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Metal-free Photocatalytic Graphitic Carbon Nitride on p-type Chalcopyrite as Composite Photocathode for Light-induced Hydrogen Evolution

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Very recently, it has been shown that an abundant material, polymeric carbon nitride, can produce hydrogen from water under visible-light irradiation in the presence of a sacrificial donor^[1]. We will present here the preparation and characterization of graphitic carbon nitride (g-C₃N₄) films on p-type semiconducting CuGaSe₂ chalcopyrite thin film substrates by thermal condensation of dicyandiamide precursor under inert gas conditions. Structural and surface morphological studies of the carbon nitride films suggest a high porosity of g-C₃N₄ thin film consisting of a network of nanocrystallites. Photo-

electrochemical investigations show upon cathodic polarization light-induced hydrogen evolution for a wide range of proton concentrations in the aqueous electrolyte. Additionally, Synchrotron radiation based photoelectron spectroscopy has been applied to study the surface/near-surface chemical composition of the utilized g-C₃N₄ film photocathodes. For the first time it is shown that g-C₃N₄ films coated on p-type CuGaSe₂ thin films can be successfully applied as new photoelectrochemical composite photocathode for light induced hydrogen evolution.

Introduction

In the past 3 decades, a variety of inorganic semiconducting, polymeric and molecular materials have been synthesized as catalytically active material for hydrogen evolution from water under visible light illumination^[2-13]. Semiconductors explored so far are assembled from transition-metal ions with d⁰ electronic configuration or post-transition-metal ions of d¹⁰ configuration, along with group VA or VIA ions as counter-anion components^[3, 7-13]. In general, the photocatalytic conversion reaction is only chemically productive if precious-metal species^[12] such as Pt and RuO₂ are used in most cases as additional co-catalysts to promote the transfer of photoinduced charge carriers from the bulk to the surface at which water molecules are converted to hydrogen gas. Organic metal-based complexes in natural enzymes (for example, a complex with four manganese ions in photosystem II (ref. 14) and a di-iron centre in hydrogenases^[15]) have been identified as being the active photocatalytic sites for water decomposition. Polymeric semiconductors such as polyparaphenylene^[16] have also been synthesized for the hydrogen production but they reveal moderate photocatalytic performance only in the ultraviolet region. Very recently, it has been shown that a further polymer-like semiconductor, made of carbon and nitrogen only, can act as metal-free photocatalyst for the evolution of hydrogen from water^[1]. It has been shown that the abundant material, polymeric carbon nitride, can produce hydrogen from water under visible-light irradiation in the presence of a sacrificial donor^[1]. Contrary to other conducting polymer semiconductors, carbon nitride is chemically and thermally stable and does not require complicated device manufacturing. Carbon nitrides can exist in several allotropes with diverse properties, but

the graphitic phase is regarded as the most stable under ambient conditions. A huge number of different preparation routes exist regarding to the synthesis of carbon nitride (see for example refs. 17 and 18). The synthesis of meso-porous graphitic carbon nitride -g-C₃N₄- via thermal polycondensation reaction of cyanamide, dicyandiamide or melamine used as precursors is thoroughly described in refs. 1 and 19.

In the present work g-C₃N₄ films have been deposited onto semiconducting substrates by thermal polycondensation of an organic dicyandiamide precursor. Photoelectrochemical investigations have been performed by applying a front-contacting to the g-C₃N₄ films. Upon cathodic polarization g-C₃N₄-films can be used as photocathode catalyzing light-induced hydrogen in aqueous electrolyte. The photoelectron spectroscopy shows the elemental surface/near surface composition of the utilized g-C₃N₄ film photocathodes.

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Results and Discussion

Preparation, structure and surface morphology of g-C₃N₄ thin films

Films of graphitic carbon nitride were synthesized onto semiconducting chalcopyrite substrates and porous silicon wafers by thermal treatment of dicyandiamide at temperatures of 550° up to 600°C. The film thickness was controlled by the employed amount of the dicyandiamide precursor. Fig.1 shows the thermal polycondensation reaction route of g-C₃N₄ films starting from dicyandiamide (see refs. 20 and 21).

