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Influence of the gas atmosphere during the synthesis of g-C₃N₄ for enhanced photocatalytic H₂ production from water on Au/g-C₃N₄ composites†

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The design of Au/g-C₃N₄ nanocomposites for enhanced H₂ production from water under solar and visible light irradiation is presented by varying the g-C₃N₄ synthesis atmosphere (air, N₂, H₂, Ar and NH₃). We showed for the first time that the synthesis of g-C₃N₄ in a pure NH₃ atmosphere led to enhanced photocatalytic performances between 3 and 9 times higher than g-C₃N₄ prepared in other gas atmospheres. The resulting, novel 0.3 wt% Au/g-C₃N₄-NH₃ photocatalyst produced up to 324 μmol h⁻¹ g_{cat}⁻¹ and 26 μmol h⁻¹ g_{cat}⁻¹ of H₂ corresponding to internal quantum yields of 1.85 and 0.60% under solar and visible light irradiation respectively, with an unusually low amount of triethanolamine used as the sacrificial agent (1 vol%). This enhanced activity was correlated to the structural, optical, porosity, and surface properties of g-C₃N₄, and to the quality of the interface with Au NPs. From an in-depth structure–activity correlation study, we highlighted the combined effects of a higher surface area with larger contribution of mesoporous volume, higher crystallization degree of g-C₃N₄-NH₃ and lower deformation of nanosheets. Additionally, the ratio between tri-s-triazine and s-triazine based C₃N₄ was determined and used for the first time to point out the effect of different continuous gas flow atmospheres during synthesis. Furthermore, the suitable surface chemistry of g-C₃N₄-NH₃ allowed more homogeneous coverage with small Au NPs yielding more intimate contact and higher quality of the interface between Au NPs and the g-C₃N₄ support.

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Introduction

Energy and environmental crises are amongst the most serious issues that mankind is facing.¹ Solar energy is an abundant and clean energy source. The vast supply of energy from the Sun to the Earth is 3.8×10^{24} joules a year corresponding to 7500 times that of the global population consumption.² The two main obstacles for widespread of solar energy usage are finding an artificial system able to efficiently convert solar energy to any other type of energy, and finding a way to properly store this energy to be used further on demand. Since water splitting was demonstrated by Fujishima and Honda in a photo-electrocatalytic cell,³ photocatalysis has been a promising technology to achieve the transformation of solar energy into storable chemical fuels.

Even though titanium dioxide exhibits many suitable characteristics, this photocatalyst suffers from important limitations, mainly its large band gap ($E_g > 3.1$ – 3.2 eV), preventing the

absorption of visible light. In order to overcome this main limitation, many strategies were implemented to improve its visible light response. In the last few decades, a large number of inorganic semiconductors with lower band gaps such as (oxy) nitrides⁴ and sulfides⁵ and transition metal or post-transition metal oxides⁶ have been investigated. More recently conducting polymer-like semiconductors have attracted a lot of interest.^{7,8} More precisely, g-C₃N₄ (band gap 2.7 eV) has revealed in a milestone study its photocatalytic H₂ and O₂ evolution capacity under visible irradiation by using a co-catalyst, in the presence of an electron donor and/or an acceptor, respectively.^{9–12} However, even though g-C₃N₄ is easily processable and presents high stability in aqueous media, the efficiency towards visible light-mediated H₂ production from water has to be enhanced.¹³ Lots of studies deal with many approaches aiming to overcome this challenging purpose.¹⁴ Exfoliated nanoporous or mesoporous g-C₃N₄ is commonly admitted to be more attractive than bulk g-C₃N₄ structures¹⁵ and lead to better photocatalytic performances. Some studies are also focused on g-C₃N₄ band gap narrowing by doping with non-metallic^{16,17} or metallic elements.^{18–21} Many investigations are also dedicated to the formation of heterojunctions²² between g-C₃N₄ and other semiconductors; amongst them, TiO₂ is certainly the most studied.²³ Post-thermal treatment is considered as a g-C₃N₄

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modification approach, however it has extra costs, since it is a secondary step. Also, the crystalline and amorphous proportion is defined during the polycondensation synthesis, not after, and this is the parameter that enables the control of the crystallite size, interlayer distance, and flat vs. deformed orientation.²⁴ Here, the photocatalytic efficiency of g-C₃N₄ towards H₂ production from water under solar and visible light irradiation has been improved by changing the synthesis gas atmosphere during the g-C₃N₄ polycondensation. Different oxidative, reductive and inert atmospheres were selected, namely air, H₂, NH₃, N₂ and Ar. The H₂ production was evaluated by coupling the modified g-C₃N₄ with a simple binary composite (Au/g-C₃N₄) with a low loading of Au NPs (*ca.* 0.3 wt%). The different materials were then evaluated toward H₂ production from water using an unusually low quantity of a sacrificial agent (1 vol% triethanolamine, TEOA). Under these optimized conditions, a novel and highly efficient g-C₃N₄ material resulting from synthesis in pure NH₃ produced between 3 and 9 times more H₂ with 3 times higher internal quantum yields, compared to the commercial reference, to the standard synthesis performed in static air and to the synthesis performed in the other atmospheres. Furthermore, we studied in depth the structure–activity correlation of the different systems. For the first time, the photocatalytic activity was correlated to the ratio between tri-s-triazine based g-C₃N₄ and s-triazine based g-C₃N₄ phases which depends on the synthesis atmosphere. This study might serve as a reference on how to modulate the g-C₃N₄ structure and activity by modifying only the synthesis atmosphere.

Experimental

Materials

Melamine (C₃H₆N₆, 99%, Sigma Aldrich), dicyandiamide (C₂H₄N₄, 99%, Sigma Aldrich), chloroauric acid (HAu^{III}Cl₄) (≥99.9% trace metal basis, Alfa Aesar), sodium borohydride (≥98%, Sigma Aldrich), methanol (CH₃OH, ≥99.6%, Sigma Aldrich), ethanol (CH₃CH₂OH, ≥96%, Sigma Aldrich), triethanolamine (TEOA, ≥99%, Sigma Aldrich), hydrochloric acid (HCl, ACS reagent, 37%, Sigma Aldrich), sodium hydroxide (NaOH, ACS reagent, ≥97.0, pellets, Sigma Aldrich), and Nicanite®, a commercial reference, carbon nitride (C₃N₄ + xH₂, high purity, Fairland Technology Ltd.) were used without further purification.

Synthesis of g-C₃N₄ and Au/g-C₃N₄ photocatalysts

Bare g-C₃N₄ was synthesized *via* thermal polycondensation of an equimolar ratio of melamine (M; 1.92 g) and dicyandiamide (D; 1.28 g) as described elsewhere.²³ The precursors were put into an alumina crucible with a top cuvette. Thermal polycondensation was carried out in a tube furnace at 550 °C for 3 h by applying a heating ramp of 5 °C min^{−1} in a continuous flow of 100 mL min^{−1} of the designated atmosphere, *i.e.* air, H₂, NH₃, N₂ and Ar. These samples were compared to g-C₃N₄ synthesized in static air in a muffle furnace, as commonly prepared by the scientific community in this domain and to a commercial reference (Fairlandtech), g-C₃N₄–commercial, synthesized

under vacuum.²⁵ The as-prepared samples were denoted as g-C₃N₄–atm, where atm stands for the nature of the atmosphere used during its synthesis or the commercial or static air sample.

