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# Titania-Carbon Nitride Interfaces in Gold-Catalyzed CO Oxidation

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**ABSTRACT:** Gold-catalyzed CO oxidation is a reaction of both practical and fundamental interest. In particular, rate-determining oxygen activation pathways have attracted a lot of attention. They have been found to depend on the surface chemistry of the catalyst support, titania providing the most active catalysts and carbon nitride leading to inactive catalysts. Here we show that  $C_3N_4$ - $TiO_2$  composites with rather similar surface chemistries can be engineered by using titania nanotubes as hard templates and by performing the polycondensation of melamine and dicyandiamide in air and in ammonia. By varying the  $C_3N_4$  content from 2 to 75wt.%, the mesoporosity can be tuned from 8 nm to 40 nm. A systematic study of CO oxidation turnover numbers in the absence and in the presence of hydrogen over the composites loaded with well-calibrated, 2-4 nm gold nanoparticles clearly shows that (1) the chemical composition of the support surface has much less impact on PROX than on dry CO oxidation (2)  $NH_2$ -terminated supports are as active as OH-terminated supports in PROX (3) hydrogen/water-mediated CO oxidation pathways are active on  $C_3N_4$ -based Au catalysts, (4) PROX activity requires a rather large porosity (40 nm), which suggests the involvement of much larger intermediates than the usually postulated peroxy-type species.

**KEYWORDS:** carbon nitride, titania, composites, gold catalysts, PROX, porosity, surface chemical composition

## INTRODUCTION

Au/ $TiO_2$  is a well-known catalyst for the low temperature oxidation of CO. Such gold-catalyzed oxidation reaction involves peculiar oxygen activation pathways,<sup>1</sup> as compared with the redox version over transition metal oxides.<sup>2-4</sup> Although oxygen can theoretically be activated on very small gold nanoparticles (Au NPs), the direct adsorption of oxygen on Au NPs of the typical catalytic size, i.e. 3-5 nm, has a much higher barrier.<sup>5</sup> Gold oxidation catalysis thus relies on the presence of an "active" support according to Schubert's terminology.<sup>6</sup> Amongst them,<sup>7</sup> titania is a benchmark. It has proven to exhibit the most suitable surface chemistry<sup>8-11</sup> which allows for complex oxygen activation pathways<sup>12-14</sup> in dry CO/ $O_2$  feeds. Non-reducible, hydroxyl-terminated metal oxide supports may be good alternatives when water or hydrogen is present in the feed, due to oxygen activation pathways via surface hydroxyl functions,<sup>15</sup> which are enhanced by the presence of hydrogen and water. These make efficient PROX catalysts (preferential oxidation of CO in excess hydrogen).<sup>16-18</sup> In general, hydrophilic oxides<sup>19</sup> are suitable supports for gold PROX catalysts, due to water-mediated oxidation pathways.<sup>20-23</sup>

The surface chemical composition of the inorganic support on which Au NPs are dispersed is thus a key parameter which determines the reactivity of gold catalysts in CO oxidation,<sup>24</sup> like in many other reactions.<sup>25</sup> In this regard,  $C_3N_4$  yields inactive gold catalysts because of its inadequate surface chemistry towards oxygen activation under hydrogen-free and water-free conditions.<sup>26</sup> However, a

heterostructured  $TiO_2$ - $C_3N_4$  support was reported to yield an active gold catalyst for the PROX reaction.<sup>27</sup>

Composites of titania and carbon nitride are more widely studied in photocatalysis,<sup>28-35</sup> due to the ability of both components to form a heterojunction which increases charge carrier lifetime, extends the absorption wavelength range and thus yields photocatalytic properties in the visible range. However it was found that the formation of a suitable heterojunction is critically dependent on the  $TiO_2$ / $C_3N_4$  interface. We have recently shown that a suitable interface could be obtained by performing the polycondensation of  $C_3N_4$  precursors in the presence of pre-formed titania crystallites in air. Such materials exhibited, after additional gold nanoparticle deposition, a state-of-the-art behavior in challenging water photoreduction to hydrogen.<sup>36,37</sup> Besides, we recently reported that the surface chemistry of  $C_3N_4$  (as well as its crystallinity, morphology and porosity) could be tuned by the atmosphere of the polycondensation process leading to its synthesis. In particular, the specific surface area and porosity of  $C_3N_4$  could be markedly enhanced by performing polycondensation in ammonia instead of air.<sup>38</sup> The importance of the porosity of functional materials designed for  $CO_2$  and  $N_2$  reductions has recently been highlighted.<sup>39</sup> Yet there is no report to date concerning the importance of the porosity of gold PROX catalysts.

By directing the growth of  $C_3N_4$  using titania nanotubes as hard template, by tuning the porosity of the composite via both the  $C_3N_4$ / $TiO_2$  composition and the polycondensation atmosphere (air vs. ammonia) and by using the resulting  $C_3N_4$ - $TiO_2$  composites as supports for

Au NPs, we here show (1) that PROX activity is observed on Au/C<sub>3</sub>N<sub>4</sub> due to active hydrogen/water-mediated oxidation pathways and (2) that the gold-catalyzed CO PROX reaction is critically dependent on the porosity of the support.