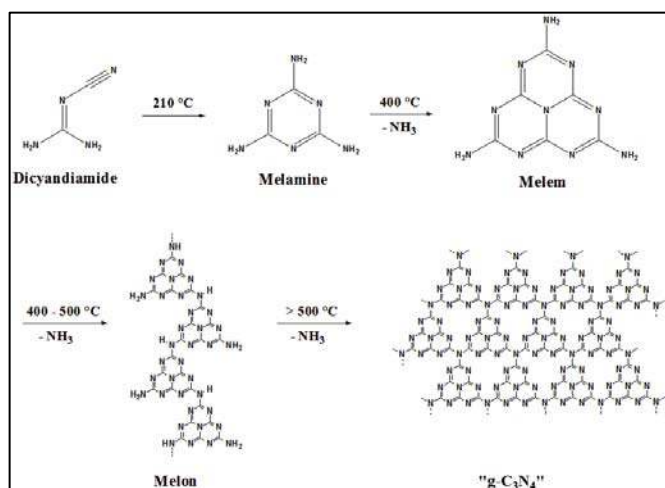


Figure 1: Schematic presentation of the thermal polycondensation reaction route of g-C₃N₄ films onto semiconducting substrates (see refs. 20 and 21).

Fig.2 shows the X-ray diffraction (XRD) patterns of g-C₃N₄ films on CuGaSe₂ substrate (red) and on porous Si(100) substrate (blue) detected under a grazing X-ray incidence angle of 1°. For comparison, a typical XRD pattern of g-C₃N₄ powder (black) detected in the conventional Debye-Scherrer 2θ-mode is also shown. There is a very good agreement of the XRD pattern of the films, the powder (as shown in Fig.2) and recent literature data^[1]. These results indicate that the synthesized films coincide with the lattice structure of single phase graphitic carbon nitride. Moreover, optical absorption and photoluminescence studies of the films confirm the single graphitic carbon nitride phase with its band gap of 2.7 eV (and its broad, defect-dominated PL-signal, not shown here). A broad nitride pores related peak appears at 13.4°, while as in graphite, the strongest XRD peak at 27.4° in Fig.2, corresponding to 0.326 nm, is due to the stacking of the conjugated aromatic system^[1, 19]. By using the Scherrer equation we assume from the corresponding full width at half maximum (FWHM) of the two diffraction peaks that the films consists of a nanocrystalline network with nanocrystals of ~ (10 x 10 x 6) nm³ in average size.

The graphitic planes are composed of tri-s-triazine (melem) units connected by planar amino groups (Fig. 1). The in-plane organization of tri-s-triazine units and the compression of aromatic planes have been found to follow the perfection of condensation. In the course of increased condensation temperature a compression of the stacking distance is found of the conjugated aromatic system. For g-C₃N₄ condensed at 773 K up to 883 K, the stacking distance of the aromatic system decreases from 0.331 nm (2θ = 27.0°) to 0.326 nm (2θ = 27.4°). Additionally, between 773 K and 883 K, the in-planar repeat

period decreases from 0.682 nm (2θ = 13.0°) to 0.662 nm (2θ = 13.4°) (not shown here). This strongly indicates that the perfection of the graphitic

carbon nitride system is improved under by release of gaseous ammonia with increasing condensation temperature.

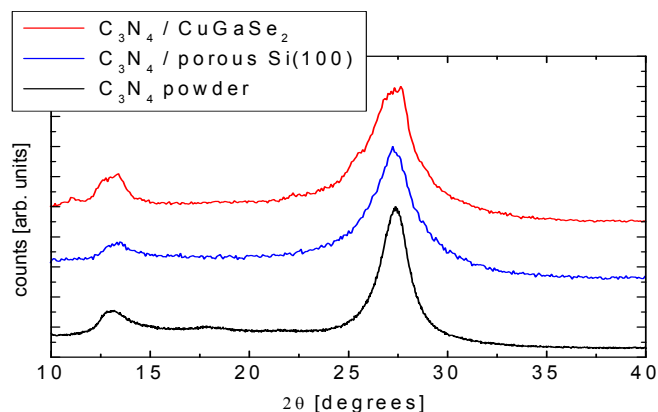


Figure 2: X-ray diffraction pattern of g-C₃N₄: films on CuGaSe₂ substrate (red) and on porous silicon substrate (blue). For comparison, the XRD pattern of g-C₃N₄ powder (black) detected in conventional Debye-Scherrer 2θ-mode is also shown.