Au/g-C₃N₄ samples were prepared by chemical reduction of HAuCl₄.²⁶ The support (300 mg) was dispersed into a methanol/ethanol mixture (91/9 v/v, 55 mL) with a tip sonicator (700 W, 20 kHz) for 30 min, using 30% of the maximum sonication power. The mixture was then transferred to a bath sonicator (280 W, 50/60 Hz) and cooled to room temperature (22 °C) before the sonicator was turned on. A given volume of a methanol/ethanol solution of HAuCl₄ ($2.5(\pm 0.2) \times 10^{-3}$ mol L^{−1}) was then added in order to target a gold loading of 0.3 wt%. Sonication was carried out for 1 h before 5 mL of a fresh methanol/ethanol solution of NaBH₄ solution (2.5×10^{-2} mol L^{−1}) was added. Sonication was then continued for 10 min. Finally, powders were recovered by filtration and dried in air at 110 °C for 12 h.

Materials characterization

X-ray diffraction (XRD) measurements were carried out on a Bruker D8-Advance diffractometer equipped with a Lynx Eye detector operating at 40 kV and 40 mA, in a θ – θ mode using K α radiation of Cu at 1.5418 Å. The datasets were acquired in the step scan mode over the 2θ range 5–35°, using a step interval of 0.0329° and a counting time of 4 s per step. Samples were deposited on a round-shaped glass plate. The average thickness of graphitic stacks of g-C₃N₄ sheets was determined using the Debye–Scherrer equation based on the full width at half-maximum and the position of the (0 0 2) reflection at $2\theta = 27.3^\circ$. The interlayer distance of the layers stack and the in-plane distance of the s-triazine and the tri-s-triazine (heptazine) were calculated using Bragg's law equation $2 \times d_{hkl} \times \sin(\theta) = n \times \lambda$, where d_{hkl} represents the distance between 2 planes of the (*hkl*) Miller index (Å), θ corresponds to Bragg's angle, n is the diffraction order and λ stands for the wavelength of the incident beam (Å). A triplicate measurement of g-C₃N₄–NH₃ was used to obtain the uncertainty of the d_{space} distances. The number of layers was calculated with a method described elsewhere,²⁷ using the ratio between the thickness of the graphitic stacks and the d spacing of the (0 0 2) planes of the graphitic material. From the peaks at $2\theta = 13.1^\circ$ (in plane diffraction peak of the g-C₃N₄ based tri-s-triazine phase; TSTCN) and $2\theta = 17.4^\circ$ (in plane diffraction peak of the g-C₃N₄ based s-triazine phase; STCN) it was possible to determine their proportion by fitting the two indicated peak areas by using Casa XPS software 1.1.

Fourier transform infrared (FT-IR) spectra were recorded with a Thermo Fisher Nicolet iS10 spectrometer in the 525–4000 cm^{−1} range. The characteristic doublet of the atmospheric CO₂ 2340/2360 cm^{−1} signal could not be totally removed from the spectra after background subtraction due to physisorbed CO₂.

Near infra-red (NIR) Raman spectra were collected with a LabRAM ARAMIS instrument equipped with a Synapse CCD detector, an Olympus BX41 microscope and a 785 nm laser (Laser Quantum MPC600 PSU) in the selected range of 300–1800 cm^{−1} (after 1800 cm^{−1} no significant peak was detected).

The working laser power (84 mW) was carefully chosen to minimize both heating effect and fluorescence. The experimental conditions used were as follow: slit opening of 200 μm , grating with 1200 lines per mm, aperture hole of 600 μm , objective 10 $\times$, no filter, and acquisition time of 5 s two times. A dual scan was applied in the x and y axes of the chosen area in order to average the signal over a $300 \times 300 \mu\text{m}^2$.

X-ray photoelectron spectroscopy (XPS) measurements were performed on an ultrahigh vacuum (UHV) Thermo-VG scientific spectrometer equipped with a CLAM4 (MCD) hemispherical electron analyzer. The Al K α line (1486.6 eV) of a dual anode X-ray source was used as incident radiation. Survey and high resolution spectra were recorded in constant pass energy mode (100 and 20 eV, respectively). The energy shift due to electrostatic charging was subtracted using the carbon adventitious signal of g-C₃N₄, i.e., the C 1s peak located at 284.6 eV. Surface atomic ratios were derived from XPS spectra using a Shirley-type background using the appropriate experimental sensitivity factors of the normalized photo ionization cross-section of the atomic subshells as determined by Scofield.²⁸

Zeta potential (ζ) measurements were obtained using a Zetasizer Nano ZS (Malvern Instruments Ltd. UK) equipped with an automatic titrator–diluter Malvern MPT-2 at room temperature. The sample container was connected through a capillary system and with a peristaltic pump with a folded capillary cell (DTS 1060). The zeta potential was obtained from the electrophoretic mobility of the suspension by using the Smoluchowski equation, due to the polar nature of the solvent. Thus, each sample was measured three times at every pH value. The pH titration was programmed from pH 8 to pH 3 using a 0.5 pH interval. The isoelectric point (IEP) was determined at the pH value where the zeta potential was zero.²⁹

Nitrogen adsorption–desorption isotherms were obtained using a Micromeritics Asap 2420 porosimeter using N₂ as an adsorbent at 77 K. The materials were outgassed at 250 °C under primary vacuum for 2 h in order to desorb impurities from their surfaces and eliminate any water. Specific surface areas were calculated by the Brunauer, Emmett and Teller (BET) method in the relative pressure (p/p_0) range 0.05–0.3 and using t -plot methods. Pore-size distributions were calculated by the Barrett–Joyner–Halenda (BJH) method, specifically for mesoporous solids.

Thermogravimetric analyses (TGA) were performed using a TA Instrument Q5000IR. Each sample was placed in a platinum crucible and heated from room temperature up to 900 °C with a heating rate of 10 °C min^{−1} under an air flow of 25 mL min^{−1}. The standard deviation of the decomposition temperature of the as-prepared samples is ± 10 °C.

Time resolved micro conductivity (TRMC) analyses were performed using a Gunn diode of the K $_x$ band at 30 GHz. The pulsed light source was an OPO laser (EKSPLA, NT342B) tunable from 225 to 2000 nm. It displays 8 ns fwhm pulses with a frequency of 10 Hz. The corresponding light energy densities received by the sample were 1.6, 6.1, and 3.3 mJ cm^{−2} at 360, 450, and 550 nm, respectively.

High resolution transmission electron microscopy (HRTEM) was performed on a JEOL 2100F LaB6 TEM/STEM microscope

operating at 200 kV with a point-to-point resolution of 0.21 nm and an X-ray microanalysis silicon drift detector (SDD). The sample was sonicated in ethanol before a drop of the suspension was deposited onto a microscopic copper TEM grid covered with a carbon film for observation. For statistical determination of the gold nanoparticles' size and for determination of relative distances (d_{hkl}) by electronic diffraction (ED) pattern analysis, ImageJ 1.43 was used. The data analysis procedure was based on the measurement of the distance from the center of the image until the respective circular points.

UV-vis absorption spectra were recorded on a PerkinElmer Lambda 950 Scan spectrophotometer equipped with a 100 mm diffuse reflectance integrating sphere. For clarity of the results, diffuse reflectance R_d spectra were converted into Kubelka–Munk units according to $F(R) = (1 - R_d)^2/2R_d$, where $R_d = R_{\text{sample}}/R_{\text{BaSO}_4}$ (BaSO₄ as the standard). For obtaining the apparent band gap (E_g) of the semiconductors, the Tauc equation was used $(F(R) \times h\nu)^s = h\nu - E_g$, where h is Planck's constant, ν is the frequency, and s is a coefficient depending on the direct or indirect nature of the band gap transition (1/2 for g-C₃N₄).