## EXPERIMENTAL

### Materials

Melamine (C<sub>3</sub>H<sub>6</sub>N<sub>6</sub>, 99%, Sigma Aldrich), dicyandiamide (C<sub>2</sub>H<sub>4</sub>N<sub>4</sub>, 99%, Sigma Aldrich), AEROXIDE® TiO<sub>2</sub> P25 (Evonik Industries), sodium hydroxide (NaOH, ≥98%, Sigma Aldrich), hydrochloric acid (HCl, fuming ≥37%, Sigma Aldrich), chloroauric acid (HAu<sup>III</sup>Cl<sub>4</sub>) (≥ 99.9% trace metals basis, Alfa Aesar), sodium borohydride (≥98%, Sigma Aldrich), methanol (CH<sub>3</sub>OH, ≥99.6%, Sigma Aldrich), ethanol (CH<sub>3</sub>CH<sub>2</sub>OH, ≥96%, Sigma Aldrich), were used without further purification.

### Synthesis of the supports

Graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) was synthesized via thermal polycondensation of an equimolar relationship of melamine (M) and dicyandiamide (D) as described elsewhere.<sup>36</sup> In brief, M and D precursors were mixed in an agate mortar and were placed in an alumina crucible, covered with a lid. Thermal polycondensation was carried in a tubular furnace at 550 °C for 3 h (ramp of 5 °C min<sup>-1</sup>) with a continuous flow of 100 mL min<sup>-1</sup> of the designated atmosphere, i.e. air or NH<sub>3</sub>.

The materials are referred to as C<sub>3</sub>N<sub>4</sub> (*atm*), where *atm* stands for the atmosphere of the polycondensation treatment (air or NH<sub>3</sub>).

Titania nanotubes (TiO<sub>2</sub>-NT) were synthesized via hydrothermal method as described elsewhere.<sup>40</sup> In brief, P25 and NaOH (10 M) aqueous solution were mixed and stirred for 1 h in a Teflon vessel. The solution was then transferred in a Teflon reactor, covered with a stainless steel jacket. A thermal treatment was applied (130 °C for 48 h) in a stove. After cooling the solution was washed with deionized (DI) water, filtrate and dry at 100 °C for 2h. The solution was re-dispersed to obtained a pH = 2, using HCl (1 M) and stir for 18h. A final washing with DI water until neutrality took place. Then, it was filtered and dried at 110 °C for 10 h. Finally, a calcination step was applied at 380 °C for 2 h (ramp of 5 °C min<sup>-1</sup>) in static air.

TiO<sub>2</sub>-NT were treated at 550°C for 3 h (ramp of 5°C min<sup>-1</sup>) in air or in ammonia (100 mL min<sup>-1</sup>) to mimic the thermal polycondensation experimental condition. They are referred to as TiO<sub>2</sub> (*atm*), where *atm* stands for the atmosphere of the heat treatment (air or NH<sub>3</sub>).

gC<sub>3</sub>N<sub>4</sub>-TiO<sub>2</sub> nanocomposites were synthesized via a two-step process as described elsewhere.<sup>36</sup> First, titania NT and an equimolar amount of melamine and dicyandiamide blend were suspended in 10 mL of distilled water at room temperature (impregnation method). The solution was evaporated under vigorous stirring and the obtained powder was dried in an oven at 100 °C overnight. A second thermal polycondensation step was carried out in an alumina crucible with a lid at 550 °C for 3 h (ramp of 5 °C

min<sup>-1</sup>, flowing gas at 100 mL min<sup>-1</sup>) to obtain the final composite. Nanocomposites were synthesized with a final g-C<sub>3</sub>N<sub>4</sub> content ranging from 2(±0.5) wt.% to 72(±2) wt.%, as determined by thermogravimetric analysis. The g-C<sub>3</sub>N<sub>4</sub> content was defined as:

$$g\text{-C}_3\text{N}_4 \text{ (wt.\%)} = \frac{m(\text{C}_3\text{N}_4)}{m(\text{C}_3\text{N}_4) + m(\text{TiO}_2)}$$

The resulting materials are denoted C<sub>3</sub>N<sub>4</sub>(X%)–TiO<sub>2</sub> (*atm*), where X stands for the wt. % of C<sub>3</sub>N<sub>4</sub> and *atm* stands for the atmosphere of the polycondensation treatment (air or NH<sub>3</sub>).

### Gold deposition

Au/support were prepared by chemical reduction of HAuCl<sub>4</sub> as gold precursor in the presence of the support.<sup>36-38,41,42</sup> 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) during 30 min, using 30% of maximum sonication power. The mixture was then transferred to a bath sonicator (280 W, 50/60Hz) and allowed to cool down to room temperature (20 °C) before the sonication was turned on. A given volume of a methanol/ethanol solution of HAuCl<sub>4</sub> (2.5(±0.2) × 10<sup>-3</sup> mol L<sup>-1</sup>) was then added in order to target a gold loading of 0.3 wt.%. Sonication was carried on for 1 h before 5 mL of a fresh methanol/ethanol solution of NaBH<sub>4</sub> solution (2.5 × 10<sup>-2</sup> mol L<sup>-1</sup>) was added. Sonication was carried on for 10 min. Finally, powders were recovered by filtration and dried at 110 °C for 12 h. The resulting materials are denoted Au/support, where support refers to one of the materials described above (C<sub>3</sub>N<sub>4</sub> (*atm*), TiO<sub>2</sub> (*atm*) or C<sub>3</sub>N<sub>4</sub>(X%)–TiO<sub>2</sub> (*atm*)).