In Fig. 3 the surface morphology of the g-C₃N₄ films is presented by optical (Figs. 3a and b) and scanning electron microscopy (SEM; Fig. 3c) pictures. The surface morphology of the films is highly porous consisting of larger (see Figs. 3a and b) and smaller craters (see Fig. 3c) and ditches in the μm scale. The averaged thickness of typical film is ~200 μm independent of the substrate (see Fig. 3b). The high porosity indicates an enlarged surface area which is required and beneficial for an enhanced photoelectrochemical performance.

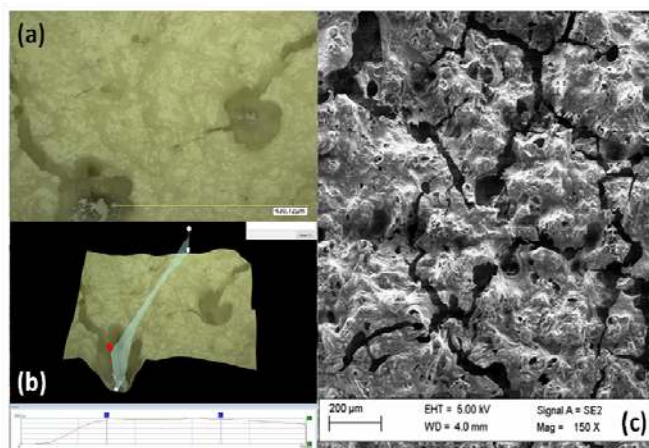


Figure 3: Surface morphology of g-C₃N₄ films as investigated by optical, (a) and (b), and scanning electron (c) microscopy (SEM). The surface morphology reveals a high porosity and, hence, an enlarged surface area with ditches and craters in the μm scale.

Photo-electrochemical application of g-C₃N₄ thin films

Photo-electrochemical investigations have been performed by applying a front-contact to the sample using a conductive carbon tape in order to exclude the influence of the semiconducting silicon or chalcopyrite substrate. Figure 4 displays the used 3-electrode-arrangement with the g-C₃N₄ film as working electrode (sample, WE), a Pt counter electrode (CE) and a Ag/AgCl reference electrode (RE).

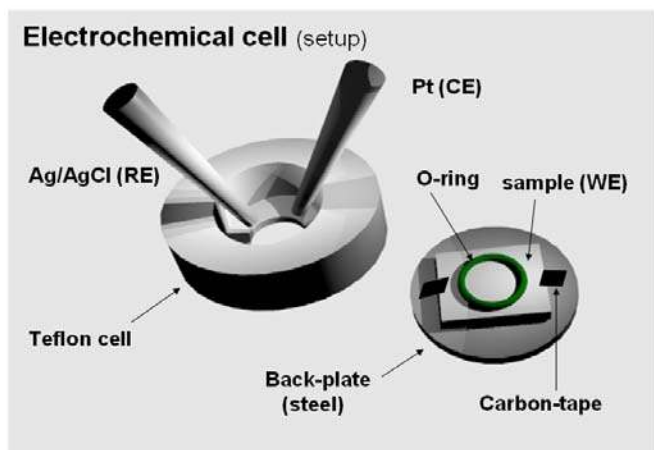


Figure 4. The used electrochemical setup consisting of a 3-electrode assembly is shown with the g-C₃N₄ film sample as working electrode.

Typical dark and photo-induced cathodic current densities in diluted sulphuric acid solution (0.1 M) are shown in Fig.5 of a g-C₃N₄ film deposited on a CuGaSe₂ chalcopyrite substrate as a function of the applied potential. The advantageous influence of extra deposited noble metal particles on the g-C₃N₄ films is also illustrated in Fig.5. In the case of a pristine film we observe a dark current density of ~10 $\mu\text{A}/\text{cm}^2$ at an applied potential of -1.0 V. Under illumination of 1 sun the current density increases to ~15 $\mu\text{A}/\text{cm}^2$ (yellow j-V curves in Fig. 5). The current densities increase by a factor of 2 and 4 due to the deposition of Pt nanoparticles (grey curves in Fig. 5) and Pt plus Rh nanoparticles (quantity of precipitated particles by electrochemical deposition: 2 mC; brown curves in Fig. 5) on the thin film surface.