Elemental analyses of the composites were performed using inductively coupled plasma atomic emission spectroscopy (ICP-AES). The limit of detection of the instrument is 0.1 mg L^{−1} for Au. Analysis of the gold component of the Au/g-C₃N₄ composite allowed us to calculate deposition yields which are defined as the ratio between the actual deposited mass of Au (deduced from ICP-AES analysis) and the mass of Au introduced during the deposition step.

Photocatalytic tests

The photocatalytic activities of the Au/g-C₃N₄–atm composites were evaluated toward H₂ production from water using a very low amount of triethanolamine (TEOA) as the sacrificial agent (1 vol%) in a photocatalytic set-up described elsewhere²³ (Fig. S1†). H₂ production was carried out in a quartz vessel containing 1 L of Milli-Q deionized water and equipped with a jacket quartz tube containing a 150 W ceramic-metal-halide Hg lamp, simulating artificial solar light (21.1 mW cm^{−2}, Fig. S2†). Simulated visible light irradiation was achieved by adding a 0.1 g L^{−1} nigrosin solution into the cooling solution flowing into the plunging quartz tube with the purpose of cutting-off the UV photons (resulting irradiance of 2.8 mW cm^{−2}, Fig. S2†). The jacket is linked to a water cooling bath to continuously cool it off (at 20 °C) with the purpose of avoiding any increase in water temperature due to the heating by the light source. The photocatalytic tests were performed by suspending 250 mg of the catalyst in ultra-pure water under a continuous nitrogen flow at 100 mL min^{−1} with mechanical stirring at 700 rpm. Prior to any experiment, residual oxygen was removed by nitrogen flushing. The reaction products were analyzed online every 100 s using a micro-gas chromatography analyzer (SRA Instruments R-3000) equipped with thermal conductivity detectors (TCD).

Stability and recycling tests were performed using the same initial photocatalyst. After each photocatalytic test (2.5 h after

reaching the plateau of H_2 production), the photocatalyst was filtered, washed and dried. The photocatalyst was then re-used as previously described in the photocatalytic reactor. It should be noticed that after each washing cycle there was a 5% mass loss.

Internal quantum yield (IQY) values were determined by measuring the absorbance of the photocatalyst suspension at the same concentration (0.25 g L^{-1}) as in the photocatalytic reactor. These absorbance values were measured at the entrance and exit port of the integrating sphere, in order to measure mainly the absorbance of the sample while minimizing the contribution of diffusion from catalyst particles. For the determination of the photon flux, the absolute irradiance of the lamp was measured by using an ILT900-R spectroradiometer (International Light Technologies).

Results and discussion

Structural characterization (XRD)

The XRD patterns of the as-prepared samples exhibited the basic diffraction peaks at around $2\theta = 13.1^\circ$ and $2\theta = 27.6^\circ$ corresponding respectively to repeating motifs of the tri-s-triazine (also referred to as heptazine) unit of the aromatic system, and to the interlayer stacking of π -conjugated aromatic systems, indexed as the (002) diffraction plane, characteristic for graphitic materials^{8,30,31} (Fig. 1a).

The diffraction peak at 17.4° (Fig. 1b) can be attributed to the diffraction plane of the repeating motifs of the s-triazine unit of the aromatic system.^{32–34} The relative proportion between TSTCN and STCN phases was determined by fitting the two corresponding peaks (Fig. S3†). First, it was observed that the main diffraction peak at 27.6° was more or less shifted to lower angles compared to the commercial $\text{g-C}_3\text{N}_4$ sample. Consequently, the $d_{\text{interlayer}}$ distances of the samples varied between 3.22 and 3.29 Å (Table 1). The less important shift was observed for $\text{g-C}_3\text{N}_4\text{-Ar}$, i.e., the sample using an inert synthesis atmosphere. It has also been reported that the decrease of $d_{\text{interlayer}}$ may be the result of the removal of nitrogen-containing species from the $\text{g-C}_3\text{N}_4$ skeleton, which is hindered when using Ar as the synthesis atmosphere.³⁵ The calculated d_{TSTCN} distance of the synthesized samples increased in the following order for the

synthesis atmosphere: Ar ($6.67 \text{ \AA}$) < H_2 < air < commercial < N_2 < $\text{static air} = \text{NH}_3$ ($6.94 \text{ \AA}$). Furthermore, it must be noticed that both $\text{g-C}_3\text{N}_4\text{-static air}$ and $\text{g-C}_3\text{N}_4\text{-NH}_3$ materials also exhibited the largest d_{STCN} among all samples. Nevertheless, these distances remained respectively smaller and higher than the theoretical size of TSTCN (*ca.* $7.13 \text{ \AA}$) and STCN (*ca.* $4.7 \text{ \AA}$), probably due to small tilt angularity in the assembly.³⁶

From Table 1, one can also observe, that the smallest $A_{\text{TSTCN}}/A_{\text{Total}}$ proportion amongst the synthesized samples was obtained for the $\text{g-C}_3\text{N}_4\text{-static air}$ and $\text{g-C}_3\text{N}_4\text{-NH}_3$ materials (0.35 and 0.47), respectively. It is noteworthy to mention that these calculations are based on the assumption that graphitic carbon nitride is constituted by only two crystalline phases, tri-s-triazine based $\text{g-C}_3\text{N}_4$ and s-triazine based $\text{g-C}_3\text{N}_4$.

Looking further at the mean crystallite size, the largest crystallites were obtained for $\text{g-C}_3\text{N}_4\text{-NH}_3$ with 8.4 nm, which is much more important than the one observed for $\text{g-C}_3\text{N}_4\text{-H}_2$ (4.6 nm) and $\text{g-C}_3\text{N}_4$ synthesized in other atmospheres, and also slightly larger than that of the commercial reference. According to some studies, this may be related to a higher polymerization degree.³⁷ The number of $\text{g-C}_3\text{N}_4$ layers followed the same tendency, the highest packing being observed for $\text{g-C}_3\text{N}_4\text{-NH}_3$ (average of 26 layers) and the lowest for $\text{g-C}_3\text{N}_4\text{-H}_2$ (average of 14 layers).

FT-IR and Raman characterization

To investigate the influence of the gas atmosphere, FT-IR and Raman spectroscopy were used. FT-IR spectra (Fig. 2a) for all samples exhibited the characteristic peaks of $\text{g-C}_3\text{N}_4$.³⁸ The broad absorption band extending from 3000 to 3500 cm^{-1} observed for all the samples was assigned primarily to the N-H stretching vibration of amine groups (secondary and primary). Secondary amines are found in the bridges of the repeating motif phases as C-NH-C, and primary amines are found in the terminating edges of each $\text{g-C}_3\text{N}_4$ layer as C-NH₂.³⁹ In the same region, a large part of the absorption is also attributed to O-H originating from physically adsorbed water species on the $\text{g-C}_3\text{N}_4$ surface resulting in a broad peak, making it difficult to distinguish the specific contribution of each amine type. The region with the majority of peaks ranging from 1240 to

Fig. 1 (a) General XRD pattern and (b) zoom of the (10–21°) region of the references and the as-prepared $\text{g-C}_3\text{N}_4\text{-atm}$.

