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Photocatalysis

Synthesis of a Carbon Nitride Structure for Visible-Light Catalysis by Copolymerization[**]

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Artificial photosynthesis holds great promise for addressing global energy and environmental problems. Extensive studies have focused on the titania-based systems since the discovery of photolysis of water into H_2 and O_2 in a photoelectrochemical Pt/TiO_2 cell, which unfortunately works only with ultraviolet radiation.[1] Doping of TiO_2 with metallic (Cr, Fe, V)[2] and nonmetallic elements (N, C, B)[3] creates localized/delocalized states in the band gap and thus extends its optical absorption to the visible region, but doping usually comes with accelerated charge recombination and lower stability of the doped materials. Meanwhile, various other inorganic, non-TiO_2-based, visible-light catalysts have been developed (e.g., metal oxides, nitrides, sulfides, phosphides, and their mixed solid solutions), whereby Ga, Ge, In, Ta, Nb, and W are the main metal constituents.[4] However, sustained utilization of solar energy calls for the development of more abundant and stable catalysts working with visible light, and this has remained challenging so far.

Recently, a polymeric semiconductor on the basis of a defecteous graphitic carbon nitride (g-C_3N_4), was introduced as a metal-free photocatalyst which fulfills the basic requirements for a water-splitting catalyst, including being abundant, stable, and responsive to visible light.[5] In the following, we use the notation "g-C_3N_4" to describe this class of materials rather than the idealized structure.

The most active system is in fact presumably an N-bridged "poly(tri-*s*-triazine)",[6] already described by Liebig as "melon".[7] A semiconductor structure with band edges straddling the water redox potential was revealed for melon by DFT calculations,[5] albeit electrochemical analysis is still awaited. g-C_3N_4 is considered to be the most stable phase of covalent carbon nitride, and facile synthesis of the melon substructure from simple liquid precursors and monomers allows easy engineering of carbon nitride materials to achieve the desired nanostructures via soft-chemical processing routes and methods. For instance, a high surface area (67–400 m^2g^{-1}) can be imparted on g-C_3N_4 materials by polymerization of cyanamide on a silica template, which results in photocatalytically more active g-C_3N_4 nanostructures.[8] Metal-doped g-C_3N_4 can also be conveniently obtained by polymerization of dicyandiamine in the presence of metal salts, and thus multifunctionalization of such materials for a variety of applications can be achieved.[9] Most importantly, the electronic and optical properties of carbon nitride, regarded as a polymer semiconductor, are in principle adjustable by organic protocols. Such organic protocols have been widely used to control the performance of traditional π-conjugated polymers, for example, to improve solar-cell efficiencies by constructing copolymerized donor–acceptor structures,[10] or to modify electronic properties by co-blending with p/n-type organic dopants.[11]

Our aim was to use such organic modifications to extend the insufficient light absorption of g-C_3N_4 (a result of its large band gap of 2.7 eV, which corresponds to wavelengths shorter than 460 nm) towards the maximum of the solar spectrum. Here we demonstrate that the optical absorption of carbon nitride semiconductor materials is extendable into the visible region up to about 750 nm by simple copolymerization with organic monomers like barbituric acid (BA). The electronic and photoelectric properties of the modified carbon nitrides were then investigated to elucidate their enhanced activity for hydrogen production from water containing an appropriate sacrificial reagent with visible light.

In principle, BA can be directly incorporated into the classical carbon nitride condensation scheme (Scheme 1). New carbon nitride structures were therefore synthesized by dissolving dicyandiamide with different amounts of BA in water, followed by thermally induced copolymerization at 823 K. For simplicity, the resulting samples are denoted CNBx, where x (0.05, 0.1, 0.2, 0.5, 1, 2) refers to the weighed-in amount of BA. The structure, texture, and electrochemical properties of these materials were characterized, and their photochemical performance analyzed.