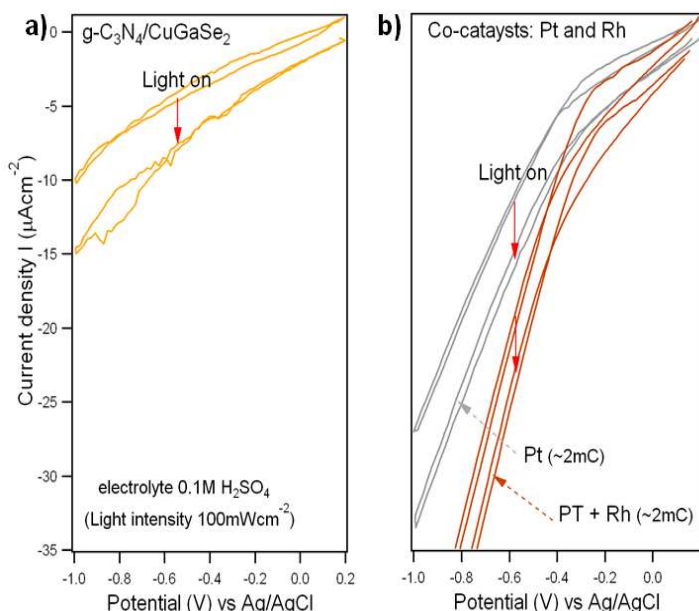


Figure 5: Dark current and photocurrent densities of a g-C₃N₄ film on CuGaSe₂ chalcopyrite substrate under cathodic conditions. The red curves show typical j-V-curves of the pristine g-C₃N₄ film and the beneficial influence on the photoelectrochemical performance of noble metal nanoparticles deposited on the g-C₃N₄ film surface is pointed out for Pt nano-particle precipitation (grey curves) and Pt+Rh nano particle precipitation (brown curves).

For the pristine g-C₃N₄ film we observe a light induced current density gain (photoeffect) under cathodic conditions of ~ 5 $\mu\text{A}/\text{cm}^2$. After noble metal particle precipitation this photoeffect is enhanced by a factor of 1.5.

A non linear increase of the photocurrent densities can be detected with raising light intensities. The non linear behavior can be attributed to inhibited charge transfer kinetics to molecules in solution -such as H₃O⁺, H₂, and H₂O- at the interface between the aqueous electrolyte and the g-C₃N₄ film surface due to a very low conductivity of the intrinsic g-C₃N₄ film ($\sigma \approx 5 \cdot 10^{-12} \text{ S}/\text{cm}^{[22]}$). Fig.6 displays the so called open circuit potential (OCP) with and without light illumination as a measure for the photoactivity of the pristine and noble metal covered g-C₃N₄ film photocathodes. The OCPs reveal a shift from light-off to light-on (illumination of 1 sun, AM1.5) of ~150 mV for all three photocathodes as shown in Fig.6. The direction of shift is positive towards the anodic potential region since the quasi-Fermi level -or the electrochemical potential- of the electrons raises under light illumination which is typical for a p-type semiconducting system.

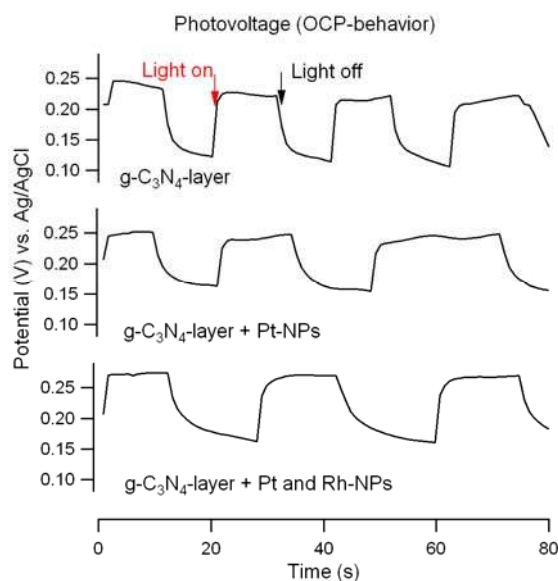
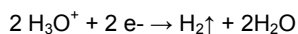


Figure 6: Detection of the so called open circuit potential (OCP) with and without light illumination of 1 sun (AM1.5) as an extent of the photoelectrochemical activity of the pristine and noble-metal covered g-C₃N₄- film photocathodes.

