SHORT REPORT

Fabrication of graphite-phase carbon nitride modified by phycocyanin with enhanced photocatalytic activity

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Graphite carbon nitride is a new type of semiconductor photocatalyst with unique stacking structure, physical and chemical properties. It can be used for degradation of pollutants, generation of H_2 and O_2 from water, and photocatalytic conversion of CO_2. However, the high recombination rate of photogenerated electrons and holes limits its large-scale application in the field of environment and energy. In this study, a series of the novel graphite-phase carbon nitrides (MCNxP, x = 5, 10, 20, 30) with different carbon doping contents in response to visible light were firstly prepared by thermal condensation polymerization using melamine and phycocyanin as precursors. The spectroscopic analysis of X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), ultraviolet visible diffuse reflectance spectroscopy, and photoelectrochemical spectra showed that phycocyanin was successfully doped in the structure of the graphite-phase carbon nitride as a carbon source. After that, the activity of the catalyst was evaluated by photocatalytic decomposition of water to produce hydrogen. The results showed that carbon doping could effectively improve the separation of photogenerated electrons and holes, and thus enhancing the photocatalytic activity. Among the prepared graphite phase carbon nitrides with or without phycocyanin modification, MCN10P exhibited the optimal photocatalytic performance at hydrogen production with 2.7-fold higher than that of the unmodified graphite-phase carbon nitride (MCN). Moreover, MCN10P showed good cyclic stability. Thus, phycocyanin could be used as the carbon source of carbon doping, which was transformed into the activated carbon substrate during the calcination process, allowing the graphite phase carbon nitride to grow on the substrate, providing more reactive active sites for photocatalytic hydrogen production, thereby improving the photocatalytic efficiency. The results thus provided new insights into the fabrication of efficient carbon doped graphite carbon nitride for generating hydrogen energy by using water.

Introduction

At present, the world's energy depends largely on fossil fuels including petroleum, coal, and natural gas, which are rapidly depleting and non-renewable. Therefore, efforts have been made to develop new energy. Hydrogen energy is a promising alternative for solving energy crisis and environmental problems owing to its advantages of no pollution and high combustion value [1]. The main applications of hydrogen energy include the following aspects: (1) as fuel, hydrogen fuel cells have strong power, strong endurance, and no pollution, and are mainly used in transportation. Besides, hydrogen can be used in power generation as a more flexible energy

storage medium and cleaner feedstock; (2) the use of hydrogen or hybrid fuels can reduce or eliminate carbon emissions while providing high temperatures; (3) as raw materials, hydrogen can be applied for the synthesis of ammonia and methanol synthesis, and hydrogenation of unsaturated components in natural edible oil, and so on. Moreover, governments around the world have introduced hydrogen energy development strategies, and hydrogen energy planning has been raised to the level of national energy strategy in some developed countries such as the United States, Japan, and Germany. China, as the world's largest producer of hydrogen, has also issued a series of supportive policies for the development of hydrogen energy. However, the hydrogen production is mainly made from fossil fuels and methanol reforming, in which the former will generate a large amount of carbon emissions, and the latter has low technology maturity except carbon emissions. In industry, hydrogen can also be prepared by using natural energy such as solar energy and wind energy to electrolyze water with remaining high energy consumption. In recent years, with photocatalyst as the "medium", hydrogen generation from water splitting by solar energy has been widely studied due to its simplicity, green, high efficiency, and low cost. In this process, the electrons in the photocatalyst are excited to transition from valence band to conduction band under illumination, forming free electrons and holes in both bands, respectively. With the electron-hole pair, water is ionized to generate H_2 and O_2.