Table 1 Size of TSTCN and STCN, d -interlayer distances and phase proportion of TSTCN, and the mean thickness of graphitic stack based g- C_3N_4 ^a

g- C_3N_4	d_{TSTCN} (Å)	d_{STCN} (Å)	$d_{interlayer}$ (Å)	A_{TSTCN}/A_{Total}	τ^* (nm)	No. layers**
Commercial	6.81 ± 0.02	4.99 ± 0.02	3.22 ± 0.01	0.54	7.9 ± 0.4	25 ± 1
H ₂	6.76 ± 0.02	4.97 ± 0.02	3.28 ± 0.01	0.59	4.6 ± 0.4	14 ± 1
N ₂	6.85 ± 0.02	4.99 ± 0.02	3.29 ± 0.01	0.54	5.9 ± 0.4	18 ± 1
Air	6.79 ± 0.02	4.96 ± 0.02	3.26 ± 0.01	0.56	6.6 ± 0.4	20 ± 1
Argon	6.67 ± 0.02	4.89 ± 0.02	3.25 ± 0.01	0.59	5.5 ± 0.4	17 ± 1
Static Air	6.94 ± 0.02	5.06 ± 0.02	3.29 ± 0.01	0.35	6.4 ± 0.4	19 ± 1
NH ₃	6.94 ± 0.02	5.04 ± 0.02	3.27 ± 0.01	0.47	8.4 ± 0.4	26 ± 1
NH ₃ [‡]	6.49 ± 0.15	4.59 ± 0.15	3.19 ± 0.15	—	—	—
Theoretical	7.13	4.70	3.26	—	—	—

^a ‡ = obtained by electron diffraction measurements; * = mean thickness of stacks; ** = calculated as described by Saner *et al.*²⁷

1640 cm⁻¹ was attributed to the fingerprint of tri-s-triazine units. The bands positioned at 1631 and 1538 cm⁻¹ were assigned to the side-chain asymmetric C-N stretch vibrations. Signals at 1455, 1396, 1312 and 1230 cm⁻¹ corresponded to the characteristic C-N bonding of secondary and tertiary aromatic amines. This group of signals are an indication of the formation of dimelem units.^{30,39}

The absorption band at approximately 890 cm⁻¹ was assigned to the characteristic deformation mode of N-H in amino groups. The sharp absorption band at 806 cm⁻¹ matched with the typical tri-s-triazine ring breathing mode.³⁹ All the as-prepared samples presented the overall peaks described, showing clear qualitative evidence for the polymeric g- C_3N_4 structure.

Fig. 2 (a) FT-IR spectra. (b) Background corrected Raman spectra of the as-prepared samples. (c–e) Normalized signals of the 950–1010 cm⁻¹, 730–790 cm⁻¹, and 440/500 cm⁻¹ ranges, corresponding to the breathing mode of the s-triazine ring, the layer–layer deformation vibration (out of plane deformation vibration of CN heterocycles), and the in plane twisting vibration of the heptazine heterocycle, respectively.

Raman spectra (Fig. 2b) exhibited the characteristic peak pattern of g-C₃N₄ for all the as-prepared samples, even for g-C₃N₄-H₂, for which the Raman spectrum barely emerged from a strong fluorescence background. The most intense peak in the spectra appeared at 707 cm⁻¹ and was attributed to the breathing 2 mode of the s-triazine ring.^{39,40} Next to 707 cm⁻¹, a weak signal at 718 cm⁻¹ could be observed. The two signals, *ca.* at 707 and 718 cm⁻¹, were predicted by theoretical simulations, ascribing them to the vibrational frequencies of g-C₃N₄ with an active Raman E'' vibration.⁴¹ The breathing 1 mode of the s-triazine unit was also present at 977 cm⁻¹.^{39,40} Other major peaks were present at 472, 752, 1150, and 1232 cm⁻¹, which were ascribed to in-plane twisting vibrations of the heptazine heterocycle, out-of-plane deformation vibrations of CN heterocycles (also referred to as layer-layer vibrations), A1' vibrations of the tri-s-triazine ring, and =C (sp²) bending vibrations, respectively.^{39,42} The weaker signal at 1310 cm⁻¹ has previously been ascribed to a C–N vibration of aromatic secondary amines, which could indicate the presence of the dimelem unit.³⁹ It could also be attributed to the C–N stretching vibration of terminal amide groups.⁴³

Significant differences may be found between the samples regarding the normalized intensities of the peaks at 470, 750 and 977 cm⁻¹ (Fig. 2c–e, Table 2). In general, g-C₃N₄-commercial and g-C₃N₄-H₂ exhibited much weaker signals than the other samples, whereas g-C₃N₄-NH₃ and g-C₃N₄-air showed the most intense signals. The *I*₇₅₀/*I*₇₀₇ ratio in particular has been discussed previously in relation with the number of layers in the sample.⁴² It was shown that bulk g-C₃N₄ exhibited much lower *I*₇₅₀/*I*₇₀₇ and *I*₄₇₂/*I*₇₀₇ ratios than a 1-layer sample. Besides, all the *I*₄₇₂/*I*₇₀₇, *I*₇₅₀/*I*₇₀₇ and *I*₉₇₇/*I*₇₀₇ ratios have been shown to decrease when the degree of polycondensation was increased by increasing the temperature of the process.³⁹ Hence it may be argued that the polycondensation was more complete in g-C₃N₄-commercial and g-C₃N₄-NH₃ materials. It is noted that the signals exhibited by g-C₃N₄-H₂, g-C₃N₄-N₂, g-C₃N₄-air and g-C₃N₄-Ar are very similar in intensities. Nevertheless, g-C₃N₄-H₂ stands out in the case of the signal at 472 cm⁻¹, by exhibiting a much larger intensity than its counterparts. This may be interpreted as a lower degree of polymerization and crystallization in accordance with XRD crystallite size results. Namely, the strong fluorescence observed for the g-C₃N₄-H₂ sample is also reminiscent of the one observed for the g-C₃N₄ monolayer⁴² and is thus consistent with a lower stacking order.

Table 2 Raman intensity ratios in the as-prepared g-C₃N₄-atm samples^a

g-C ₃ N ₄	<i>I</i> ₉₇₇ / <i>I</i> ₇₀₇	<i>I</i> ₇₅₀ / <i>I</i> ₇₀₇	<i>I</i> ₄₇₂ / <i>I</i> ₇₀₇
Commercial	0.07	0.08	0.25
H ₂	0.44	0.46	1.79
N ₂	0.24	0.56	0.29
Air	0.21	2.04	0.32
Argon	0.23	0.36	0.32
Static Air	0.10	0.89	0.25
NH ₃	0.08	0.16	0.18

^a *I* = Raman peak intensity.

Thermal stability (TGA)

TGA profiles (Fig. S4†) revealed a one-pot decomposition with a maximum located between 585 and 640 °C, suggesting the construction of heptazine-base units in all samples, in accordance with the reported literature.^{9,44} However, depending on the synthesis atmosphere, the g-C₃N₄ decomposition temperature increased in the order g-C₃N₄-static air (585 °C), g-C₃N₄-H₂ (590 °C), g-C₃N₄-N₂ (595 °C), g-C₃N₄-NH₃ (600 °C), g-C₃N₄-air (615 °C), g-C₃N₄-Ar (615 °C), and g-C₃N₄-commercial (640 °C). Thus, the highest and lowest decomposition temperatures were obtained for g-C₃N₄-commercial and g-C₃N₄-static air, respectively. This highest decomposition temperature may be correlated with the largest graphitic stack thickness increasing with the number of sheets, which confers stronger van der Waals interactions between the single layers. Moreover, thermal stability is also related with ideal condensation of g-C₃N₄ as graphitic structure materials.³⁰ Thus, g-C₃N₄-static air presented the lowest decomposition temperature, *ca.* 585 °C, presumably for presenting the lowest *A*_{TSTCN} proportion, *ca.* 0.35, confirming the energetic stability of the tri-s-triazine unit over the s-triazine unit with a 30 kJ mol⁻¹ difference.⁴⁵ It must be underlined that a wider range of decomposition temperature (difference between the starting and the finishing decomposition temperature) among the samples (Fig. S4 inset†) was presented for g-C₃N₄-NH₃ (Δ*T* = 145°), presumably for the combination of the largest graphitic stack thickness and flatter in-plane organization (less tilt angularity).