Their XRD patterns (Figure S1, Supporting Information) are dominated by the characteristic (002) peak at 27.4° of a graphitic, layered structure with an interlayer distance of $d =$

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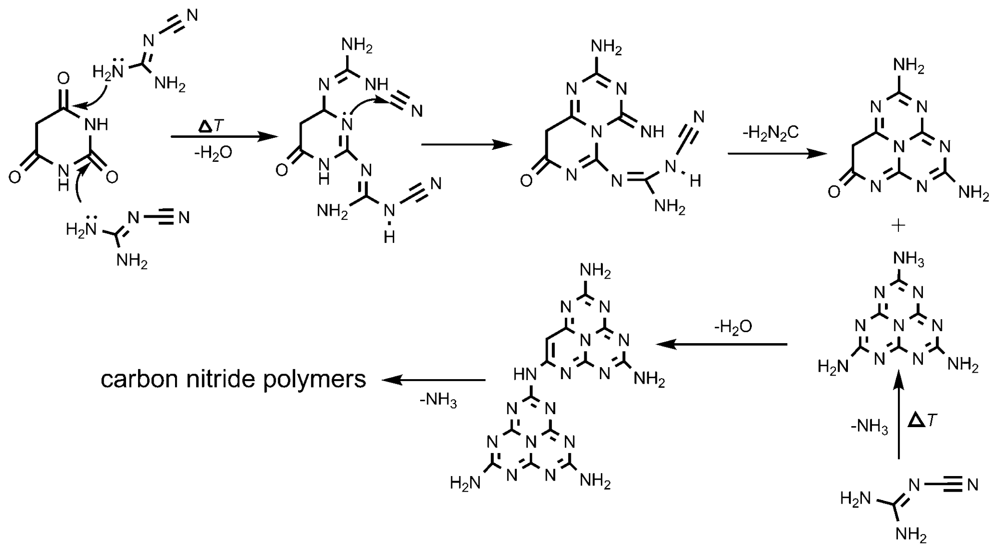

Scheme 1. Proposed copolymerization processes of dicyandiamide with barbituric acid at high temperature.

0.326 nm, as is well known for unmodified carbon nitride. However, the (002) peak becomes broader and gradually less intense with increasing amount of BA, which indicates disturbance of graphitic structure, potentially by the additional carbon functionality introduced by BA. The FTIR spectrum (Figure S2, Supporting Information) of CNB samples features characteristic stretching bands of aromatic CN heterocycles at 1200–1600 cm^{-1} and the breathing mode of the triazine units at 800 cm^{-1}, but the peaks for $CNB_{2.0}$ are broader and less resolved. This again reflects the lower structural order when using large amounts of BA.

Elemental analysis revealed a C/N molar ratio of 0.73 for g-C_3N_4; this ratio gradually increases with increasing amount of BA, from 0.74 to 0.96 for $CNB_{0.05}$ and $CNB_{2.0}$, respectively (see Table 1). This clearly proves that carbon is incorporated into the melon-based carbon nitride structures, likely through replacement of one of the ring nitrogen atoms by carbon, as proposed in Scheme 1. Solid-state ^{13}C NMR spectra (Figure S3, Supporting Information) confirm a heptazine-based structure for g-C_3N_4[6] and also for CNB, except for a weak peak appearing at $\delta \approx 95$ ppm for CNB, which reflects incorporation of new carbon into the structure. Note that this idealized structure has C/N ≈ 1:1.

Table 1: Physicochemical properties and photocatalytic activity of Pt/CNB for the hydrogen evolution reaction with UV and visible light.[a]

Catalyst	Surface area [m^2g^{-1}]	C/N molar ratio	Band gap[b] [eV]	H_2 evolution rate [$\mu mol\,h^{-1}$] $\lambda > 300$ nm	$\lambda > 420$ nm
g-C_3N_4[c]	10	0.73	2.67	148.2	6.5
$CNB_{0.05}$	22	0.74	2.57	253.1	29.4
$CNB_{0.1}$	19	0.75	2.45	218.8	16.4
$CNB_{0.2}$	14	0.76	2.26	175.7	12.7
$CNB_{0.5}$	12	0.80	1.86	115.3	8.9
$CNB_{1.0}$	11	0.88	1.68	53.9	5.1
$CNB_{2.0}$	12	0.96	1.58	8.5	1.6

[a] See Experimental Section for reaction conditions. [b] Estimated from optical measurements. [c] Synthesized by using dicyandiamine as precursor.

The XRD peak at 13° corresponding to in-plane ordering of tri-*s*-triazine units which form 1D melon strands[6] also slowly vanishes with increasing amount of BA. Indeed, replacement of some ring nitrogen atoms by CH_2 groups would weaken the H-bonding network and lead to lower in-plane order. Note that all carbon nitrides feature some residual amount of hydrogen, attributable to uncondensed amino groups. The presence of structured hydrogen in principle favors fast proton exchange in aqueous solution.