### Characterization

Nitrogen adsorption–desorption isotherms were obtained at 77 K using a Micromeritics Asap 2420 porosimeter. Powder materials were outgassed at 250 °C under primary vacuum for 2 h prior to analysis. Specific surface areas were calculated by the Brunauer, Emmett and Teller (BET) method in the relative pressure (p/p<sub>0</sub>) range 0.05–0.3 and using t-plot methods. Pore volumes and pore size distributions were calculated by the Barrett, Joyner and Halenda (BJH) method on desorption isotherms.<sup>43</sup>

Fourier transform infrared (FTIR) spectra were recorded by Attenuated Total Reflectance with a Thermo Fisher Nicolet iSio spectrometer in the 525 – 4000 cm<sup>-1</sup> range. Powders (few mg) are placed directly on the 2 mm × 2 mm diamond window and cover the whole surface.

Transmission Electron Microscopy (TEM) was carried out on a JEOL 2100F LaB<sub>6</sub> TEM/STEM microscope working at 200 kV accelerating voltage and equipped with a probe corrector for spherical aberrations, giving a point-to-point resolution of 0.21 nm. The sample is dispersed in ethanol by ultrasonication for 5 min. A drop of the solution is subsequently deposited on a copper grid covered with a holey carbon membrane for observation. Statistical Au NPs size distributions are obtained on bright field images using populations of 16-200 nanoparticles and the ImageJ software.<sup>44</sup>

X-ray diffraction (XRD) measurements were carried out on a D8-Advance diffractometer equipped with a LynxEye detector and operated at 40 kV and 40 mA, in a  $\theta - 2\theta$  mode using the  $K\alpha$  radiation of Cu at 1.5406 Å. The datasets are acquired in stepscan mode over the  $2\theta$  range 5–60°, using a step interval of 0.0329° and a counting time of 4 s per step. Samples are deposited on a round-shaped glass plate. Average size of titania crystalline domains is determined using the Scherrer formula from the full width at half-maximum of the main  $\text{TiO}_2(101)$  reflection at  $2\theta = 25.3^\circ$ .

### Catalytic study

Catalytic tests are performed in a previously described<sup>3,4,45,46</sup> fully automated (CETRIB SARL, Andlau, France) fixed-bed flow reactor (i.d. 10 mm) loaded with 26 mg of the composites (i.e. 0.24–0.36  $\mu\text{mol}$  Au in the bed). The gas mixtures balanced in He, i.e. 1% CO / 1% O<sub>2</sub> for

CO oxidation, and 24% H<sub>2</sub> / 1% O<sub>2</sub> / 1% CO for the oxidation of H<sub>2</sub> in the presence of CO are introduced at a total flow rate of 100 mL min<sup>-1</sup> (1 atm, GHSV ~ 15,000 h<sup>-1</sup>). The composite is heated at 1° min<sup>-1</sup> from 20 to 300 °C and then cooled down at the same rate. O<sub>2</sub> (and CO) conversions are determined on the basis of on-line Compact Gas Chromatograph (Interscience, Belgium) analysis, using external calibration. Selectivity to CO<sub>2</sub> is defined as the ratio between the number of moles of O<sub>2</sub> used to convert CO over the total number of moles of converted O<sub>2</sub>. It is calculated by the ratio of half the CO conversion over the conversion of O<sub>2</sub>. Turnover frequencies (TOF) are defined as the number of mole of CO or O<sub>2</sub> converted per number of mole of surface gold per second. The fraction of surface gold (gold dispersion) is determined by geometric calculations for cuboctahedral particles<sup>47</sup> using the average particle size measured by TEM before reaction.

