Title	**Light-triggered catalytic conversion of nitrogen-containing species for environmental remediation and sustainable synthesis of value-added chemicals**

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Ammonia (NH_3) is an indispensable chemical feedstock for various important end-uses, encompassing fertilizers, chemicals, medicines. Thanks to its high hydrogen content (≈17.7 wt %), gravimetric energy density ($3\ kWh\cdot kg^{-1}$), and safety (in comparison to H_2), as well as the convenient transportation (easily liquefied), NH_3 has been highlighted as a promising zero-carbon energy carrier for extensive applications such as direct NH_3 fuel cells and H_2 production (through NH_3 cracking). Indeed, the strategic "ammonia-hydrogen" roadmap has been well outlined with the items of ammonia synthesis, storage/transportation, and $NH_3 \rightarrow H_2$ utilization/conversion. In this regard, NH_3 preparation is of key importance and, consequently, significant efforts have been aimed at developing technologies for ammonia production compliant with the ever more stringent environmental regulations. Beside conventional hydrogen production with reduced CO_2 emissions by coupling with carbon capture and storage (*blue* ammonia), a prominent role is played by *green* ammonia, obtained through electrolytic processes using renewable electricity through the activation of nearly limitless molecular nitrogen (N_2). Nonetheless, the direct use of solar irradiation for N_2 conversion is a highly challenging approach plagued by low yields, still very far from reaching industrial viability. In a different way, a sustainable and more feasible alternative involves the conversion of nitrate (NO_3^-) into ammonia, strategically appealing in the framework of waste valorisation (e.g. nitrate-containing wastewaters) for the obtainment of resources. However, the NO_3^--to-NH_3 reaction involves multi-step electron transfer and complex intermediates, and driving an efficient NO_3^- reduction with high NH_3 selectivity is far from being straightforward. Various concurrent advantages in this regard are offered by photocatalytic and photoelectrocatalytic processes, whose optimization still requires significant research efforts concerning the development of suitable catalyst materials. Among the various investigated candidates, graphitic carbon nitrides (gCN) have recently emerged as very valuable workhorses for similar end-uses, especially after tuning their N-vacancy content and/or upon coupling with suitable transition metal oxides [1,2]. The introduction of nitrogen vacancies, working as active centres for N_2 activation, has been pursued by various complementary approaches, including annealing, chemical treatments under different conditions, or plasma exposure [3]. A complementary approach involves the construction of heterojunctions between gCN and suitable partner materials, enabling to benefit from the mutual chemical and electronic interplay between the system constituents [4,7]. The best results in terms of functional performances are obtained when the strategies of defect engineering and heterojunction formation are combined [1,2].

In this context, the present PhD project will be focused on frontier research activities aimed at the development of innovative gCN-based materials for photo-activated ammonia synthesis either from N_2 or NO_3^-. The corresponding research activities can be summarized as follows:

1) As far as the N_2-to-NH_3 reaction is concerned, nitrogen vacancies can be generated either by thermal condensation of melamine, cyanuric acid or thiourea to gCN under controlled conditions, or by cold-plasma treatment of pre-synthetized gCN. In this regard, the proposing research group has matured a solid and internationally recognized know-how over the last decades [4, 6, 7]. In addition, the decoration with noble metals (such as Au, Ag or their alloys), either in form of nanoaggregates or atomically dispersed species, could favourably contribute to the enhancement of material photoactivity through the concurrence of optical, electronic and chemical effects. Following recent results [6], a similar functionalization can be successfully accomplished by sputtering under mild operating conditions. Heterojunction formation with transition metal oxides or chalcogenides will also be investigated through hydrothermal synthesis, in *situ* electrochemical deposition or by plasma enhanced CVD.
2) Regarding catalysts for the photo-electro-reduction of NO_3^-, gCN will be coupled with suitable transition metal oxides, to be used as photocathodes in multi-junctions structures like Cu_2O/CuO/gCN, that have recently been proven to be very effective in the HER under visible light [7].

The prepared materials will be used as photocathodes in the proposing MFN group for the electrochemical synthesis of ammonia, and, in a complementary approach, as photocatalysts in the group of prof. L. Sánchez at Cordoba University (see scheme below). This group, that has already a well-established scientific collaboration with the MFN one, possesses a long-standing experience in the development and testing of photocatalysts for the conversion of nitrogen oxides into harmless nitrates (DeNO$_x$ processes) [8]. After a multi-technique characterization of material structure, morphology, chemical composition and optical properties by means of complementary analytical tools, attention will be dedicated to the investigation of material functional properties, and to their optimization through a feedback loop with their chemico-physical characteristics A detailed photo-electrochemical characterization will be performed in the proposing group, whereas the photocatalytic mechanism of the target processes will be investigated in detail in coordination with prof. Sánchez group.

PADOVA: Liquid-phase photoelectrochemical generation of ammonia

$$N_2 \longrightarrow NH_3$$

$$NO_3^- \longrightarrow NH_3$$

CORDOBA: Gas- and liquid-phase photocatalytic generation of ammonia

$$N_2 \longrightarrow NH_3$$

In particular, the samples will be employed as photocatalysts in air and aqueous media under UV-Vis and Visible light irradiation. The production of radical species, charge transfer mechanism and intermediates will be investigated by using EPR, PL and DRIFTS techniques, so that a detailed elucidation of the catalytic mechanism can be obtained. Standard photoelectrochemical techniques will be employed (Chopped Light LSVs, IPCE, EIS and Mott-Schottky analysis) as well as Intensity Modulated Photocurrent Spectroscopy (IMPS) measurements to gain insights on the electron-hole life time and charge transfer kinetic constants [5, 9]. The analysis of the possible reduction products and intermediates, such as ammonia and hydrazine, will be carried out by chromatographic methods in cooperation with the group coordinated by prof. Valerio Di Marco at DiSC, Padova. In this regard, the method displaying the best performances together with adequate detection limit appears to be ionic chromatography [10]. Alternatively, hydrazine can also be determined by HPLC ion-pair chromatography [11]. Attention will be dedicated to optimizing the target analytical method and to adapt it to the investigated process, to achieve a reliable and reproducible quantification.

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