Substitution of N by C changes structural and electronic aspects and consequently the optical/electronic properties of the resulting CNB polymers. The UV/Vis reflectance spectrum (Figure 1, left) shows a remarkable redshift of optical absorption from 470 to 750 nm with increasing BA content compared to g-C_3N_4. This would allow wavelengths in which the solar photon flux is maximal to be covered.

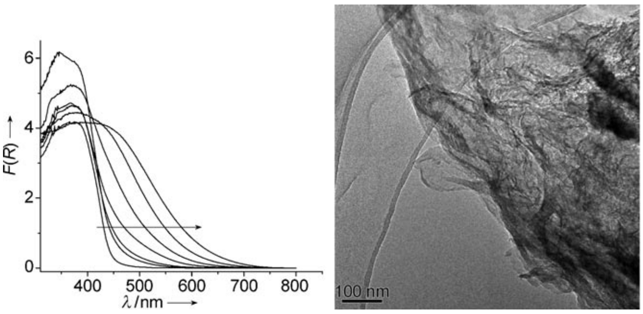

Figure 1. Left: UV/Vis diffuse-reflectance spectra of g-C_3N_4 and CNB samples; arrow direction: g-C_3N_4, $CNB_{0.05}$, $CNB_{0.1}$, $CNB_{0.2}$, $CNB_{0.5}$, $CNB_{1.0}$ and $CNB_{2.0}$. Right: a typical TEM image for $CNB_{0.05}$.

A typical TEM image (Figure 1, right) shows that the surface morphology of CMB is layered and platelet-like, which is similar to that of bulk g-C_3H_4, indicating that the modification of the polymeric subunits by copolymerization with BA does not significantly change the texture of carbon nitride polymer.

We also carried out electrochemical analysis of g-C_3N_4 and CBN samples, including Mott–Schottky plots, electrochemical impedance spectroscopy (EIS) Nyquist plots, and photocurrent response to investigate their electronic properties. Figure 2a shows typical Mott–Schottky plots in the dark for g-C_3N_4 and $CNB_{0.2}$, which suggest n-type characteristics of these organic semiconductors due to the positive slope of the linear plots.[12] Another important parameter derived from

