Self-Sensitized Carbon Nitride Microspheres for Long-Lasting Visible-Light-Driven Hydrogen Generation

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A new type of metal-free photocatalyst is reported having a microsphere core of oxygen-containing carbon nitride and self-sensitized surfaces by covalently linked polymeric triazine dyes. These self-sensitized carbon nitride microspheres exhibit high visible-light activities in photocatalytic H₂ generation with excellent stability for more than 100 h reaction. Comparing to the traditional g-C₃N₄ with activities terminated at 450 nm, the polymeric triazine dyes on the carbon nitride microsphere surface allow for effective wide-range visible-light harvesting and extend the H₂ generation activities up to 600 nm. It is believed that this new type of highly stable self-sensitized metal-free structure opens a new direction of future development of low-cost photocatalysts for efficient and long-term solar fuels production.

1. Introduction

Solar driven hydrogen generation through a photocatalytic process has been attracting strong research attentions as one of the most promising strategies to obtain sustainable energy resources. Among all types of photocatalysts, metal-free semiconductors such as graphitic carbon nitride (g-C₃N₄) and its derivatives (e.g., C₃N₃, C₃N₂, and C₃N₃S₃) are of particular interest because they have tailorable band structures with visible-light activities and contain only low-cost earth-abundant elements. In most previous reports, the graphitic carbon nitride photocatalysts were commonly prepared through annealing molecular precursors (e.g., cyanamide, urea, melamine, etc.) at 400–600 °C. The traditional bulk g-C₃N₄ has low visible-light photocatalytic activities due to the limited response to visible light and rapid recombination of photogenerated charge carriers, which are indeed quite common for most semiconductor photocatalysts.

In order to promote visible-light activities for the semiconductor-based photocatalytic process, dye-sensitization has been widely used as an effective strategy in the past decade. For example, Takanabe et al. reported that introducing magnesium phthalocyanine dye to mesoporous carbon nitride could enhance photocatalytic H₂ evolution under visible light irradiation. Xu et al. also found that Eosin Y-sensitized g-C₃N₄ showed improved visible-light-driven H₂ generation rate. Nevertheless, the charge transfer processes between the additionally introduced dye molecules and carbon nitride are inefficient due to the weak physisorption of dyes on carbon nitride surfaces. In addition, when exposed in air, most dyes used for sensitization in previous reports could not be stable for long-time reaction under solar irradiation.

In recent years, several groups have tried to synthesize polymeric carbon nitride by using solvothermal approaches at relatively low temperature. Our previous studies also confirmed that condensation and polymerization of melamine and cyanuric chloride can occur under solvothermal condition toward formation of graphitic carbon nitride microspheres. All previous efforts indicate that the solvothermal methods provide an opportunity to control the microstructure of graphitic carbon nitride. In this work, we report a new structure of self-sensitized carbon nitride (SSCN) microspheres prepared via one-pot solvothermal polymerization of cyanuric chloride and cyanuric acid. The “self-sensitization” originates from...
the covalently attached 1,3,5-triazine based oligomer (TBO) which acts as the “dye” and formed in-situ on the surface of carbon nitride microsphere during the polymerization process. As illustrated in Scheme 1, the condensation between cyanuric chloride and cyanuric acid leads to formation of TBO dyes with strong and wide visible light absorption. Further polymerization and condensation of these oligomers eventually results in oxygen-containing carbon nitride microspheres, on which there are always TBO dye moieties covalently conjugated.

As a result, under visible light irradiation, the as-prepared carbon nitride microspheres with self-sensitization by the surface TBO dyes exhibit highly enhanced visible-light activities for H₂ generation as compared to traditional g-C₃N₄. Significantly, the long-wavelength absorption of TBO allows for extension of the visible-light activity up to 600 nm with still observable H₂ generation. More importantly, the excellent stability of TBO enables long-lasting H₂ generation by SSCN with maintained rate for more than 100 h. This new type of highly stable self-sensitized metal-free semiconductor opens a new direction of future development of low-cost photocatalysts for efficient and long-term solar fuels production.