**Table 1. Physico-chemical characteristics of Au/C<sub>3</sub>N<sub>4</sub>-TiO<sub>2</sub> composites.**

Entry	Composite support	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	Pore volume (cm <sup>3</sup> g <sup>-1</sup> )	Au content (wt.%) <sup>a</sup>	Deposition yield (%) <sup>b</sup>	Au NPs size (nm)	Au dispersion	N° counts	CO TOF at 250°C (s <sup>-1</sup> )		O <sub>2</sub> TOF Selectivity at 250°C (s <sup>-1</sup> ) (%)	
									COox	PROX	PROX	PROX
0	TiO <sub>2</sub> -380 (air)	144	1.11	-	-	-	-	-	-	-	-	-
1	TiO <sub>2</sub> -550 (air)	107	1.25	0.18	60	3.7±0.9	0.36	16	1.71	0.20	1.55	7
2	TiO <sub>2</sub> -550 (NH <sub>3</sub> )	103	n.a.	0.21	70	3.1±1.1	0.42	44	2.37	0.40	1.47	14
3	C <sub>3</sub> N <sub>4</sub> (2%)-TiO <sub>2</sub> (air)	64	0.69	0.19	63	3.1±0.6	0.42	27	2.79	0.35	1.44	12
4	C <sub>3</sub> N <sub>4</sub> (2%)-TiO <sub>2</sub> (NH <sub>3</sub> )	78	n.a.	0.25	83	4.1±1.4	0.33	76	0.10	0.02	0.58	2
5	C <sub>3</sub> N <sub>4</sub> (75%)-TiO <sub>2</sub> (air)	29	0.15	0.26	87	4.2±1.7	0.32	119	0.14	0.31	1.47	11
6	C <sub>3</sub> N <sub>4</sub> (75%)-TiO <sub>2</sub> (NH <sub>3</sub> )	33	n.a.	0.27	90	2.3±0.4	0.54	76	0.04	0.12	1.36	5
7	C <sub>3</sub> N <sub>4</sub> (air)	10	0.05	0.24	81	5.1±2.4	0.27	200	0.07	0.24	2.06	6
8	C <sub>3</sub> N <sub>4</sub> (NH <sub>3</sub> )	32	n.a.	0.24	80	3.2±1.1	0.41	200	0.05	0.30	2.72	6
9	C <sub>3</sub> N <sub>4</sub> <sup>26,c</sup>	16	n.a.	0.39	n.a.	2.8±0.9	0.49	497	0	n.a.	n.a.	n.a.
10	SiO <sub>2</sub> <sup>6,d</sup>	220	n.a.	1.8	n.a.	30	0.05	n.a.	0.04	n.a.	n.a.	n.a.
11	TiO <sub>2</sub> <sup>6,e</sup>	40	n.a.	2.4	n.a.	2.9	0.46	n.a.	1.3	n.a.	n.a.	n.a.

<sup>a</sup> Determined by ICP measurements

<sup>b</sup> Defined as the ratio between the real Au content as measured by ICP and the targeted Au content (0.3 wt.%) derived from the amount of gold used in the synthesis

<sup>c</sup> P<sub>O<sub>2</sub></sub> = 6 kPa, GHSV = 5000 h<sup>-1</sup>

<sup>d</sup> P<sub>CO</sub> = 4.9 kPa, P<sub>O<sub>2</sub></sub> = 4.8 kPa, T = 80°C, GHSV = 3330 h<sup>-1</sup>

<sup>e</sup> P<sub>O<sub>2</sub></sub> = 20 kPa, T = 80°C

## RESULTS AND DISCUSSION

### Morphology of C<sub>3</sub>N<sub>4</sub>-TiO<sub>2</sub> composites (Nitrogen physisorption).

Full nitrogen physisorption isotherms were recorded on TiO<sub>2</sub> and C<sub>3</sub>N<sub>4</sub> references, as well as on the low and highly

loaded C<sub>3</sub>N<sub>4</sub>-TiO<sub>2</sub> composites obtained in air (Figure 1a) and in ammonia (Figure 1c).

After synthesis, titania nanotubes exhibit a Type IV isotherm, according to the IUPAC nomenclature, with a H<sub>3</sub> hysteresis which corresponds to mesoporous materials.<sup>43</sup> The mesoporosity originates from the intertube void, as

well as the open space inside the tube. The pore size distribution (Figure 1c) exhibits two maxima at 7 nm and 20 nm. The lower pore size is consistent with the inner tube diameter determined by TEM (Figure S1). The larger pore size is attributed to the empty space created by the aggregation of nanotubes. It is consistent with the dimensions of the tubes (outer diameter of 15 nm, length of about 130 nm) and TEM observations. The measured BET surface area of  $144 \text{ m}^2\text{g}^{-1}$  (Table 1) is also quite close to the calculated geometric surface of tubes of those dimensions ( $128 \text{ m}^2\text{g}^{-1}$ ).

After further calcination at  $550^\circ\text{C}$ , the overall surface area decreases by about 30% (to  $105 \pm 2 \text{ m}^2\text{g}^{-1}$ ), regardless of the atmosphere of calcination (Table 1), due to partial collapse and sintering of the tubes (Figure S1). The population of smaller pores is decreased and shifted to larger sizes, with maxima at 10 nm (Figure 1c,d), but the pore volume remains similar.

