# Metal-free photocatalytic polymeric carbon nitride on p-type chalcopyrite as new thin film composite photocathodes for hydrogen evolution under visible light illumination

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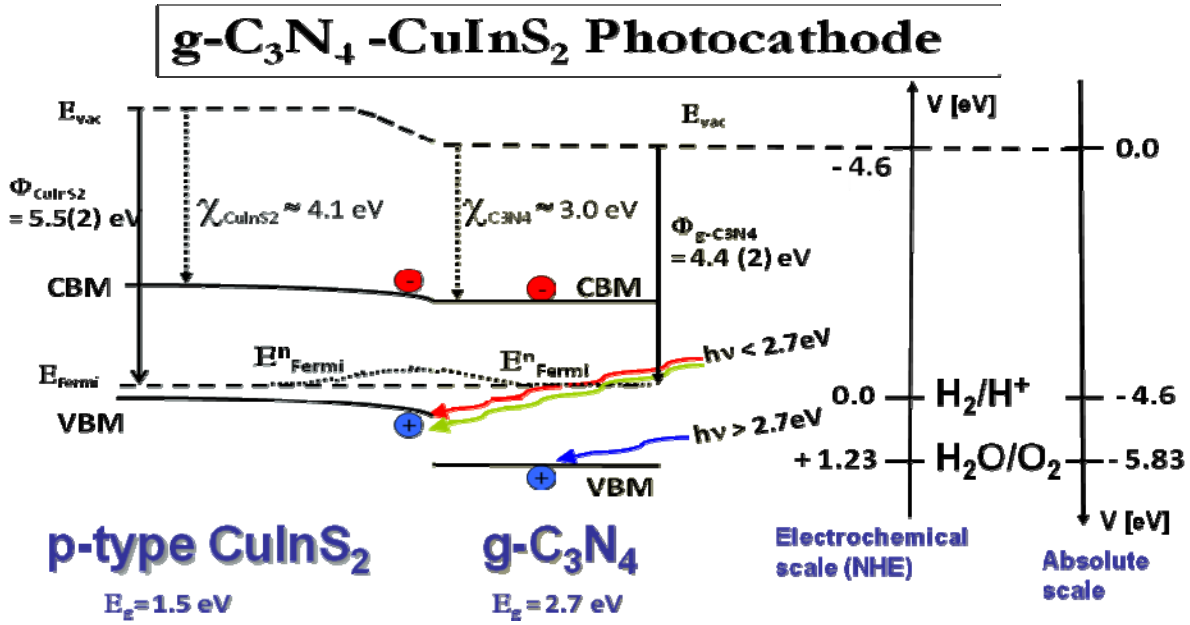
Very recently, it has been shown that an abundant material, polymeric carbon nitride, can produce hydrogen from water under visible-light irradiation in the presence of a sacrificial donor [1]. We will present here the preparation and characterization of graphitic carbon nitride (g-$C_3N_4$) films on semiconducting 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-$C_3N_4$ thin films 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-$C_3N_4$ film photocathodes. For the first time it is shown that g-$C_3N_4$ films can be successfully applied as photoelectrochemical material for light induced hydrogen evolution [2]. Additionally, polycrystalline $CuInS_2$ semiconducting chalcopyrite thin films used as photocathodes showed a cathodic photocurrent density of 25 $\mu A/cm^2$ at a potential of -1.5 V. Surface modification with g-$C_3N_4$ films strongly enhanced the cathodic photocurrent by one order of magnitude to 250 $\mu A/cm^2$ and also revealed long term stability for duration more than 24h in 0.1 M $H_2SO_4$ solution. Water splitting into $H_2$ evolution under visible light can be successfully achieved from g-$C_3N_4$ films on polycrystalline $CuInS_2$ chalcopyrite photocathodes [3] (see Figure).




Proposed band alignment of g-$C_3N_4$ - $CuInS_2$ photocathode is given together with the electrochemical and the absolute scale of both the hydrogen reduction potential $\mu_e^{H+/H2}$, and the water oxidation potential, $\mu_e^{H2O/O2}$, on the right hand side. The derived energetic position of the CBM of ~3 eV -i.e. the electron affinity- is negative versus the hydrogen reduction potential $\mu_e^{H+/H2}$ which allows a performance of the g-C3N4 film as photocathode.

[1] X. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen, M. Antonietti, Nature Mat. **2009**,*8*, 76-80.

[2] F. Yang, M. Lublow, S. Orthmann, C. Merschjann, T. Tyborski, M. Rusu, M. Kanis, A. Thomas, R. Arrigo, M. Hävecker, Th. Schedel-Niedrig, ChemSusChem (submitted 2.11.2011).

[3] F. Yang, M. Lublow, V. Kuznietsov, Ch. Merschjann, M. Kanis, A. Thomas, M. Antonietti, J. Klaer, Th. Schedel-Niedrig, J. Chem. Phys. C. (in preparation).