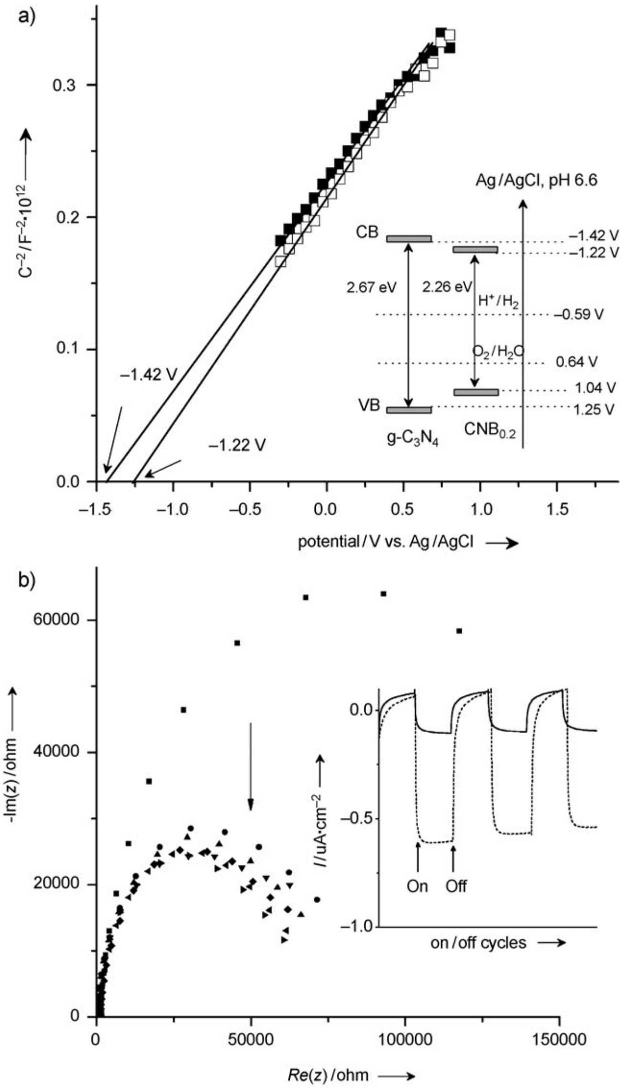

Figure 2. a) Mott–Schottky plots and band structure (inset; CB: conduction band, VB: valence band) of g-C_3N_4 (■) and $CNB_{0.2}$ (□), and b) EIS Nyquist plots for CNB samples (arrow direction: g-C_3N_4, $CNB_{0.05}$, $CNB_{0.1}$, $CNB_{0.2}$, $CNB_{0.5}$, $CNB_{1.0}$ and $CNB_{2.0}$), with the inset showing the periodic on/off photocurrent response of g-C_3N_4 (solid line) and $CNB_{0.2}$ (dotted line) electrodes in 0.2 M Na_2SO_4 with −0.2 V bias versus Ag/AgCl.

these measurements is the flat-band potential,[13] which is roughly −1.42 and −1.22 V versus Ag/AgCl for g-C_3N_4 and $CNB_{0.2}$, respectively, which thermodynamically enables photocatalytic water reduction (H^+/H_2: −0.59 V vs. Ag/AgCl at pH 6.6).

Anodic shifts in the flat-band potential observed for CNB samples compared to g-C_3N_4 reflect alterations due to copolymerization with BA. The band structure (inset of Figure 2a) can be determined by using the band gap determined from the $(ahv)^2$ versus photon-energy plots.[14] The experimental band structure revealed here is very close to the result of our previous DFT calculation.

Electrochemical impedance spectroscopy (Figure 2b) studying the charge transfer rate in the dark revealed the expected semicircular Nyquist plots for g-C_3N_4 and CBN, but with a significantly decreased diameter for the latter. The electron-transfer conductivity calculated with an equivalent circuit was found to increase by a factor of four for the CBN samples. This is further confirmed by the measurements of the photocurrent I_{ph} (inset of Figure 2b), which shows a remarkable improvement in I_{ph} of $CBN_{0.2}$ over g-C_3N_4. Large enhancement of I_{ph} was indeed observed over the entire bias potential ranging from −0.3 to 0.8 V versus Ag/AgCl, indicating faster transport of charged carriers. The photocurrent measurements however reveal an ambipolar nature of the materials, and thus the n-type nature revealed by the Mott–Schottky plots probably reflects the average of those particles in the dark.

Table 1 lists the photocatalytic activity of CNB samples toward hydrogen evolution from water/triethanolamine mixtures with visible light and Pt (3 wt %) as cocatalyst. Indeed, some CNB samples show a remarkable improvement in H_2 evolution activity (also in specific activity) over g-C_3N_4 both under UV irradiation and especially with visible light. The H_2 evolution rate, however, is maximal for the most weakly doped sample, that is, $CNB_{0.05}$. We interpret this finding to mean that excessive doping spoils the indirect character of the semiconductor and offers potential recombination sites. This is not unexpected for heavily doped semiconductors in general. At this point, further optimization of organocatalyst layout and photoreaction conditions as well as design of cocatalysts are certainly still desirable to achieve more efficient photocatalysis by a stable polymer semiconductor with a suitably narrow gap that still exhibits sufficient catalytic performance.

We also tested the stability of organic photocatalysts (Figure 3a). After the first run of photocatalytic reaction, the reaction mixture was kept for 60 d to examine the stability of the organic semiconductor in contact with water and dissolved oxygen. The mixture was then subjected to the four consecutive runs of photochemical reaction, and the activity was virtually identical to that in the initial run, without noticeable deterioration.

The total amount of 1.2 mmol H_2 gas (27 mL) produced during the entire operation, including the UV experiment, exceeded the amount of catalyst used (0.5 mmol). This is a strong indication that the reaction proceeds catalytically. Wavelength dependence of H_2 evolution by g-C_3N_4 and $CNB_{0.05}$ reveals that the activity of both samples corresponds to their optical absorption (Figure 3b). $CNB_{0.05}$ exhibits enhanced activity over g-C_3N_4 at corresponding wavelengths through the spectrum up to 590 nm, that is, in addition to absorption, the general photocatalytic properties have also been improved.