Comparing to the traditional photocatalysts such as TiO_2, SnO_2, and ZrO_2, graphite phase carbon nitride (g-C_3N_4) as a new non-metallic photocatalyst material is non-toxic and harmless with a wider absorption spectrum range, which can work photocatalysis under ordinary visible light without ultraviolet light. Together with its band structure matching the redox potential of water, high physicochemical stability, easy synthesis, and abundant sources, g-C_3N_4 has been considered as one of the most promising next-generation photocatalysts [2]. However,

drawbacks such as easy recombination of photogenerated charges and holes, single absorption of blue light restricted the application of graphite-phase carbon nitride [3]. Carbon doping is a common and effective modification method for improving the light absorption range of g-C_3N_4 and promoting the separation of photogenerated carriers, thereby improving the photocatalytic performance of g-C_3N_4. It has been reported that manganese-phosphorus, cobalt, and carbon were co-doped with carbon nitride [4, 5]. Inspired by the previous research, this study was firstly proposed to design a novel carbon-doped g-C_3N_4 (MCNxP) by thermal condensation polymerization using melamine and phycocyanin as precursors. Phycocyanin from *Spirulina* is a navy-blue pigment protein with abundant carbon content, which can help to adjust the band structure of g-C_3N_4, improving its photocatalytic activity. Therefore, phycocyanin-modified g-C_3N_4 was expected to be an efficient and green photocatalyst. Through spectral characterization and photocatalytic activity analysis, the obtained results were expected to provide a reliable basis for further development of photocatalysts with excellent and stable photocatalytic performance.

Materials and methods

Preparation of graphite-phase carbon nitride modified by phycocyanin

One gram of melamine (analytic grade) (Sinopharm Chemical Reagent Co., Shanghai, China) and 5-30 mg of phycocyanin (the purity of 70%, Zhejiang Binmei Biotechnology Co., Linhai, Zhejiang, China) were dissolved in 30 mL of deionized water *via* ultrasonication using KQ-200KDE Ultrasonic Cleaner (Kunshan Ultrasonic Instrument Co., LTD, Shanghai, China) for 10 min, followed by removing water *via* heating in a water bath to obtain a well-mixed powder of melamine and phycocyanin. To perform the thermal polymerization of cyanamide molecules, the resulting mixture was successively kept in a ceramic crucible with a cover and heated from 25°C to 550°C at 5°C/min in SX2-4-10 muffle

furnace (Shenyang Industrial Electric Furnace Factory, Shenyang, Liaoning, China), and afterwards were held for 2 h. After cooling, the functionalized product (MCNxP) in the crucible was ground into powder. Four MCNxPs were prepared with different amount of phycocyanin (5 mg, 10 mg, 20 mg, and 30 mg) and they are denoted as MCN5P, MCN10P, MCN20P, and MCN30P, respectively. In addition, the pure graphite-phase carbon nitride (MCN) was also prepared as described above.

Characterization of synthesized samples

The phase and composition of the samples were analyzed by X-ray diffraction (XRD) using an X-ray powder diffractometer (Rigaku Smartlab, Tokyo, Japan). The molecular structure of the samples was analyzed by using Shimadzu FTIR 8300 Fourier transform infrared spectroscopy (FT-IR) (Shimadzu, Kyoto, Japan). The UV-vis diffuse reflectance spectrum was recorded by using Shimadzu UV-2450 UV-vis spectrophotometer (Shimadzu, Kyoto, Japan). Barium sulfate (analytic grade) (Sinopharm Chemical Reagent Co., Shanghai, China) was employed as the reflectance reference standard. X-ray electron spectroscopy (XPS) was measured by using Kratos XSAM800 X-ray electron spectrometer (Kratos Analytical Ltd, Manchester, UK). The photocurrent and electrochemical impedance spectra were performed on CHI660D electrochemical analyzer (Shanghai Chenhua, Shanghai, China).