Unlike titania, air-derived  $\text{C}_3\text{N}_4$  exhibits a type II isotherm (Figure 1a), i.e. a reversible isotherm with virtually no hysteresis typical of non-porous materials,<sup>43,48</sup> and a low surface area of  $10 \text{ m}^2\text{g}^{-1}$  (Table 1). Virtually no mesoporous volume ( $0.05 \text{ cm}^3\text{g}^{-1}$ , Table 1) is created when  $\text{C}_3\text{N}_4$  is produced in air, in accordance with previous results.<sup>38</sup> This indicates a highly packed and compact structure.<sup>49</sup>

Morphology of the  $\text{C}_3\text{N}_4$ -rich composite grown in air is similar to that of bare  $\text{C}_3\text{N}_4$ . Nevertheless, the composite appears a little more porous. It exhibits a Type IV isotherm with a H3 hysteresis loop (Figure 1a). The pore volume and the surface area are about three times higher than those found for raw  $\text{C}_3\text{N}_4$  (Table 1), which shows that titania acts as a dispersing agent for  $\text{C}_3\text{N}_4$ . The maximum at 7 nm in the pore size distribution (Figure 1c) suggests that the porosity of the composite may correspond to the inner volume of the incorporated titania tubes. The intensity of the peak, which is decreased by about 75% in the  $\text{C}_3\text{N}_4(75\%)\text{-TiO}_2$  composite, as compared with pure titania NT (heated at  $550^\circ\text{C}$ , i.e. at the same temperature than that used in the polycondensation process), is consistent with this model. Further, the absence of larger pores, as those found in pure titania NTs agglomerates, suggests that  $\text{C}_3\text{N}_4$  fills the intertube space in the composite.

Morphology of the low loaded  $\text{C}_3\text{N}_4$ -titania composite resembles more that of titania. Nevertheless, surface area and pore volume are about 40% lower. The absence of the peak at 7 nm in the pore size distribution (Figure 1c) suggests that the  $\text{C}_3\text{N}_4$  has polycondensed within titania NTs, filling the inner space. It is interesting that the outer volume also decreases, by about 50% as compared with pure titania NT, despite the very low  $\text{C}_3\text{N}_4$  loading of 2wt.%. Besides, high resolution TEM images show coverage of titania by very thin layers of  $\text{C}_3\text{N}_4$  (Figure 2b-c). This is attributed to a molecular interaction between  $\text{C}_3\text{N}_4$  precursors and/or their gaseous decomposition products ( $\text{NH}_3$ , HCN, cyanuric acid, isocyanate)<sup>50</sup> and the hydrophilic, OH-terminated  $\text{TiO}_2$  surface.<sup>51,52</sup> We speculate that the polycondensation process is then directed by the titania surface,<sup>53</sup> which drives/controls the morphology of

the resulting composites, and that  $\text{C}_3\text{N}_4$  acts as a glue that makes the titania NTs agglomerated structure more compact.

When grown in ammonia, raw  $\text{C}_3\text{N}_4$  exhibits a Type IV isotherm with a H3 hysteresis (Figure 1b). The surface area is three times higher than that of the raw air-derived carbon nitride (Table 1), in accordance with previous results.<sup>38</sup> More importantly, the porous volume is one order of magnitude higher with a much larger pore size distribution centered at about 40 nm (Figure 1d). Such a large mesoporous volume is indicative of the loose packing of extended  $\text{C}_3\text{N}_4$  layers.<sup>49</sup> It is consistent with the high "crystallinity" of ammonia-derived  $\text{C}_3\text{N}_4$ , i.e. the growth of 2D layers instead of the 1D linear melon and dimelem structures produced upon polymerization in air, as shown by a previous XRD study.<sup>38</sup>

Morphology of the  $\text{C}_3\text{N}_4$ -rich composite grown in ammonia is similar. It is characterized by a similar surface and an only slightly lower pore volume (Table 1). The pore size distribution exhibits two local maxima, one at 10 nm and one at 40 nm (Figure 1d). The first one is attributed to the inner porosity of the incorporated titania tubes. The second one is attributed to mesoporosity of  $\text{C}_3\text{N}_4$ . The slightly lower intensity of this larger pore size is consistent with partial filling of the  $\text{C}_3\text{N}_4$  mesoporosity by titania, which is supported by the observation of embedded titania NTs on TEM images (Figure 3c, d). Yet, the large pore size remains the most significant feature of the porosity of this composite.

Morphology of the low loaded ammonia-derived  $\text{C}_3\text{N}_4$ -titania composite is peculiar. Its surface area is similar to that of its air-derived counterpart (Table 1). However the pore size distribution obtained in ammonia significantly differs from all other size distribution patterns (Figure 1d). It consists in small mesopores ranging from 2 to 30 nm with local maxima at 9 nm, 14 nm and 21 nm. The intensity of this event is much larger than the one that could be expected from the inner tube porosity of titania. It has been observed before upon splitting of  $\text{C}_3\text{N}_4$  sheets, i.e. decrease in the  $\text{C}_3\text{N}_4$  2D layers dimensions.<sup>49</sup> It suggests that, at high concentration,  $\text{TiO}_2$ -NTs act as inhibitors of the ammonia-driven growth of  $\text{C}_3\text{N}_4$  planes. At the same time, the large mesoporosity observed for titania NTs aggregates is markedly reduced. It suggests that the intertube void is largely filled by  $\text{C}_3\text{N}_4$ . The partial filling of the pores (i.e. not just increase in the percolation state of the structure, like in the air-derived counterpart) also creates a smaller porosity, which contributes to the peculiar porous profile observed (Figure 1d). Given the low amount of  $\text{C}_3\text{N}_4$  present in the composite, a reasonable model that could fit these observations is the growth of stacks of very small  $\text{C}_3\text{N}_4$  sheets normal to the tubes. Hence, the titania-inhibited 2D structures of  $\text{C}_3\text{N}_4$  obtained in ammonia exhibit the narrowest pore size distribution with the lowest average pore size.