In conclusion, we have shown that the optical and electronic properties of carbon nitride polymer can be easily modified by standard organic protocols, here exemplified by copolymerization with barbituric acid. However, we believe that the diversity of organic chemistry will allow the rational design of a much broader set of carbon nitride polymers with controlled functions, opening a new pathway for the development of light-harvesting semiconductors. The distinct advantage of "flexibility" (easily adjustable electronic and textural

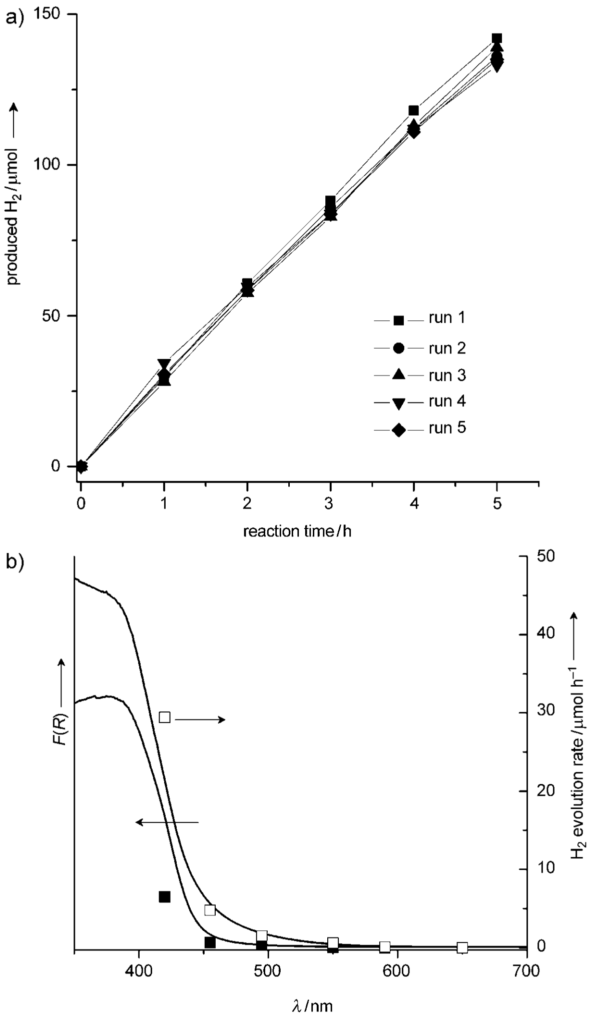

Figure 3. a) Stability test for Pt/$CNB_{0.05}$ under visible-light irradiation (> 420 nm) and b) wavelength dependence of hydrogen evolution rate on Pt/g-C_3N_4 (■) and Pt/$CNB_{0.05}$ (□).

structures) of carbon nitride polymers makes them particularly interesting for solar-energy application.

Experimental Section

Synthesis: CNB samples were synthesized by mixing dicyandiamide (3 g) with different amounts of BA in 15 mL water with stirring at 373 K to remove water. The resultant solids were calcined at 550 °C for 4 h in air to obtain the final samples.

Characterization: XRD measurements were performed on a Bruker D8 Advance diffractometer with $Cu_{K\alpha 1}$ radiation. The UV/Vis spectra were recorded on a Varian Cary 500 Scan UV/Vis system. FTIR spectra were recorded on a BioRad FTS 6000 spectrometer. TEM was performed on a FEI Tencai 20 microscope.

Photocatalytic tests: Reactions were carried out in a Pyrex top-irradiation reaction vessel connected to a closed glass gas-circulation system. H_2 production was studied on a dispersion of 0.1 g of catalyst in an aqueous solution (100 mL) containing triethanolamine (10 vol %). Pt was photodeposited on the catalysts by using H_2PtCl_6 dissolved in the reactant solution. The reactant solution was evacuated several times to remove air prior to irradiation under a HBO 500 W lamp and a water filter. The reactant solution was first irradiated for 2 h without the optical filter to facilitate deposition of Pt on the catalyst, and during these 2 h the H_2 evolution rate under UV irradiation ($\lambda > 300$ nm) was determined. Then, the system was evacuated to remove H_2 completely and exposed to visible-light irradiation ($\lambda > 420$ nm) by attaching a 420 nm cutoff filter at the light source. The evolved gases were analyzed by gas chromatography with a thermal conductive detector.

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