2. Results and Discussion

2.1. Structure Identification of SSCN

After 20 h solvothermal treatment of cyanuric chloride and cyanuric acid, the red solid product was collected through centrifugation, and showed a morphology of microsphere with diameters 0.5–1.5 μm (Figure 1A) and broad visible-light absorption up to 700 nm (Figure 1B). The X-ray diffraction (XRD) analyses (Figure 1C) show a broad and weak peak at 27.0° (d ≈ 0.332 nm) corresponding to the stacking of conjugated hexatomic heterocyclic system, which is slightly smaller than that of g-C₃N₄ (at 27.3°, d ≈ 0.323 nm). But the microspheres do not show the characteristic peak of in-planar repeat packing at ≈13°, suggesting the imperfect and disordered crystal structure of the SSCN microspheres. The disordered structure will affect the transport of photogenerated charge carriers and the electron-hole recombination process, and consequently influences the photocatalytic activities.

The intermediate products at different reaction time were also examined by scanning electron microscopy (SEM). As shown in Figure S1A (Supporting Information), after 4 h reaction, well-defined spheres with diameters of ≈330 nm formed through self-assembly of the small nanoparticles (≈25 nm in diameter) that were probably generated from condensation of precursor molecules. Extending reaction time led to enlarged microspheres with less particulate on the surface. After 8 h reaction, the spherical products showed smooth surface and the diameters are more close to the final product. The diameter variation with respect to the reaction time is plotted in Figure S1F (Supporting Information). These observations suggest that the solvothermal treatment leads to gradual polymerization and condensation of the precursors.
toward a microsphere with a solid core of carbon nitride and incompletely condensed oligomers as shells on the microsphere surface. Moreover, these surface oligomers may have very different chemical structures with the core.

To verify this “core–shell” hypothesis for the microsphere structure, we have treated the microspheres by the base Piranha solution (NH₃/H₂O₂/H₂O solution with volume ratio of 1:1:5) at 60 °C for 3 h, which led to a color change from red to bright yellow, corresponding to a clear blue-shift of the absorption range in the UV–vis spectra (Figure 1B). This yellow product, denoted as SSCN-P, showed almost no change in the XRD pattern, and well retained the microsphere morphology with smooth surface (Figure S2, Supporting Information), suggesting that the microsphere “core” has very stable chemical composition with strong resistance to oxidation by Piranha. As such, the color change could be attributed to the removal of surface oligomers having a chemical structure vulnerable to Piranha treatment. It is critical to identify the molecular structure on the microsphere surface in order to figure out the chemical composition of these microspheres. Therefore, we have compared the two samples, SSCN and SSCN-P, by using different characterization techniques.

The X-ray photoelectron spectroscopy (XPS) analyses of SSCN (Figure 2 and Table S2 (Supporting Information)) indicate the surface elements including C, N, O, and Cl. The C 1s signals can be fitted into two peaks centered at 284.6 and 288.0 eV attributed to the adventitious or contaminant carbon and sp²-hybridized carbon in the unit of N—C—N, respectively. The C 1s peak at around 286.8 eV might be owing to the oxidized carbon in the form of N—C(NH)—O. Consistently, the O 1s spectrum shows two peaks at 531.7 and 533.4 eV, corresponding to C—OH and C=O oxygen species. The N 1s signals can be also fitted into three peaks located at 398.6, 399.9, and 401.0 eV for sp²-hybridized nitrogen in triazine rings (C=N=C), tertiary nitrogen N—(C)₃, and nitrogen bonded with hydrogen, respectively. These results indicate that the polymerization and condensation of cyanuric chloride and cyanuric acid can eventually form oxygen-containing CN framework consisting of tri-s-triazine repeating units.

After Piranha treatment, the microsphere sample (SSCN-P) shows decreased C 1s peak at 286.8 eV and O 1s peak, suggesting that the surface of SSCN microspheres is oxygen-rich as compared to the core. Moreover, the SSCN sample exhibits clear Cl 2p signals with two pairs of Cl 2p₃/2 and Cl 2p₁/2 peaks at 200.3 and 201.9 eV for the C—Cl species and 196.9 and 198.9 eV corresponding to ionic Cl species, respectively, while the SSCN-P shows much weaker Cl 2p signals. This observation suggests that the Cl-species mostly exist on the surface of SSCN microspheres, and are hardly embedded in the core of CN framework.
The solid-state 13C NMR spectra (Figure 3) of the SSCN sample show two distinct peaks at 155.9 and 162.4 ppm, and a clear shoulder at ≈150 ppm. The signal at 155.9 ppm, corresponding to the C atoms bonded to three N atoms (−CN3), is almost identical to the value (155.6 ppm) of g-C3N4,[7,39–44] which indicates the existence of characteristic poly(tri-s-triazine) structures in the SSCN microspheres. However, the other strong peak at 162.4 ppm shows a lower shift as compared to that of g-C3N4 at 164.3 ppm for the C atoms in the N2C-NH2 unit, and also might be attributed to the C atoms in the oxygen-containing unit (N2-C-O) as shown in Scheme 1. The shoulders at ≈150 ppm disappeared after Piranha treatment, thereby should be related to the C atoms bonding with O (C=O) or Cl (C−Cl) in triazine units on SSCN surfaces since the triazine units are readily removed by Piranha solution.