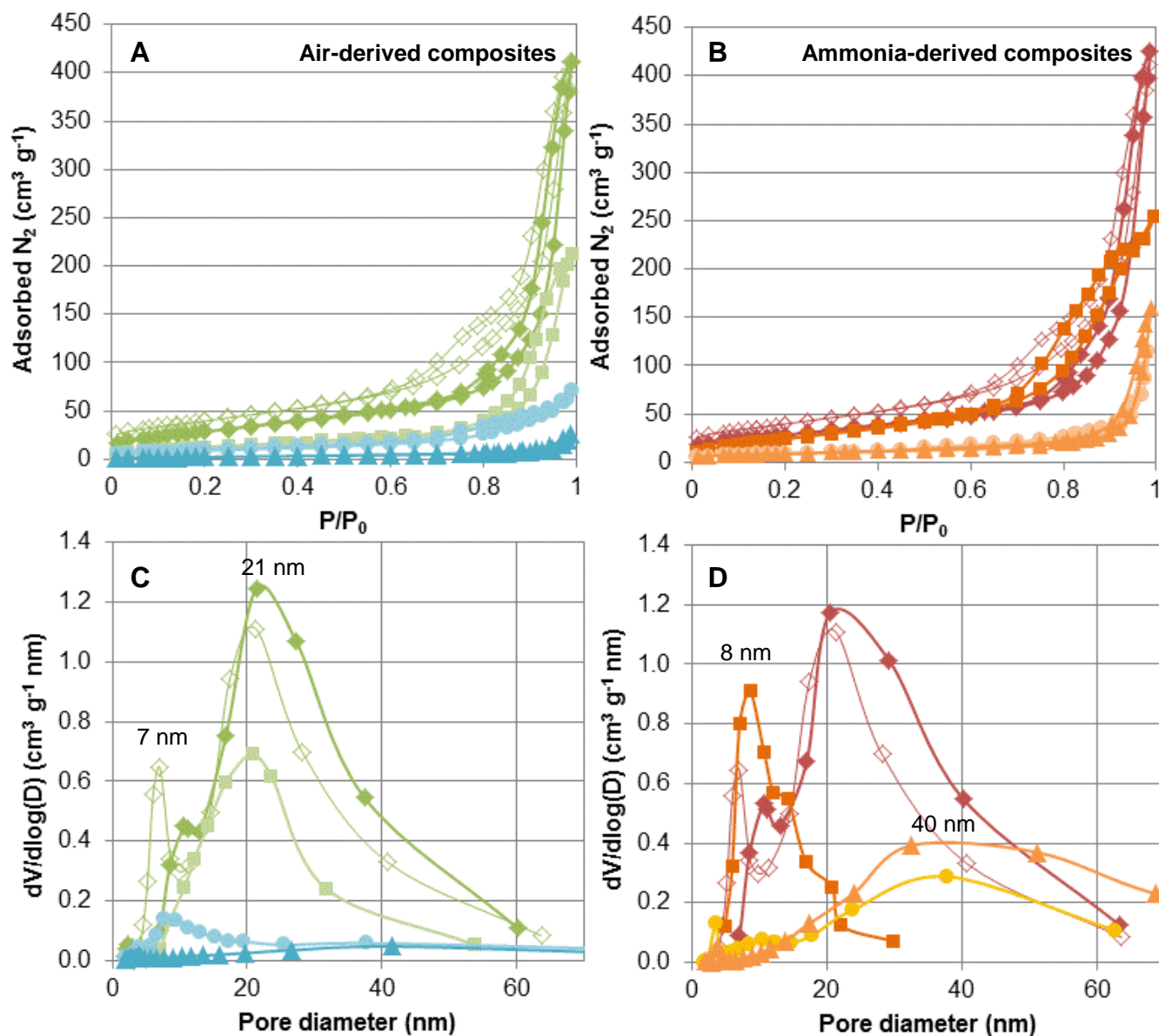
In summary:

- At high  $\text{C}_3\text{N}_4$  loadings, the morphology and porosity of  $\text{C}_3\text{N}_4\text{-TiO}_2$  composites is essentially dominated by  $\text{C}_3\text{N}_4$