Surface characterization

BET surface area measurements. From Brunauer, Emmett, and Teller (BET) measurements (Table 3, Fig. 3a), it can be observed that all the references and the as-prepared samples exhibited a type-IV adsorption-desorption isotherm profile characteristic of mesoporous materials. Moreover, for all synthesized g-C₃N₄ samples, the hysteresis loop exhibited a type-H4 profile characteristic of slit-like pores⁴⁶ which is in good agreement with the (002) facet ascribed from XRD for graphitic materials, constituted by stacked layers.

Thus, the BJH pore-size distribution exhibited a bimodal type, *ca.* 4 nm and 33–47 nm, with small narrow and broad distribution, respectively (Fig. 3a inset). The large mesopore size distribution of the synthesized samples increased depending on the synthesis atmosphere from Ar (36 ± 3 nm), H₂, N₂, commercial, air = NH₃, to static air (47 ± 5 nm). One can say that the mesopore size tendency differed from the pore volume, which increased following the respective order air–Ar–N₂–H₂ (0.05 cm³ g⁻¹), static air, commercial and NH₃ (0.39 cm³ g⁻¹). Amongst the synthesized g-C₃N₄ materials, g-C₃N₄-NH₃ exhibited the largest pore volume, which is in correlation with the largest surface area obtained. Pore volume and size values suggested that g-C₃N₄-NH₃ has a different spatial arrangement with the largest average mesopore size and pore volume. This phenomenon is attributed to a profound deep channel and/or the high amount of mesopores, which make us speculate that the NH₃ atmosphere participates in the polycondensation, with a positive impact on mesoporosity.

Table 3 Specific surface area (S_{BET}), pore volume (V_{pore}), pore size, C/N ratio, and IEP of the as-prepared samples^a

g-C ₃ N ₄	S_{BET}^* (m ² g ⁻¹)	V_{pore} (cm ³ g ⁻¹)	Pore size** (nm)	C/N***	IEP (pH)
Commercial	33 ± 3	0.27 ± 0.02	40 ± 4	0.76 ± 0.05	5.35
H ₂	6 ± 1	0.04 ± 0.02	39 ± 4	0.70 ± 0.05	6.00
N ₂	7 ± 1	0.05 ± 0.02	39 ± 4	0.75 ± 0.05	5.30
Air	10 ± 1	0.05 ± 0.02	42 ± 4	0.76 ± 0.05	5.20
Argon	10 ± 1	0.05 ± 0.02	36 ± 4	0.75 ± 0.05	5.50
Static Air	15 ± 2	0.14 ± 0.02	47 ± 5	0.76 ± 0.05	5.00
NH ₃	32 ± 3	0.39 ± 0.02	42 ± 3	0.75 ± 0.05	5.90

^a * = specific surface area calculated using the BET method; ** = calculated using the BJH method; *** = obtained by XPS measurements; IEP = isoelectric point.

Zeta potential measurements. From the auto-titration measurements (Table 3, Fig. 3b), it can be observed that all the references and the as-prepared samples exhibited the same tendency at various pH values. g-C₃N₄ particles presented positive and negative charged values at pH values below and above the IEP, respectively. The references and as-prepared samples obtained an IEP in the range of pH 5–6, which was in good agreement with previous studies.⁴⁷ These values confirmed the amphoteric functionality of g-C₃N₄ (ref. 9) associated with the capacity of g-C₃N₄ for protonation and deprotonation of specific groups on the g-C₃N₄ surface, namely, physisorbed O–H hydroxyls, and primary (C–NH₂) and secondary (C₂–NH) amines (already described by FT-IR, Raman, and XPS for some of them). Amino groups preferentially act as proton acceptors under basic conditions, due to the available lone pair of electrons of the nitrogen atom, to obtain a positive surface charge.⁴⁸ But under acidic conditions, hydroxyl groups can be transformed into hydroxyl ions, to obtain a negative surface charge. The IEPs of most of the samples vary slightly,

ranging from 6.00 to 5.00 for g-C₃N₄–H₂ and g-C₃N₄–static air, respectively. Furthermore, the lowest IEP might be associated with the lowest tri-s-triazine phase proportion, *ca.* 0.35. Due to the presence of amino groups on the edge of each C₃N₄ sheet and considering the size difference between s-triazine and tri-s-triazine building blocks, a higher number of local charges is expected for the STCN phase. However, for the other samples (for example g-C₃N₄–NH₃) the tendency of IEP might also be correlated to other parameters.

XPS characterization. From the survey spectra in Fig. 4a, it can be observed that the major contributions corresponded to N 1s and C 1s at a binding energy of *ca.* 400 and 280 eV, respectively. For all samples, a small peak attributed to O 1s appeared approximately at 530 eV. The C 1s signal (Fig. 4b) displayed two contributions, a minor one at 284.6 eV and a major one at binding energies varying between 287.9 and 288.2 eV. The first contribution can be assigned to C=C (sp²) from adventitious carbon and to sp³ defects on the edge of graphitic domains. The second contribution was attributed to sp²-bonded C of (N)₂–C=

Fig. 3 (a) Nitrogen adsorption–desorption isotherms. (Inset) BJH pore-size distribution of the references and the as-prepared samples. (b) Auto-titration of the references and the as-prepared samples to obtain the IEP.

Fig. 4 XPS spectra analysis of the references and the as-prepared g-C₃N₄ samples. (a) XPS survey spectra showing the three contributions for the g-C₃N₄ components. (b) N 1s spectra, (c) C 1s spectra and (d) O 1s spectra.

N from the heterocyclic ring.^{1,11} One may observe that the binding energy of the second contribution was significantly shifted to lower binding energy for the g-C₃N₄-H₂ sample, meaning that the sp²-carbon may also be bonded to more reduced N species. It can also be mentioned that amongst the synthesized materials, the percentage of the second contribution is higher in g-C₃N₄-Ar and g-C₃N₄-NH₃ samples. The N 1s signal (Fig. 4c) displayed two contributions, a major one at 398.5 eV and a minor one at 400.4 eV, assigned to sp²-hybridized pyridine nitrogen of C=N-C from the heterocyclic ring and to the N-(C)₃ tertiary nitrogen, respectively.^{49–51} One can also notice that there is no evidence for the presence of a third contribution due to the presence of terminal amino groups at higher binding energies. However, knowing the complexity of XPS deconvolution for small contributions, one cannot exclude the presence of small amounts of terminal amino-groups. As the O 1s signal (Fig. 4d) presented a lower intensity, it was not deconvoluted, but it displayed the contribution assigned to -OH surface groups at 532.1 eV. Almost all the as-prepared g-C₃N₄ samples exhibited a C/N ratio very close to the theoretical value of C/N = 0.75, thus, indicating high quality g-C₃N₄, except for

g-C₃N₄-H₂ presenting a ratio of 0.70 suggesting that there is less nitrogen content (less amino groups), being consistent with XRD and Raman results.