To figure out the origination of this shoulder at ≈150 ppm, we have checked the NMR spectra of supernate (denoted as S−CN) after solvothermal reaction and centrifugation. As shown in Figure S4A (Supporting Information), the precursors before solvothermal reaction showed two strong 13C peaks at 150.06 and 150.16 ppm, corresponding to the C atoms in cyanuric chloride and cyanuric acid, respectively. After reaction, though the supernate might contain oligomers with different levels of polymerization, its 13C NMR spectrum only showed three sharp peaks at 150.12, 150.24, and 150.36 ppm, which may be attributed to the C atoms in N−C(NH)−Cl, N−C(NH)−O, and C−O−C units bridging two triazine rings, respectively. This result suggests that the initial polymerization between cyanuric chloride and cyanuric acid leads to a large network of triazines bridged by oxygen (C−O−C) (confirmed by Fourier transform infrared spectra (FTIR) results in Figure S4B, Supporting Information). These polymeric triazines not only exist in the reacted solution, but also are the major component on the SSCN microsphere surface.

The elemental analyses of SSCN microspheres also indicate different chemical composition between the surface and the core. As shown in Table S3 (Supporting Information), the as-prepared SSCN sample contains 5.4 wt% Cl which were almost completely removed after Piranha treatment. This verifies that the majority of Cl-contained units is existing on the microsphere surface, while the core consisting of tri-s-triazine units is nearly free of Cl. Moreover, upon Piranha treatment, the atomic N/C ratio changed significantly from 1.07 to 1.24, but the atomic C/O ratio maintained as around 1.93. Since the N/C ratios in triazine and tri-s-triazine (with one side group of −NH−) are 1.0 and 1.33, respectively, the surface oligomers removed by Piranha should contain mostly polymeric triazine units, and the microsphere core is composed by condensed tri-s-triazine units. The vast content of oxygen in the tri-s-triazine units results in smaller N/C ratio of SSCN-P (1.24) as compared to that of standard g-C3N4 (1.33).

Based on the above characterization results, we can confirm chemical reactions during the solvothermal process as shown in Scheme 1. At the beginning, the polymerization between cyanuric chloride and cyanuric acid generates large network of triazines bridged by C−O−C bonds. Further condensation driven by high-pressure solvothermal process would result in formation of tri-s-triazine units which eventually create small particles as nuclei. Subsequently, the nuclei coalescence and continuous condensation of these polymeric triazines on small particle surface lead to larger microspheres. Nevertheless, even after 20 h reaction, there are always a number of polymeric triazines, which are incompletely condensed to tri-s-triazine units, existing in solution and also covalently attaching on the microsphere surface as a loose layer of “oligomer dyes.” As such, it is believed that the resulted microsphere has an oxygen-containing carbon nitride core composed by tri-s-triazine units with high stability, and decorated surfaces by TBO dyes.