For the first time, we show here a clear proof for the photoelectrochemical performance of g-C₃N₄ film photocathodes under illumination of 1 sun. Under illumination we detect at the NHE (Normal hydrogen electrode) potential of -0.20 V (vs Ag/AgCl) an already existing cathodic photocurrent density of ~5 $\mu\text{A}/\text{cm}^2$ which can be assigned to the reduction of hydronium ions, H₃O⁺, to hydrogen:



Additionally, a bubbling of gaseous hydrogen can be monitored on the long term time scale under cathodic conditions or under a higher cathodic potential. The investigated g-C₃N₄ thin film photocathodes exhibit a high stability under the applied photoelectrochemical conditions of 1 sun illumination under acidic conditions. The presented photocurrent densities are detected over several hours without losses.

Photoelectron spectroscopy of g-C₃N₄ thin films

Synchrotron-based X-ray photoemission spectroscopy (SXPS) was performed at BESSY to assess the surface chemical composition of g-C₃N₄ films deposited on CuGaSe₂ and silicon substrates with variable photon energies. Here we will show our very recent SXPS data of the two working photocathodes as presented in the last section. The samples have been heated up to 300°C for 5 min. in order to thermally decompose the surface oxide and to increase the conductivity of the samples.

In Fig. 7 SXPS survey scans are shown of g-C₃N₄ films on CuGaSe₂ after electrodeposition (i) of Pt nanoparticles (NPs) (red) and (ii) Pt+Rh NPs (gray) on the surface. The spectra reveal that only carbon and nitrogen can be observed at the surface/near-surface region of the photocathodes together with very small amounts of the Pt and Rh co-catalysts.

After the annealing process, no surface oxygen could be observed. The overall C/N ratio of 0.67 obtained from the SXPS data indicates the presence of excess nitrogen in comparison to carbon atoms. Thus, the g-C₃N₄ film photocathodes of the present study are characterized by a slight nitrogen-rich concentration of about 4% in comparison to the ideal theoretical value of g-C₃N₄ (0.71) as calculated from the structure shown in Fig.1.

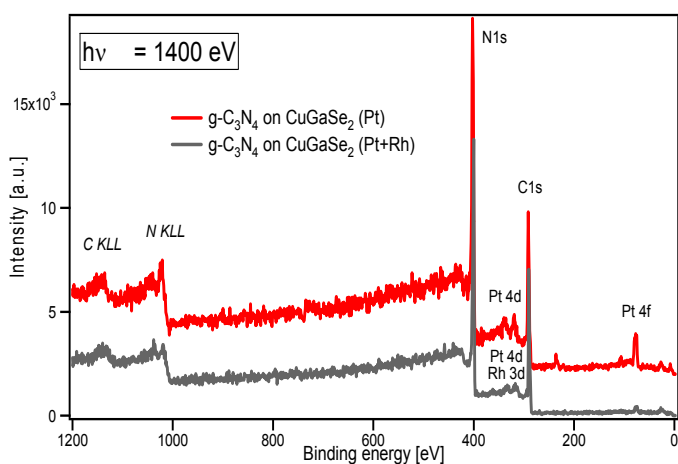


Figure 7: XPS Survey scans (excited with $h\nu = 1400$ eV photon energy) of the two working photocathodes: g-C₃N₄ film on CuGaSe₂ with Pt NPs (red curve) and with Pt+Rh NPs (gray curve) detected after annealing up to 300°C for 5 min, respectively.

