and more effective separation rate, causing the higher photocatalytic 105 H₂O₂ production ability and stability.

Conclusions

In this work, g-C₃N₄ coated CuO nanorods heterojunction catalyst with outstanding photocatalytic H₂O₂ production ability was synthesized. Compared with traditional polycondensation ¹¹⁰ method, the catalyst prepared via molten salt-assisted microwave process exhibits larger area of heterojunction and more effective separation rate, causing the higher photocatalytic H₂O₂

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production ability and stability. CN@CuO(4) with the largest area of heterojunction displays the highest photocatalytic H_2O_2 production ability of 6.9 mmol·L⁻¹. According to "Z-scheme" mechanism, not only the CB electrons of CN@CuO(4) reduce O_2 s to form H_2O_2 , but the VB holes can oxidize OH⁻ to form •OH,

which subsequently react with each other to form H_2O_2 . Such "two channel pathway" causes the remarkably promoted H_2O_2 production ability.

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Notes and references

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This work reports a $g-C_3N_4$ coated CuO nanorods catalysts with outstanding photocatalytic H_2O_2 production ability via "two channel pathway".