### 2.2. Photocatalytic Activities for H2 Generation

Prior to the photocatalytic test, each sample was loaded with Pt (3 wt%) nanoparticles through wetness impregnation as described in previous reports.[25,45] Photocatalytic tests of the Pt-loaded sample (10 mg) for H2 generation were carried out in the solution containing triethanolamine (TEOA, 15 vol%) as the sacrificial agent under visible light (>420 nm) irradiation. The standard g-C3N4 sample prepared by annealing melamine and the Piranha treated standard g-C3N4 (g-C3N4-P) were used as references for comparison. As shown in Figure 4A, the prepared SSCN sample showed a hydrogen generation rate of 4.96 μmol h⁻¹, which is about 3 and 2.5 times of the rate (1.69 μmol h⁻¹) over g-C3N4 and (1.97 μmol h⁻¹) g-C3N4-P, respectively. Comparing to SSCN, the Piranha treated sample (SSCN-P) showed half reduced H2 generation rate (2.45 μmol h⁻¹), which is still higher than that over g-C3N4. The influence of surface area can be excluded because the g-C3N4 sample has much larger surface area (3.93 m² g⁻¹) than the SSCN sample (1.85 m² g⁻¹), but lower photocatalytic activity. This result suggests that the microsphere core as oxygen-containing carbon nitride is active for photocatalytic H2 generation, but more importantly, the surface TBO dyes can provide additional light-harvesting
capability and be sensitized for H\textsubscript{2} generation, leading to greatly enhanced overall activity. However, the TBO dyes without support of carbon nitride cores are inactive for photocatalytic H\textsubscript{2} generation because the supernate sample (S-CN) could not show observable activity for H\textsubscript{2} generation. We also tested the prepared sample at 4 h reaction (SSCN-4h), which showed very low activity for H\textsubscript{2} generation (0.03 μmol h\textsuperscript{-1}). These observations suggest that the solid carbon nitride core is required to serve as the acceptor for the excited electrons from sensitized TBO dyes, which is critical for the high photocatalytic activity.

The stability of SSCN in the photocatalytic test was evaluated by recycling the reaction under the same conditions. As shown in Figure 4B, the H\textsubscript{2} generation rate well preserved after four test cycles over 4 d, and the structure and morphology of the CN still remains no change after 4 d photocatalytic reaction (Figure S5, Supporting Information). This test indicated excellent stability of SSCN microspheres for long-lasting H\textsubscript{2} generation.

To explore more details on the visible-light-driven activity, we have estimated the apparent quantum efficiency (AQY) at different irradiation wavelength, as shown in Figure 4C and Table S4 (Supporting Information). The SSCN showed consistently higher AQY than g-C\textsubscript{3}N\textsubscript{4} at all wavelengths above 420 nm. The g-C\textsubscript{3}N\textsubscript{4} only showed activity at irradiation wavelength below 450 nm. In comparison, the action spectrum threshold for SSCN is up to 600 nm. Although the absorption of SSCN spans more than 700 nm, the photons at wavelengths over 600 nm absorbed by SSCN cannot result in H\textsubscript{2} generation, which implies that the photogenerated electrons of surface TBO dyes by excitation at >600 nm light could not reach sufficient energy level to transfer to the conduction band of the carbon nitride core for proton reduction.

2.3. Principles of Photocatalytic H\textsubscript{2} Generation over SSCN

Based on the above observations, we propose that the photocatalytic H\textsubscript{2} generation over Pt-loaded SSCN is contributed by two major processes, direct excitation of the carbon nitride core and sensitization of the surface TBO dyes, as illustrated in Figure 5. Under visible light irradiation, the photogenerated electrons from the carbon nitride core would be trapped by the loaded Pt catalyst for H\textsubscript{2} generation. Meanwhile, the excited electrons of TBO dyes on the microsphere surface would transfer to the conduction band of carbon nitride core and subsequently transport to the nearby Pt catalyst for proton reduction. The excitation of carbon nitride core might increase its conductivity, and thereby facilitate the transport of injected electrons from TBO to Pt. Meanwhile, TEOA in the solution would quench the photogenerated holes and recover the excited state of TBO dyes.

The electron transfer from TBO to the carbon nitride core can be verified by the photoluminescence (PL) studies. The free TBO dyes in the supernate (S-CN sample) exhibited a clear PL peak at ~450 nm (Figure S6, Supporting Information), but the SSCN sample containing TBO dyes on surfaces did not show any observable PL signal. This observation suggests that the carbon nitride core quenches the PL of TBO, which verifies the transfer of excited electrons from TBO to the carbon nitride core.

Further, the polymeric degree of TBO influences its energy level and absorption feature. Normally larger polymeric degree is associated with higher highest occupied molecular orbital (HOMO) level and lower lowest
unoccupied molecular orbital (LUMO) level, which results in small gap between HOMO and LUMO level and thus longer visible light absorption.\cite{40,46} Comparing to the S-CN sample with an absorption edge at ≈590 nm, the SSCN sample exhibits longer absorption edge, indicating that some portions of TBO dyes on SSCN surfaces have larger polymeric degree than that in the S-CN sample. However, the LUMO level of those TBO with high degree of polymerization might become lower than the conduction band of the carbon nitride core, which explains why the long wavelength light (>600 nm) irradiation over SSCN could not lead to H₂ generation even though the SSCN has certain absorption in this range.