Figure 8 depicts the corresponding high-resolution SXPS spectra of the C1s (top) and N1s (bottom) core levels of g-C₃N₄ films deposited on CuGaSe₂ substrates. Corresponding data for

g-C₃N₄ powder are shown for comparison. In order guarantee similar photoelectron escape depths, the C1s and N1s core level spectra of the films have been excited with photon energies of $h\nu = 450$ and 550 eV, respectively. Hence, the information depth –i.e. three times the mean free path of photoelectrons in the material– is quasi equal due to similar kinetic energies of the C1s and N1s photoelectrons of 170 eV and 150 eV, respectively. For comparison, the C1s core levels of the powder spread onto conducting carbon tape are given (excited with Mg K_α radiation; $h\nu = 1253.6$ eV). The core level spectra have been deconvoluted by a fitting procedure using Voigt line shapes (combination of Gaussian-Lorentzian functions) after a Shirley background subtraction. We found a shift of the core level binding energy (BE) of 4.0 eV due to a homogenous positive electric charging of the photocathode surface by measuring the Pt 4f core levels (not shown here). Hence, the presented spectra in Fig. 8 have been shifted towards lower BE.

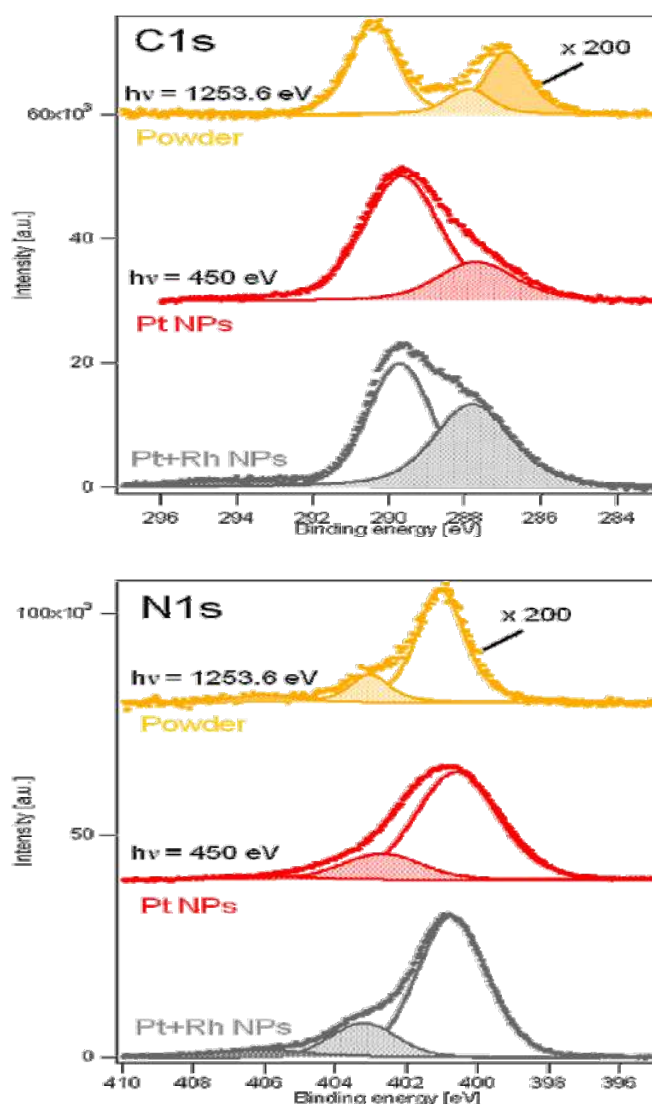


Figure 8: High resolution SXPS spectra of the C 1s (top) and N 1s (bottom) core level of g-C₃N₄ film on CuGaSe₂ with Pt NPs (red curves) and Pt+Rh NPs (gray curves), respectively. The spectra of the films were excited with a photon energy of $h\nu = 450$ and 550 eV, respectively, after annealing of the samples up to 300°C for 5 min. The corresponding core levels of the powder (yellow curves) are shown for comparison at the top. Afterwards,

the spectra were fitted with a Voigt function (convolution of Gaussian-Lorentzian sum functions) after a Shirley background subtraction.