Electronic diffraction (ED) and TEM

The distances related to the main diffraction planes corresponding to tri-s-triazine units, to s-triazine units and to the interlayer stacking of π -conjugated aromatic system distance (002) were measured by electron diffraction for only the most crystalline g-C₃N₄-NH₃ sample (Fig. 5g inset). One can see that the values obtained from XRD and ED for the size of d_{TSTCN} (6.94 and 6.49 Å), and d_{STCN} (5.04 and 4.59 Å) phases, and $d_{\text{interlayer}}$ (3.27 and 3.19 Å) were consistent, confirming the use of the two characterization techniques as a complementary analysis. Yet, compared with the theoretical values of 7.13 Å, 4.70 Å, and 3.26 Å, one can see lower and higher experimental values for the d_{TSTCN} and d_{STCN} (Å), respectively, which presumably indicated a tilt angularity in the assembly, also discussed previously in the XRD section.

HRTEM images (Fig. 5) revealed the typical lamellar-type structure with entangled nanosheets⁵² for all the Au/g-C₃N₄-

Fig. 5 HRTEM images for the Au/g-C₃N₄-atm composites, including the mean particles sizes with their standard deviation, (a) 0.3 wt% Au/g-C₃N₄-commercial, (b) 0.3 wt% Au/g-C₃N₄-H₂, (c) 0.3 wt% Au/g-C₃N₄-N₂, (d) 0.3 wt% Au/g-C₃N₄-air, (e) 0.3 wt% Au/g-C₃N₄-Ar, (f) 0.3 wt% Au/g-C₃N₄-static air, and (g) 0.3 wt% Au/g-C₃N₄-NH₃; (inset) the electron diffraction image of the g-C₃N₄-NH₃ grain lattice planes. (h) Au NP size distribution determined from HRTEM characterization of 0.3 wt% Au/g-C₃N₄-atm samples (obtained from a selection of 200 Au NPs for each sample).

atm samples. TEM micrographs further showed that Au NPs were round in shape in all samples. However, Au NP coverage, dispersion and size differ from sample to sample. The most homogeneous coverage was observed on the $g\text{-C}_3\text{N}_4\text{-NH}_3$ surface (Fig. 5g). The $\text{Au/g-C}_3\text{N}_4\text{-NH}_3$ composite also exhibited the smallest Au NP mean size (3.2 nm), associated with the smallest standard deviation (1.1 nm). All other composites exhibited larger mean particle sizes (3.7–5.1 nm), but maybe more importantly, larger standard deviations on the average size and significantly less homogeneous dispersions (Fig. S5†). $\text{Au/g-C}_3\text{N}_4\text{-air}$ and $\text{Au/g-C}_3\text{N}_4\text{-Ar}$ in particular showed the largest standard deviation of all (2.4 nm), resulting from a significant contribution of bigger Au NPs, *ca.* 6–10 nm and for the case of $\text{Au/g-C}_3\text{N}_4\text{-air}$, it displayed a quasi-bimodal distribution with local maxima at 3.5 nm and 6.5 nm. All catalysts, except $\text{Au/g-C}_3\text{N}_4\text{-NH}_3$, also presented aggregates of Au NPs. $\text{Au/g-C}_3\text{N}_4\text{-Ar}$ exhibited a particularly inhomogeneous distribution of Au NPs over the support. In this catalyst, like in most catalysts, extensive areas with no particles may be found, associated with areas containing a high density of particles, which can also explain the presence of aggregates in these samples. In contrast, no aggregate or NP-free areas are observed in $\text{Au/g-C}_3\text{N}_4\text{-NH}_3$. This sample displayed a particularly homogeneous density of Au NPs throughout the sample, of about 2000 particles per μm^2 (average distance of 23 nm between 2 Au NPs). Therefore, one can conclude that the nature of the support has a direct impact on the growth, final size and distribution of Au NPs over the support. More specifically, these results suggest that the specific surface chemistry of NH_3 -derived C_3N_4 provides stronger interactions with the gold precursor used in the synthesis, as

well as with the resulting seeds and particles, leading to better size control of the final Au NP size and coverage.

UV-Vis absorption properties

Fig. 6a presents the color of each $g\text{-C}_3\text{N}_4$ after synthesis. One can notice the diverse range of colors obtained as a function of the atmosphere used for $g\text{-C}_3\text{N}_4$ synthesis, from light yellow for $\text{NH}_3\text{-N}_2$, Ar, air-static air, or reddish and brownish for the H_2 atmosphere and the commercial sample, respectively. These color changes showed that the $g\text{-C}_3\text{N}_4$ synthesis atmosphere (oxidative, inert or reductive) directly impacts the optical and electronic properties of the $g\text{-C}_3\text{N}_4$ semi-conductor.⁵³

From the UV-Vis spectra (Fig. 6b) one can observe that all the 0.3 wt% $\text{Au/g-C}_3\text{N}_4$ composites exhibited a maximum absorption in the UV/blue range of the spectra, with an absorption band edge at 450–460 nm, characteristic of $g\text{-C}_3\text{N}_4$ semi-conductors.^{53–56} It is attributed to $\pi \rightarrow \pi^*$ electronic transitions⁵³ found in π -conjugated systems of tri-s-triazine and s-triazine units. It must also be pointed out that $\text{Au/g-C}_3\text{N}_4\text{-H}_2$ and $\text{Au/g-C}_3\text{N}_4\text{-commercial}$ samples presented an absorption tail at higher wavelengths. This behavior might be explained by the occurrence of additional $n \rightarrow \pi^*$ electronic transitions,⁵³ which are attributed to a more pronounced layer deformation, as already experimentally and theoretically described elsewhere.⁴⁴ The $n \rightarrow \pi^*$ transition is indeed a characteristic of the presence of lone pairs of electrons of the N atoms in the $g\text{-C}_3\text{N}_4$ skeleton. A second contribution with a maximum located at *ca.* 550 nm was ascribed to the presence of a surface plasmon induced effect (SPIE) of Au NPs. Nevertheless, Fig. 6b (inset), shows that the absorption of the SPIE is quite weak for all the composites due to

Fig. 6 (a) Color of the powders of the bare $g\text{-C}_3\text{N}_4$ samples. (b) UV-Vis spectra of the 0.3 wt% $\text{Au/g-C}_3\text{N}_4\text{-atm}$ composites. (Inset) zoom of the spectral domain corresponding to the SPIE signal of Au NPs at approximately 550 nm. (c) Tauc plot to determine the apparent band gap of the 0.3 wt% $\text{Au g-C}_3\text{N}_4\text{-atm}$ composites.

the low loading of Au NPs (0.3 wt%) and the small particle size (≤ 5.1 nm). For the Au/g-C₃N₄-H₂ and Au/g-C₃N₄-commercial materials, the SPIE overlaps with the $n \rightarrow \pi^*$ electronic transitions of g-C₃N₄ and thus cannot be distinguished.