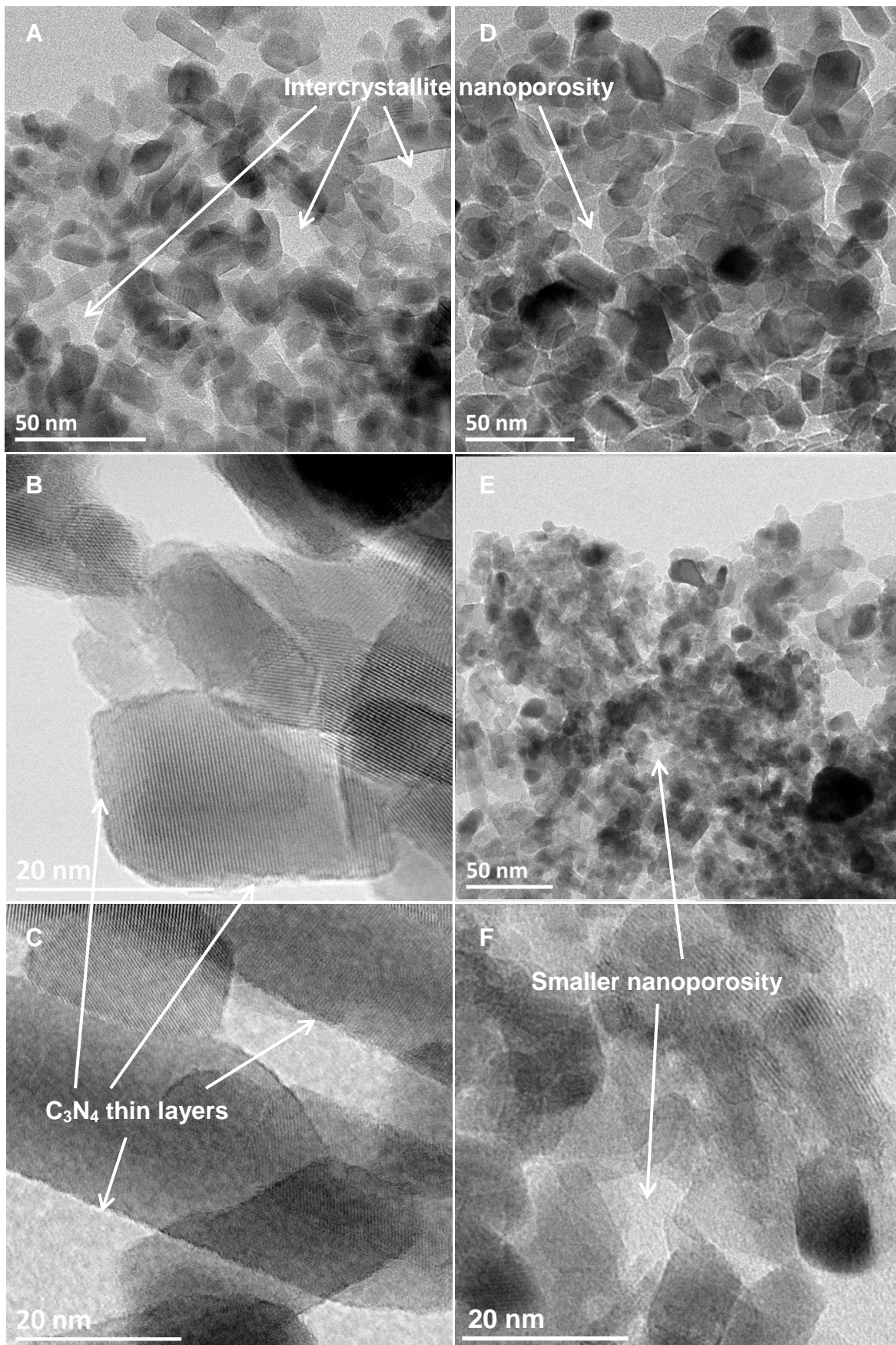
features, i.e. the growth of porous stacks of extended 2D sheets in ammonia (large pores) and the growth of a more compact, intricate structure composed of entangled less perfect 2D sheets and 1D chains in air (poorly porous), as illustrated by TEM images (Figure 3). The presence of titania thus barely affects the growth of  $C_3N_4$ . Titania creates some small porosity in the air-derived composite and occupies part of the large mesoporosity in the ammonia-derived composite.

- At low  $C_3N_4$  loadings, the growth of  $C_3N_4$  seems driven by both the polycondensation atmosphere and titania, somehow acting as hard template.<sup>54,55</sup> TEM images of such low loaded  $C_3N_4$ - $TiO_2$  composites are clearly dominated by quite similar titania aggregates with more (ammonia, Figure 2e,f) or less (air, Figure 2c,d) filled intercrystallite porosity, associated with markedly different pore size