Photocatalytic activity assay

The photocatalytic reaction was carried out by using an on-line photocatalytic hydrogen production system with equipping a CEL-SPH2N gas chromatography (CEAULIGHT, Beijing, China). A xenon lamp (power of 300 W) equipped with a 420 nm filter (to filter out ultraviolet light) was used as the light source. In the reactor, 15 mg of MCNxP was ultrasonically dispersed in 15 mL of the aqueous solution containing 10% (v/v) triethanolamine (analytic grade) (Sinopharm Chemical Reagent Co., Shanghai, China) as a sacrificial agent and 3wt% of chloroplatinic acid (analytic grade) (Sinopharm Chemical Reagent

Co., Shanghai, China) as a cocatalyst, followed by sealing with vacuum grease. Subsequently, the reactor was connected to the reaction system, and the temperature was maintained at 6°C by cycling cooling water. After vacuuming, the reaction solution was irradiated by the light source, allowing the photocatalytic decomposition of water to produce hydrogen by MCNxP. The resulting gas was fed directly into gas chromatography through a four-way valve for detecting hydrogen production. The photocatalytic activity (μmol/g·h) was defined as the quantity of photocatalyst that generated 1 μmol hydrogen per hour under the assay condition.

Statistical analysis

The average values of three replicate experiments with standard deviations were reported. Statistical analysis were performed by using OriginPro 2016 (OriginLab Corporation, Northampton, Massachusetts, USA). The analysis of variance (ANOVA) with a statistical comparison using Tukey test was employed. Statistical significance was expressed as $P < 0.05$.

Results and discussion

XRD characterization

The XRD patterns of MCN and MCNxPs were shown in Figure 1. All catalysts demonstrated two typical graphite-phase carbon nitride diffraction peaks at 13.11° and 27.41°, corresponding to the stacking of repeated s-triazine (002) and interlayers in the (100) plane, respectively [6]. Besides, no other characteristic diffraction peaks were found in the pattern, indicating that the phycocyanin completely reacted with melamine to form MCNxP without impurities. With the increase of phycocyanin content, the position and intensity of the diffraction peaks at 13.11° and 27.41° almost remained unchanged, indicating that the structure (including in-plane units and layer spacing) of the synthesized g-C_3N_4 was not affected by phycocyanin modification, which might be due to the limited amount of carbon doping.
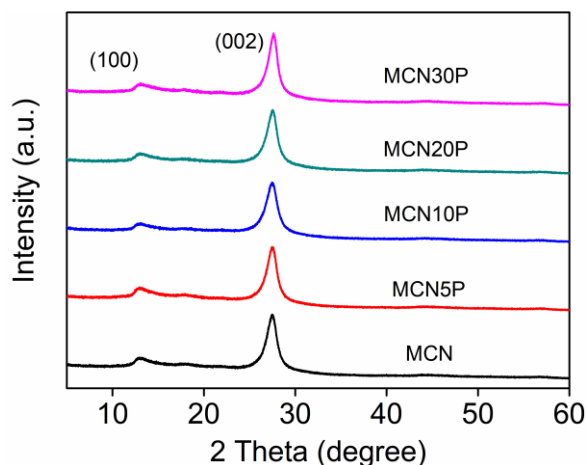
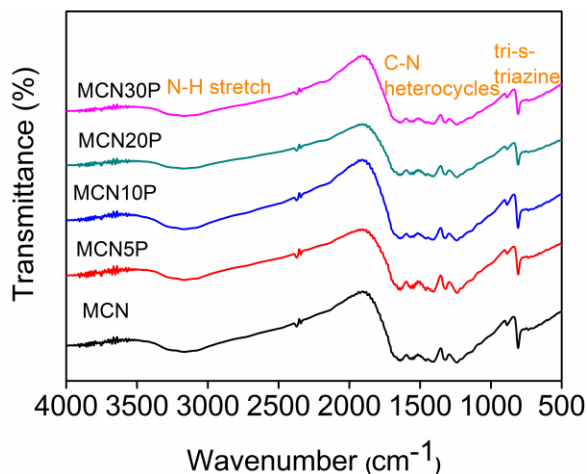**Figure 1.** XRD patterns of MCN, MCN5P, MCN10P, MCN20P, and MCN30P.