C1s spectra of g-C₃N₄ films with Pt and Pt+Rh nanoparticles (NPs) deposited on CuGaSe₂ substrates reveal a broad asymmetric feature centered at 289.6 eV which can be fitted by two peaks at 287.9 and 289.7 eV, respectively. Additionally, a small peak occurs at 294.5 eV for the CuGaSe₂ substrate with Pt and Rh nanoparticles (NPs) which can be attributed to remaining carbonyl (C=O) groups. The C1s core level spectrum of the powder shows a two peaks at BE of 287 eV and 290.4 eV. The main dominant peaks at 289.7 eV of the films and at 290.4 eV of the powder is assigned to sp² carbon-nitrogen bondings of the aromatic ring system –i.e s-triazine unit-. The peak at lower BE of 287.9 eV in the films and the powder are ascribed to tertiary nitrogen N-(C)₃ groups, i.e. trigonally bonded to three sp² carbon atoms in the C–N network (bridge, graphitic-like nitrogen structure). The peaks in the films are somewhat broader compared to the powder which can be related either to a lesser electron shielding of the photo-excited positive holes in the film or to a residual inhomogeneous charging.

The N1s spectra show a broad peak centered at 400.8 eV with a shoulder at higher BE. A deconvolution of the feature reveals contributions of two peaks at 400.76 and 403.26 eV, respectively. The dominant nitrogen peak at 400.8 eV is attributed to nitrogen atoms sp²-bonded to two carbon atoms (s-triazine rings, pyridine-like nitrogen atoms) while the other peak is due to tertiary nitrogen N-(C)₃ groups, i.e. trigonally bonded to three sp² carbon atoms in the C–N network (bridge, graphitic-like nitrogen structure). Here again, the N1s core levels of the films are in good agreement with the g-C₃N₄ powder. The region at 401-403 eV is generally referred to quaternary nitrogen, i.e. like “graphitic” nitrogen when the nitrogen atom is incorporated into the graphene layer replacing the carbon atom [29]. Another small contribution peak at ~406 eV can be assigned to residual nitrite-like (NO₂) groups at the surface/near-surface.

Films of g-C₃N₄ utilized as photoelectrochemical semiconducting material in the light-induced water and/or hydronium ion reduction must accomplish (i) the adsorption of water molecules and/or hydronium ions at the catalyst surface (ii) light-induced electron transfer from the surface to the adsorbed species –i.e. a chemical reduction-, (iii) the subsequent dissociation of the adsorbed species and, (iv) finally, the desorption of molecular hydrogen. Hence, an essential requirement for the photoelectrochemical reduction and the generation of molecular hydrogen is the energetic position of the conduction band minimum (CBM) of the g-C₃N₄ film photocathode which must be located at negative potential versus the hydrogen reduction potential $\mu_e^{H_2/H^+}$ (see Fig.9).

A band alignment of the g-C₃N₄ /CuGaSe₂ film photocathode is presented in Fig. 9 together with the electrochemical and the absolute scale of both the hydrogen reduction potential $\mu_e^{H_2/H^+}$, and the water oxidation potential, $\mu_e^{H_2O/O_2}$, on the right hand side. Recent values from the literature are in the range of 4.4 and 4.7 eV for $\mu_e^{H_2/H^+}$ referred to the vacuum level, E_{vac} [23-26]. For g-C₃N₄ films used as photocathode, the electron affinity of g-C₃N₄ films has to be smaller than the hydrogen reduction potential, $\mu_e^{H_2/H^+}$, of 4.6 eV –redox potential of the normal hydrogen electrode, NHE. Our very recent photoemission results of g-C₃N₄ films show a workfunction, Φ_{WF} , of (4.4 ± 0.4) eV and an energetic distance,

Δ_{VBM-EF} between the valence band maximum, E_{VBM} , and the Fermi level, E_F , of (1.5 ± 0.3) eV [27]. With an optical band gap energy, E_g , of (2.7 ± 0.1) eV, the latter value is a strong hint for an intrinsic g-C₃N₄ semiconductor. Hence, the electron affinity of g-C₃N₄ films is about 3 eV –referred to E_{vac} -. It follows from the foregoing that the hydrogen redox potential $\mu_e^{H_2/H^+}$ is energetically positioned below the CBM of g-C₃N₄.