3. Conclusion

We have demonstrated a new structure of self-sensitized photocatalyst (SSCN) which is composed by a core of oxygen-containing carbon nitride microsphere and a loose shell of polymeric triazine dyes covalently linking on the core surface. This new self-sensitized photocatalyst exhibits high visible-light activities for photocatalytic H₂ generation with excellent stability of more than 100 h. Comparing to the traditional g-C₃N₄ with activities terminated at 450 nm, the polymeric triazine dyes on SSCN surfaces allow for effective visible light harvesting with extended photocatalytic activities up to 600 nm. We believe that this new type of highly stable self-sensitized metal-free semiconductor opens a new direction of future development of low-cost photocatalysts for efficient and long-term solar fuels production.

4. Experimental Section

Sample Preparation: All chemicals used in the experiments were used as received without further purification. The SSCN microspheres were prepared via a solvothermal process by using cyanuric chloride (Sigma-Aldrich, 99%) as the precursor. Due to the high tendency of hydrolysis, the cyanuric chloride precursors were partly converted into cyanuric acid when exposed in air. In the actual precursor powder for solvothermal treatment, the molar ratio of cyanuric chloride and cyanuric acid was estimated as ≈1.8 by elemental analyses (see Table S1 in the Supporting Information). In a typical solvothermal process, the precursors (150 mg) were completely dissolved in 15 mL acetonitrile and then the solution was put into a 20 mL teflon-lined autoclave. The autoclave was sealed and maintained at 200 °C for 20 h. After reaction, the powder product at the bottom of autoclave (SSCN) was collected via centrifugation, washed with distilled water and ethanol, respectively, and dried in a vacuum oven. The supernate after centrifugation was separated and dried through rotary evaporation for characterizations of chemical composition.

For comparison, the obtained SSCN sample was treated by the base Piranha solution (NH₄OH:H₂O₂:H₂O with volume ratio of 1:1:5) at 60 °C for 3 h to remove the TBO on the sample surface. Thereafter, the obtained sample (denoted as SSCN-P) was washed with distilled water and ethanol, and dried in a vacuum oven.

Characterizations: The XRD patterns of all samples were collected on XRD-6000 X-ray diffractometer (Cu Ka source) at a scan rate of 2° min⁻¹. SEM images were obtained on a JEOL JSM-6390F microscope at an acceleration voltage of 5 kV. Transmission electron microscopy measurements were carried out on a JEM-2100 microscope. UV–vis absorption spectra were recorded on the Lambda 750 spectrophotometer (Perkin-Elmer, USA) using BaSO₄ as reference. FTIR were measured by Perkin Elmer Spectrum GX FTIR spectrometer. PL spectra were recorded by a Shimadzu RF5301 Spectrofluorophotometer with an excitation wavelength of 380 nm. Solid-state 13C NMR experiments were performed on a Bruker Advance DRX500 spectrometer. XPS was carried out on a VG ESCALAB 250 XPS system with a monochromatized Al Ka X-ray source (15 kV, 200 W). Nitrogen adsorption–desorption isotherms were performed at 77 K using Micromeritics ASAP 2010 equipment. Elemental analysis results were collected from a Vario MICRO system.

Photocatalytic H₂ Generation: The different photocatalyst samples were all loaded with Pt nanoparticles (3.0 wt%) via a wetness impregnation process. Typically, the samples were impregnated by H₂PtCl₆ solution (1.0 mg Pt mL⁻¹) with ultrasonic treatment for 5 min. Subsequently, the slurry was dried and the obtained solid samples were reduced by NaBH₄ (0.5 x) followed by centrifugation, washing, and drying. The test of photocatalytic hydrogen production was carried out in a quartz reactor under visible light irradiation. Typically, 10 mg of the Pt-loaded sample was dispersed into 10 mL aqueous solution of TEOA (15 vol%). The suspension was degassed with N₂ for 15 min to drive off residual O₂ in the system. A 300 W Xenon Lamp (MAX-302, Asahi Spectra, USA) coupled with UV cut-off filter (λ > 420 nm) was adopted to provide the visible light source. The amount of produced H₂ was measured by thermal conductivity detector (TCD). All reactions were accomplished at room temperature. The apparent quantum efficiency (AQE) value was calculated according to the following equation\cite{36,47,48}.
QE = \frac{2 \times \text{number of evolved } H_2 \text{ molecules}}{\text{number of incident photons}} \times 100\% \quad (i)

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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