Figure 2. FT-IR spectra of MCN, MCN5P, MCN10P, MCN20P, and MCN30P.

FT-IR characterization

The FTIR spectra of different catalysts were shown in Figure 2. The absorption peak at 3,200/cm represented the stretching vibration of N-H formed by incomplete polycondensation of melamine. The peaks at 1,200 - 1,700/cm corresponded to the stretching of carbon-nitrogen aromatic heterocycle compound, while the peak at 810/cm was assigned to the characteristic of the triazine ring, which was the basic structural unit [7]. In addition, it could be obviously seen from Figure 2 that the absorption peaks of MCNxPs with different phycocyanin

modification presented similar absorption peaks with MCN, indicating that carbon doping did not change the skeleton structure of graphitic carbon nitride, leading to the identical structure of MCNxPs and MCN [8]. These results indicated that the addition of phycocyanin could introduce a small amount of carbon into the synthesized graphite-phase carbon nitride, but it did not affect the polycondensation of melamine to form the heptazine ring, which was consistent with the XRD results (Figure 1).

XPS test

Taking MCN10P as the representative, the elemental composition of the prepared graphite-phase carbon nitride with or without phycocyanin was analyzed by XPS. The XPS spectra of MCN and MCN10P were shown in Figure 3. Both catalysts were mainly composed of C and N, while the C/N molar ratio of MCN10P was estimated to be 3.07 that was higher than 1.26 of MCN (Figure 3a). That was attributed to the incorporation of carbon elements into g-C_3N_4 from the thermal decomposition of phycocyanin during preparation, resulting in the increased carbon content in MCN10P. The C1s and N1s of the catalyst were analyzed by XPS peak fitting, in which the C1s was fitted to the peaks at the binding energy of 284.8 eV, 286.5 eV, and 288.2 eV (Figure 3b), corresponding to C-C bond, C-NH$_2$, and N=C-N of sp2 hybrid in triazine ring, respectively [9]. Besides, the N1s was fitted to the three peaks at 398.6 eV, 399.5 eV, and 400.8 eV (Figure 3c), representing the characteristics of C=N-C, N-(C)$_3$, and C-N-H, respectively. Compared with the XPS spectra of MCN, the great alteration in the peak areas was found for the three peaks of C1s of MCN10P (Figure 3b), in which the increase of peak area at 284.8 eV indicated that carbon elements from phycocyanin were embedded in the skeleton structure of MCN10P [10]. Besides, the C=N-C ratio was decreased from 78.7% for MCN to 56.3% for MCN10P, demonstrating that the doped carbon atom replaced the N atom in the C=N-C. In addition, the signal of nickel element was almost invisible in the Ni 2p spectrum of MCN10P (Figure 3d), revealing no interference of nickel element.
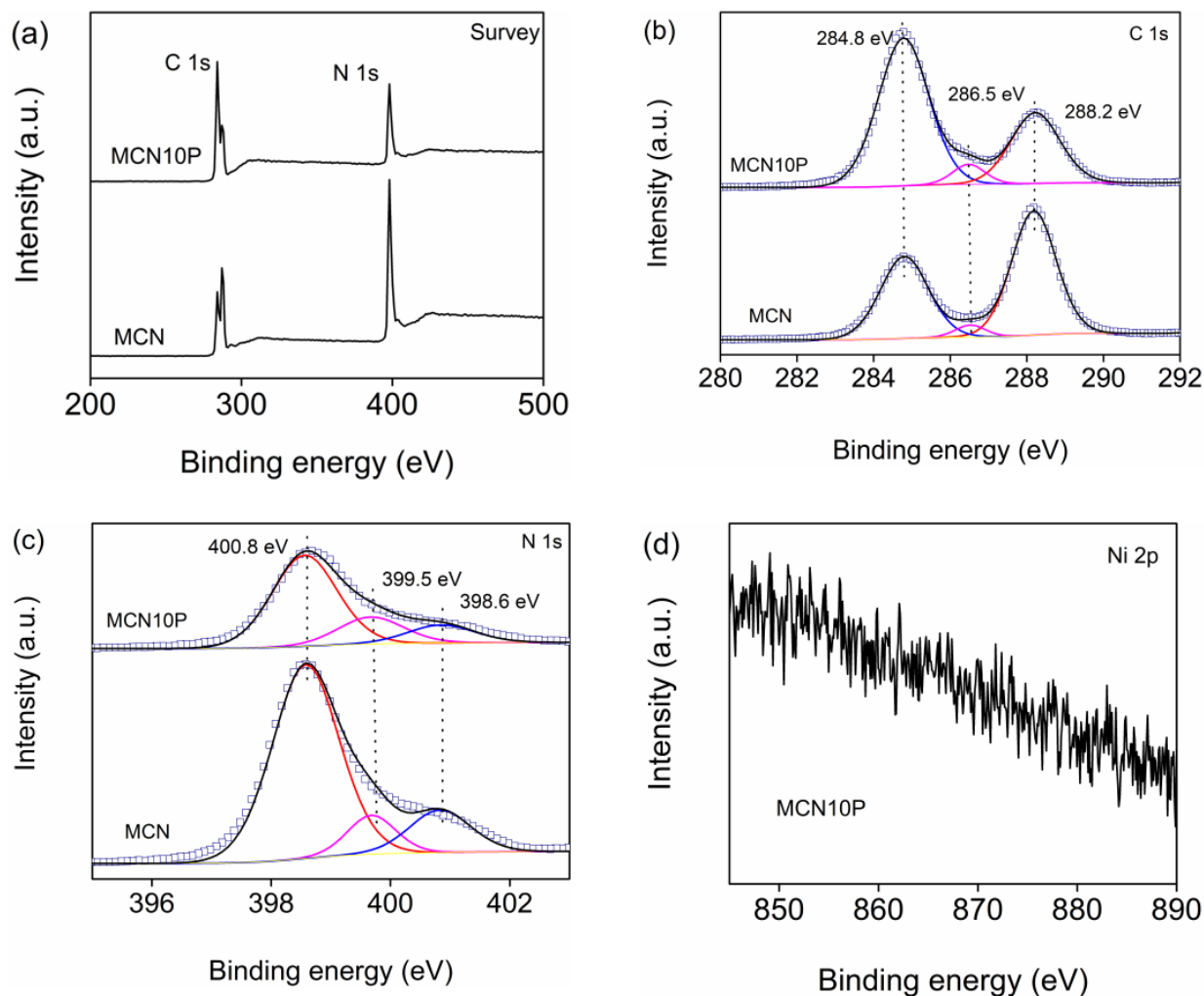
Figure 3. Spectra of MCN and MCN10P. **(a)** XPS total spectrum. **(b)** C1s spectrum. **(c)** N1s spectrum. **(d)** Ni 2p spectrum.

Therefore, the main role of phycocyanin was to introduce carbon into the structure of MCN10P.

UV-vis absorption characterization
The UV-visible absorption spectra of five samples were shown in Figure 4a. The absorption edge experienced a red-shift from 451 nm for MCN to 455 nm for the four MCNxPs along with the significantly enhanced peak values, indicating that the introduction of carbon could effectively improve the light absorption capacity of the catalyst. Meanwhile, the absorption peak value of MCNxP was also positively correlated with the content of phycocyanin, further demonstrating the increased carbon in MCNxP originated from phycocyanin. To calculate the band gap (Eg), the

plot of $(\alpha h\nu)^2$ versus hν was obtained from the following equation (Equation 1) based on the absorption spectrum data:

$$(\alpha h\nu)^{1/m} = B(h\nu - E_g) \tag{1}$$

where α, h, ν, and B were absorption coefficient, Planck constant, incident photon frequency, and proportional constant, respectively, while the value of m depended on the semiconductor material and the transition type. The tangent line along the curve was then made and extended to the X axis. The resulting intersection was just its band gap. As shown in Figure 4b, the band gap of MCN was 2.75 eV, while the band gaps of MCN5P, MCN10P, MCN20P, and MCN30P were
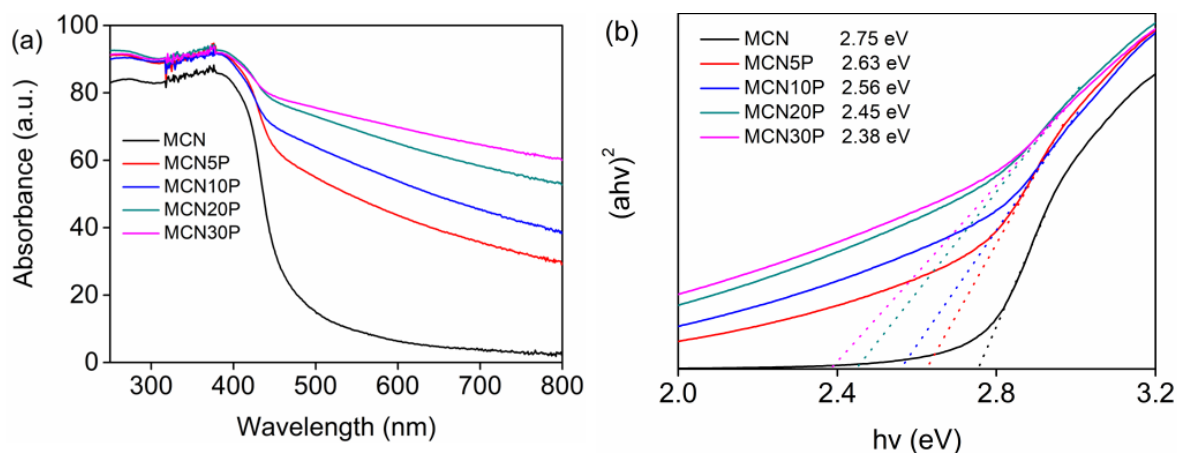
Figure 4. UV-visible absorption spectra **(a)** and $(\alpha h\nu)^2$-hν plots **(b)** of MCN, MCN5P, MCN10P, MCN20P, and MCN30P composites.
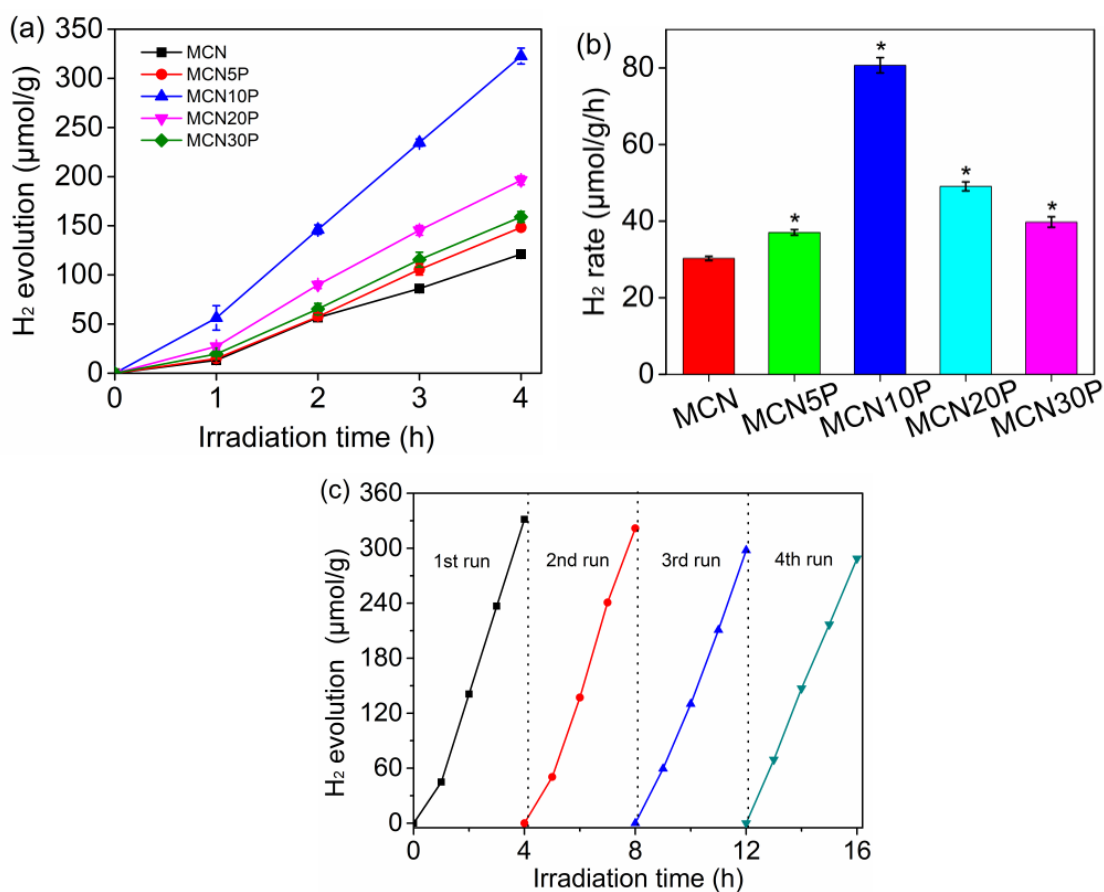