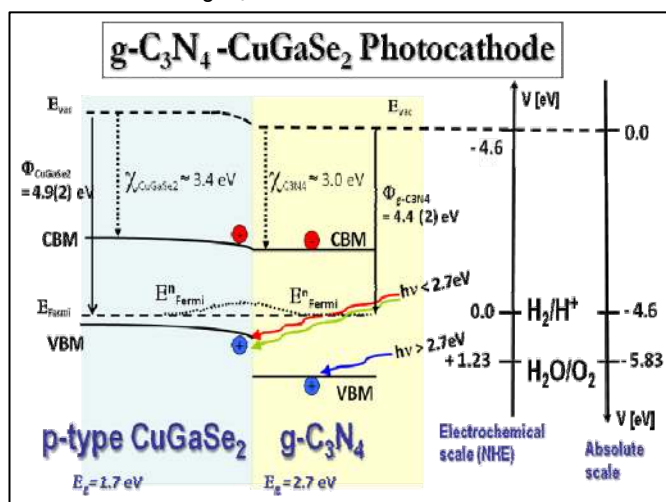


Figure 9. Proposed band alignment of g-C₃N₄ - CuGaSe₂ photocathode is given together with the electrochemical and the absolute scale of both the hydrogen reduction potential $\mu_e^{H_2/H^+}$, and the water oxidation potential, $\mu_e^{H_2O/O_2}$, on the right hand side [23-26]. The derived energetic position of the CBM of ~3 eV –i.e. the electron affinity- is negative versus the hydrogen reduction potential $\mu_e^{H_2/H^+}$ which allows a performance of the g-C₃N₄ film as photocathode.

Under the illumination of light with energies higher than the band gap energy of 2.7 eV, the photo-excited electrons in the conduction band are able to diffuse to the surface and to reduce protons, H⁺, or hydronium ions, H₃O⁺ in a solution. Furthermore, photon with energies below 2.7 eV can be absorbed in the CuGaSe₂ chalcopyrite substrate and the photo-generated electrons drifts to g-C₃N₄. If the g-C₃N₄ film thickness is in the range of the charge carrier diffusion length, these photo-generated electrons are also available for a proton reduction at the g-C₃N₄ surface.

In agreement with a recent publication^[1], we found here for the first time evidence that g-C₃N₄ films are an appropriate photocatalyst and can be used as photocathode for the light-induced hydrogen evolution from water and/or hydronium ions. Furthermore, the presented g-C₃N₄ film photocathode is chemically stable under the applied acid conditions in the presence of light for several hours.

Conclusion

Films of g-C₃N₄ have been prepared onto semiconducting substrates and they exhibit a highly porous morphology consisting of a nanocrystalline network with an averaged crystallite size of ~(10 x 10 x 6) nm³. For the first time, we show here a clear proof for the photoelectrochemical performance of g-C₃N₄ film photocathodes under illumination of 1 sun. The photoelectrochemical investigations reveal a photo-catalytical behavior

of these films with corresponding photocurrent densities of $\sim 5 \mu\text{A}/\text{cm}^2$ and an open circuit potential of $\sim 150 \text{ mV}$. We found some increase of the photo-electrochemical performance by using noble-metal co-catalysts. The overall C/N ratio of 0.67 of the utilized photocathodes indicates the presence of excess nitrogen in comparison to carbon atoms. Remaining surface oxides could be thermally decomposed. Hence, the g-C₃N₄ film photocathodes of the present study are characterized by a slight nitrogen-rich concentration of about 4% in comparison to the ideal theoretical value of g-C₃N₄ (0.71).

Experimental Section

Thin films of graphitic carbon nitride were synthesized onto semiconducting p-type CuGaSe₂ and p-type CuInS₂ chalcopyrite substrates and porous silicon wafers by thermal treatment of dicyandiamide (C₂N₄H₄) utilized either in the solid state powder or as solution in water or ethanol at temperatures of 550° up to 600°C under an inert nitrogen or argon gas atmosphere.

Sulphuric acid solutions with varying molarities (0.1 up to 1M) and deionized water were used as electrolyte and a W-I lamp was employed as light source with varying light intensities (88 - 100 mW/cm²; 100 mW/cm² \equiv 1 sun \equiv AM1.5).

The photoemission core levels of the films have been excited by monochromatized light of the ISSS-beamline at the Berliner Synchrotron radiation source BESSY^[28]. The photon excitation energies of $h\nu = 450 \text{ eV}$, 550 eV and 680 eV have been chosen in order to detect the C1s, N1s and O1s core levels of g-C₃N₄ thin films with a similar kinetic energy of the photoelectrons.

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Keywords: (graphitic carbon nitride · photocatalysis · photoelectrochemical hydrogen evolution · XPS)

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