From the band-gap determination (Fig. 6c) calculated using the Tauc equation, one can observe that the Au/g-C₃N₄-H₂ and Au/g-C₃N₄-NH₃ photocatalysts presented respectively the lowest (2.50 eV) and the highest (2.75 eV) band-gap. The main difference relies on the potential of deformation of the in-plane motifs. The lower absorption of the Au/g-C₃N₄-NH₃ sample in the visible range might be explained by a less pronounced layer deformation of the nanosheets. This phenomenon might be the result of the larger abundance of A_{STCN} with respect to A_{TSTCN} (as already mentioned in the XRD section), the former one presenting a higher stability toward the tilt angularity effect. Furthermore, using NH₃ as the synthesis atmosphere can lead to the occurrence of another phenomenon. As NH₃ is one of the by-products of the polycondensation, the saturated NH₃ environment inside the crucible may provide suitable conditions for growing well-planar nanosheets, thereby favoring stacking of the layers (and $\pi \rightarrow \pi^*$ transitions) and minimizing $n \rightarrow \pi^*$ transitions (due to layer deformation or distortion). In contrast, using H₂ as the synthesis atmosphere of g-C₃N₄ may promote the insertion of H atoms in between layers leading to strong interactions by H bonding with other skeleton atoms,⁵⁷ preferentially edged or bridged N atoms. Thanks to this new interaction forces an interplanar layer distortion is induced, allowing $n \rightarrow \pi^*$ transition to be present. On the other hand, the g-C₃N₄-commercial-N₂-air-Ar-static air samples presented

similar band gap values in reference to the theoretical polymeric semiconductor value, *ca.* 2.70 eV.^{8,30}

Photocatalytic performances

The photocatalytic H₂ production was acquired by using a photocatalytic set-up (Fig. S1†).^{58,59}

Internal quantum yield (IQY) was calculated using the following equation:

$$\text{IQY} = 2 \times \frac{r_{\text{H}_2}}{q_{\text{p(Abs)}}} \quad (1)$$

where r_{H_2} is the hydrogen formation rate (mol h⁻¹) and $q_{\text{p(Abs)}}$ is of the photon flux absorbed by the photocatalytic material calculated according to the following equation:

$$q_{\text{p(Abs)}} = \int_{\lambda_{\text{min}}}^{\lambda_{\text{max}}} \frac{P(\lambda) \times (1 - 10^{-A(\lambda)l})}{E(\lambda)} d(\lambda) \quad (2)$$

where $P(\lambda)$, $E(\lambda)$, and $A(\lambda)$ respectively are the irradiation power, the photon energy and, the absorbance of the nanoparticle suspension at a given wavelength (λ) of each sample used in the photochemical reactor which has an optical path $l = 5$ cm. Stable H₂ production was considered as the value attained after reaching a stable plateau. From the H₂ production results under artificial solar-light irradiation (Fig. 7a) the samples can be divided into three main categories as a function of their activity magnitude: the most active one, 0.3 wt% Au/g-C₃N₄-NH₃ (leading to 324 H₂ $\mu\text{mol h}^{-1} \text{g}_{\text{cat}}^{-1}$), the ones exhibiting moderate activity, 0.3 wt% Au/g-C₃N₄-commercial-N₂-static air-Ar (yielding 125, 101, 99, and 75 H₂ $\mu\text{mol h}^{-1} \text{g}_{\text{cat}}^{-1}$,

Fig. 7 (a) Mean hydrogen formation rate per hour and per mass of the 0.3 wt% Au/g-C₃N₄-atm photocatalyst using 10 mL TEOA (1 vol%) as the sacrificial agent under solar and visible-light irradiation. (b) Internal quantum yield (IQY, %) of the as-prepared composites under solar and visible-light irradiation. (c) Cumulative evolution of hydrogen with 1 vol% TEOA under solar-light irradiation. (d) Cycling tests on 0.3 wt% Au/g-C₃N₄-NH₃ with 1 vol% TEOA under solar-light irradiation.

respectively), and the less performing materials, 0.3 wt% Au/g-C₃N₄-air-H₂ (producing 41 and 36 H₂ μmol h⁻¹ g_{cat}⁻¹, respectively). One can notice the superiority of Au/g-C₃N₄-NH₃, exhibiting an activity between 3 and 9 times higher than the second most active composite (Au/g-C₃N₄-commercial) and the least active photocatalyst (Au/g-C₃N₄-H₂), respectively. In case of artificial visible-light irradiation, the Au/g-C₃N₄-NH₃ nanocomposite was the only one to exhibit a measurable activity with 26 μmol h⁻¹ g_{cat}⁻¹ H₂ produced. However, it must be pointed out that the utilization of Nigrosin as cut-off filter yields a decrease of the overall photon flux emission, besides cutting-off the UV-photons.

From Fig. 7b showing the cumulative H₂ produced during the complete photocatalytic test (over 2.5 h of simulated solar-light irradiation after reaching the plateau of H₂ formation), the best photocatalyst, *i.e.*, Au/g-C₃N₄-NH₃ produced up to 175 μmol H₂.

From the cycling tests carried out on the best performing Au/g-C₃N₄-NH₃ material (Fig. 7c), one can observe a relative decrease of H₂ production of 20 and 26% after the second and third cycle, respectively, compared to the first test. This behavior could be explained by means of TEOA degradation and by-product formation that may poison the catalyst.⁶⁰

Fig. 7b summarizes the internal quantum yields (IQY) determined under both solar-light and visible-light irradiation. Under simulated solar-light activation, Au/g-C₃N₄-NH₃ revealed the highest IQY of 1.85, compared to 0.55 for the Au/g-C₃N₄-commercial material and to 0.20 for the least performing one (Au/g-C₃N₄-H₂). This value was higher than the ones calculated for all the other samples under solar-light irradiation (also including UVA contribution). It must also be highlighted that the Au/g-C₃N₄-NH₃ photocatalyst showed an IQY of *ca.* 0.60% under visible-light irradiation.

Role and influence of the sacrificial agent

To compare and discuss the photocatalytic activities, different contributions and effects have to be considered.

The addition of a sacrificial agent (TEOA) as the hole scavenger or for O₂ consumption should avoid O₂ evolution. Consequently, the resulting solution reached a pH of 11; at this value the potentials for water oxidation and proton reduction are 0.58 V and -0.65 *vs.* NHE, respectively.^{9,61-63} It must also be considered that TEOA is an aliphatic tertiary amine with an oxidation potential of 0.6–0.7 *vs.* NHE. As TEOA presents a low oxidation potential, it may be easily oxidized and act as efficient trap hole sites.⁶⁴ TEOA can undergo an irreversible oxidation of the amine to cause a dealkylation to form a secondary amine and an aldehyde in the presence of water.^{60,65} However one can mention that protons generated during TEOA degradation may also be involved in H₂ production mechanism in addition to water-splitting. Furthermore the three alcohol functions can also be a source of H₂ production through photo-reforming processes, thus overestimating pure water-splitting contribution. However, in our case the use of very small amounts of TEOA may strongly limit the contribution of these other

pathways of H₂ production making water-splitting the predominant one.

Since TEOA is an aliphatic tertiary amine, the lone pair of electrons of its N atom may interact with the N atoms of the g-C₃N₄ skeleton, possibly modifying the overall surface charge. Moreover, one cannot exclude a theoretical uplift band bending on the suspended semiconductor in contact with the TEOA diluted solution.^{65,66}

Role of Au NPs

Most of the studies have shown that even if the position of the conduction band of g-C₃N₄ materials is suitably disposed with regard to the HER, they poorly undergo direct reduction of H⁺ into H₂ alone, and for that reason a co-catalyst is mandatory. Au NPs can generally act as (1) electron traps leading to better charge separation, (2) co-catalyst for the reduction of H⁺ into H₂ (ref. 67) or/and (3) a plasmonic promoter *via* surface plasmon-induced effects (SPIEs). When Au NPs are deposited onto a semiconductor (SC) support, the SPIEs were essentially explained by means of hot electron injection from the conduction band of Au NPs to the conduction band of the SC or enhancement of the intensity of the electric field around Au NPs thus leading to increased photon absorption by the SC at the vicinity of Au NPs.^{68,69} Therefore, Au NP size and dispersion,^{70,71} Au NP loading⁷² and quality of the interface with the SC⁷³ are crucial for these properties. In turn, the coverage of the SC by Au NPs may play a key role in the photocatalyst global activity, due to the potential role of Au in all the above mentioned phenomena.