Figure 5. Photocatalytic activity of MCNxP samples. **(a)** photocatalysis hydrogen evolution. **(b)** hydrogen production rate of the five samples. **(c)** Cyclic stability of MCN10P. (*: $P < 0.01$ as compared to the pure graphite-phase carbon nitride (MCN)).

2.63, 2.56, 2.45, and 2.38 eV, respectively. The decreased band gap after phycocyanin modification was conducive to the light absorption of sample at larger wavelength, to improve their photocatalytic performance.
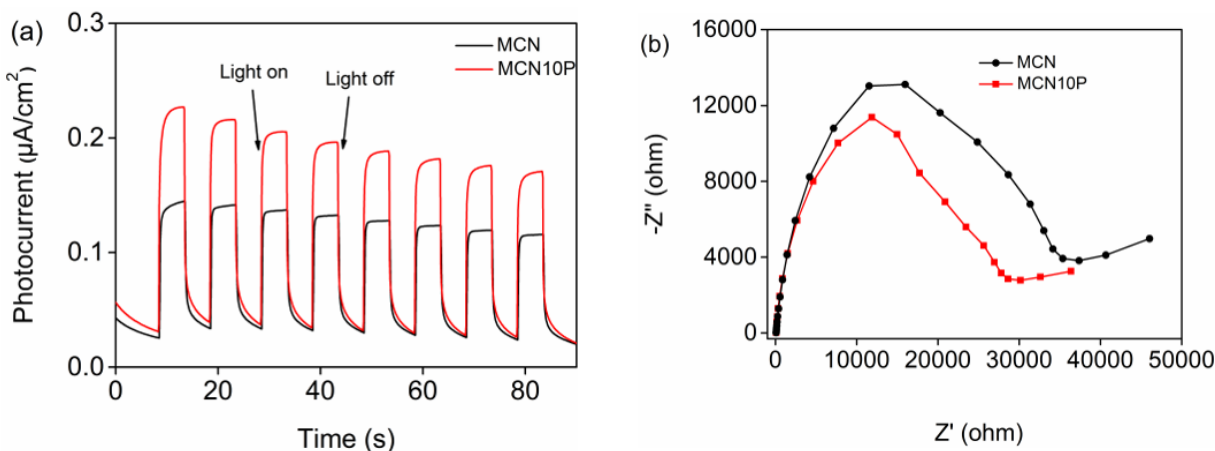
Figure 6. Response curves of transient photocurrent **(a)** and impedance spectra **(b)** of MCN and MCN10P composites.

Evaluation of photocatalytic activity

The photocatalytic properties of MCN and MCNxP samples directly reflect the effect of phycocyanin on the performance of photocatalytic decomposition of water to produce hydrogen by g-C$_3$N$_4$. As shown in Figure 5a, all MCNxPs exhibited significantly higher hydrogen evolution rate than that of MCN under visible light irradiation. Of those, MCN10P reached the highest H$_2$ evolution rate of 322.7 μmol/g at 4h, which was 2.7-fold higher than that of MCN (121.1 μmol/g). The corresponding hydrogen production rate was shown in Figure 5b. MCN10P displayed the highest H$_2$ production performance as well (80.7 μmol/g·h). The results indicated that the phycocyanin modification could effectively improve the photocatalytic activity of the synthesized g-C$_3$N$_4$. In addition, the hydrogen production of MCNxPs showed a trend of first increase and then decrease with the increase of phycocyanin addition (Figures 5a and 5b). Together with the previous characterization, these results indicated that a small amount of carbon doping could enhance the separation efficiency of photogenerated electron/hole pairs, and thereby, improving the absorption of visible light by the catalyst, resulting in higher photocatalytic activity. However, excessive carbon doping would make carbon act as the composite center of photogenerated electrons and holes, leading to the deceased charges in the photocatalytic reaction, and lower photocatalytic

activity [10]. The photocatalytic stability of MCN10P was also evaluated and the results were presented in Figure 5c. After four cycles, MCN10P still maintained a higher hydrogen evolution performance with a slight decrease in hydrogen production, which further indicated that the MCN10P composite had excellent resistance to light corrosion.

Photoelectric chemical test

In this study, MCN and MCN10P were selected as the representatives to test the photocurrent and AC impedance. Figure 6a demonstrated the transient photocurrent response of MCN and MCN10P. Once the light was turned on, both samples displayed a rapid photocurrent response, indicating the good photoelectric conversion of g-C$_3$N$_4$. However, the higher photocircuit intensity was observed for MCN10P due to the additional π orbitals generated by the introduction of carbon, increasing delocalization of interlayer electrons in MCN10P, leading to more photocarriers under light. In Figure 6b, the AC impedance of MCN10P was lower than that of MCN, indicating easier charge transfer in MCN10P, owing to the enhanced conductivity of the sample by the introduction of carbon [11]. Due to its high optical circuit intensity and low AC impedance, the photogenerated electrons were more conducive to be transported in the photocatalytic reaction, resulting in the better photocatalytic performance of MCN10P.

Conclusion

In this study, the new carbon doped graphite-phase carbon nitrides (MCNxPs) were prepared by thermal polycondensation method using melamine and phycocyanin as a precursor. A series of characterizations in terms of XRD, FTIR, XPS, UV-visible absorption spectra, and photoelectrochemical spectra demonstrated that phycocyanin as a carbon source was successfully doped in the structure of g-C_3N_4. During preparation, these phycocyanin could be converted to an activated carbon substrate, allowing MCN to grow on the substrate and providing more reactive active sites for the photocatalytic hydrogen production. Besides, the activated carbon substrate was also beneficial to the migration of photogenerated charges, enhancing the separation efficiency of photogenerated electron/hole pairs and then improving the absorption of visible light by the catalyst. The photocatalytic activity assay showed that MCN10P with the feed ratio of phycocyanin to melamine at 10 mg/1 g exhibited optimal photocatalytic hydrogen production, improving 2.7-fold higher than that of MCN. Moreover, MCN10P displayed excellent catalytic stability. The results indicated that graphite-phase carbon nitride modified by phycocyanin deserved further development for green and efficient photocatalysts.

Acknowledgments

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