The main reaction steps that might be involved in the global photocatalytic process can be summarized in the following equations:

Correlation of structure/optical properties/photocatalytic activity

For all materials, the 0.3 wt% Au/g-C₃N₄-NH₃ photocatalyst allowed enhanced photocatalytic activity toward H₂ production under both solar (324 μmol h⁻¹ g_{cat}⁻¹, IQY: 1.85) and visible-light (26 μmol h⁻¹ g_{cat}⁻¹, IQY: 0.60) irradiation. This enhanced photocatalytic performance is between 3 and 9 times higher in comparison to the two references and to the synthesis performed in the other gas atmospheres, using unusually low vol% of the sacrificial agent (1 vol%). These enhanced performances might be correlated to its specific properties.

g-C₃N₄ materials. XRD showed that the g-C₃N₄-NH₃ sample exhibited the largest crystallite size and a thicker stack of layers. In contrast, g-C₃N₄-H₂ exhibited the lowest crystallite size and a narrower stack of layers. The set of XRD measurements revealed the strong influence of the synthesis atmosphere on the g-C₃N₄ formation. It appears that inert gases (Ar and N₂) and also the reductive H₂ gas resulted in g-C₃N₄ sheets with fewer layers than an oxidative atmosphere. In contrast, even if NH₃ is a reductive gas, it resulted in thicker g-C₃N₄ particles, suggesting that NH₃ is involved in a reaction with the precursors or the reaction intermediates. From the overall comparison of ED, XRD and theoretical values obtained by simulations, one can notice that the d_{TSTCN} is even smaller than the theoretical reference value, indicating the presence of tilt angularity. Nevertheless, for the d_{STCN} the behaviour is the opposite—the XRD values are higher than the theoretical one, presumably due to the presence of tilt angularity too. Furthermore, the size value determination of the TSTCN and STCN phases revealed the clear presence of tilt angularity in the assembly, which might be explained by layer distortion. However in the case of the g-C₃N₄-NH₃ sample the size of the tris-s-triazine phase exhibited the smallest deviation compared to the theoretical value of the perfect g-C₃N₄ structure. For the g-C₃N₄-H₂ material, it has been described in the literature⁵⁷ that the insertion of H₂ molecules in-between the layers affects the van der Waals forces and promotes an in-plane distortion.

From the surface characterization, one can underline that the BET area of both g-C₃N₄-NH₃ and g-C₃N₄-commercial materials showed the same highest value (32 m² g⁻¹). However, both samples presented a difference in activity of factor three, suggesting that the surface area is not the only parameter influencing the activity. g-C₃N₄-NH₃ exhibited the largest pore volume, mainly constituted of mesoporous contribution, contrarily to the other g-C₃N₄-atm samples. It has already been

suggested elsewhere²⁴ that during post-synthesis NH₃ annealing NH₂^{*} and NH^{*} species were formed after the degradation of NH₃ at high temperatures, and these active radicals might be responsible for the increase of the porosity in terms of mesoporosity.

From UV-vis results, one can notice that the samples presenting the more pronounced red shift were not precisely the more active ones. In contrast, the g-C₃N₄-NH₃ sample exhibiting the lowest absorption in the visible range was the one with the highest activity. It may thus be argued that another parameter, *i.e.*, the additional $\pi \rightarrow \pi^*$ electronic transition, only existing when lone pairs of electrons of N atoms are in a close vicinity to promote it, and resulting from layer deformation, may also inhibit the photocatalytic activity.

In TRMC measurements performed at 360, 450 and 550 nm (Fig. S6†), no significant signal has been observed. These results might suggest that either no significant free electrons are photogenerated or that they recombine too fast to be detected. Therefore, we thus believed that it was not necessary to carry out for further PL or electrochemical measurements.

Au/g-C₃N₄ composites. The surface amino functions might certainly drive the interaction of the g-C₃N₄ support with the HAuCl₄ precursor and consequently the Au NP size (the lowest one, *ca.* 3.2 nm) and their well distributed dispersion. Some studies already mentioned that this Au NP size may be the optimal size to present quantum confinement effects,⁷⁴ optimal charge transfer to and from the support⁶⁹ and a good spatial corner position for Au⁰ atoms to interact efficiently with the external environment species.⁷⁵ It may be thus argued that the presence of Au in the binary nanocomposite is essentially co-catalytic, presenting an enhancement of diffusion/migration of hydrogen atoms, facilitating the half reaction reduction from H⁺ to H₂.²³ It may thus be mentioned that this study showed evidence that monodisperse and well distributed Au

Fig. 8 Schematic illustration of the proposed H₂ production mechanism for the Au/g-C₃N₄-NH₃ binary nanocomposite, pointing out the two half reactions of water splitting and the different electron transfer pathways.

NPs directly contribute to the photocatalytic activity, since a higher quantity of available nanoparticles on the g-C₃N₄ surface increases the number of active sites for co-catalytic H⁺ reduction. Therefore, one can conclude that there is a direct impact of the nature of the catalyst-support on the growth, geometry shape and size of Au NPs.

Optical measurements evidenced the two expected absorptions for the two components, *i.e.*, g-C₃N₄ ($\lambda \approx 460$ nm) and the Au plasmon ($\lambda \approx 550$ nm). From HRTEM, it can be noticed that all samples followed a more or less monodisperse distribution of Au NPs, with different surface distributions. In the case of the most active sample, it was found that the distribution of Au NPs presented the narrower monomodal distribution with the best surface coverage and the lowest average Au NP size. This result suggests that well distributed and small NPs (≤ 5 nm) might determine the global co-catalytic effect, since they determine the availability and amount of Au NPs. Besides, one cannot exclude a possible Z-scheme mechanism when using the Au NPs as electron shuttles.⁶⁶

From the different complementary characterization and analyses carried out, one could not confirm the presence of the SPIE on the synthesized and studied Au/g-C₃N₄ nanocomposites. Fig. 8 summarizes a detailed scheme of the possible charge transfer pathways.

Conclusions

The engineered design of Au/g-C₃N₄ binary nanocomposites allowed us to study the influence of the gas atmosphere during the synthesis of g-C₃N₄. It was highlighted that the gas atmosphere impacted the photocatalytic activity. The 0.3 wt% Au/g-C₃N₄-NH₃ composite exhibited an enhanced photocatalytic activity toward H₂ production under both solar and visible-light irradiation using low amounts of the sacrificial agent and co-catalyst. The resulting enhanced H₂ production was related to the structural organization and optical, electronic, surface and porous properties of the support (g-C₃N₄). Specific characterization revealed very relevant pieces of evidence such as the thicker stack of the graphitic domain, the largest crystallite size, and the largest mesoporous pore volume. Detailed determination and relative contribution of TSTCN and STCN phases led to underline that this Au/g-C₃N₄-NH₃ catalyst also exhibited a lower s-triazine content and consequently lower tilt angularity and thus layer deformation with respect to the theoretical values for perfect g-C₃N₄.

Conflicts of interest

There are no conflicts to declare.

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