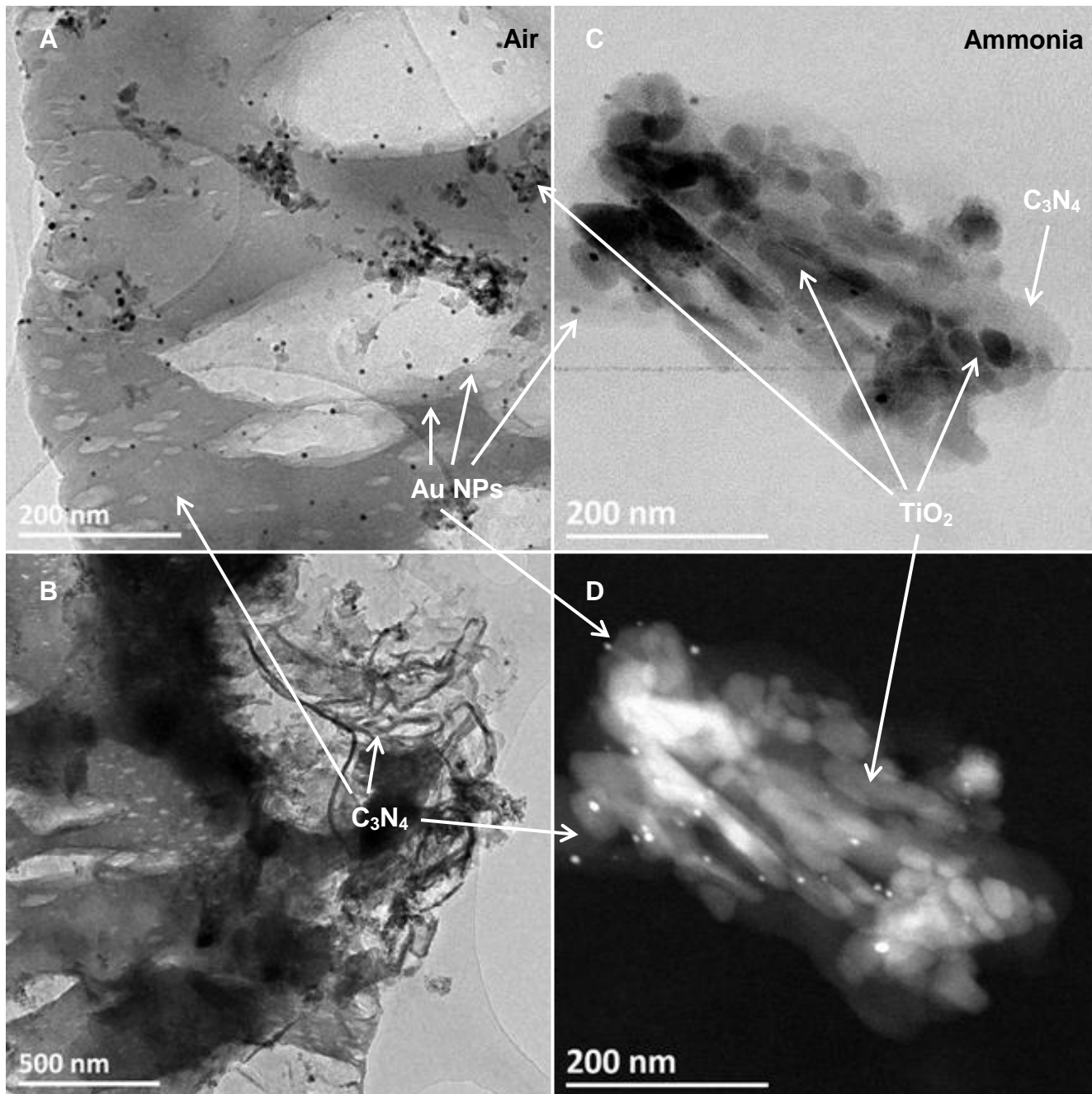
distributions. While the air-derived composite exhibits a pore size distribution (at larger pore sizes) similar to that of  $C_3N_4$ -free, pure titania, the ammonia-derived composite exhibits smaller pores than both its titania and  $C_3N_4$  counterparts. Hence, under constrained conditions (low ratio of  $C_3N_4$  precursors vs.  $TiO_2$ ), filling of the titania intertube void by  $C_3N_4$  is critically dependant on the polycondensation atmosphere. The porous profiles of low loaded  $C_3N_4$ - $TiO_2$  composites suggest that air drives the growth of  $C_3N_4$  alongside titania structures (filling the inner void and covering the outer surface without filling the external volume), while ammonia drives the growth of  $C_3N_4$  composites normal (or at least with a much higher angle relative) to the titania surface (partially filling the external porosity, which decreases the average pore size).



**Figure 1. Texture and porosity of  $C_3N_4$ - $TiO_2$  composites.**  $N_2$  physisorption isotherms (a, b) and pore size distributions (c, d) of the composites prepared in air (a, c) and in ammonia (b, d).  $C_3N_4$  ( $\blacktriangle$ ),  $C_3N_4(75\%)-TiO_2$  ( $\bullet$ ),  $C_3N_4(2\%)-TiO_2$  ( $\blacksquare$ ),  $TiO_2-550$  ( $\blacklozenge$ ),  $TiO_2-380$  ( $\diamond$ ).



**Figure 2. Morphology of low loaded  $\text{C}_3\text{N}_4\text{-TiO}_2$  composites.** TEM images of air-derived  $\text{TiO}_2$ -550 (A), air-derived  $\text{C}_3\text{N}_4(2\%)\text{-TiO}_2$  (B-D) and ammonia-derived  $\text{C}_3\text{N}_4(2\%)\text{-TiO}_2$  (E, F).



**Figure 3. Morphology of highly loaded  $C_3N_4$ - $TiO_2$  composites.** TEM images of air-derived (A, B) and ammonia-derived (C, D)  $Au/C_3N_4(75\%)-TiO_2$  composites.

**Interaction between  $C_3N_4$  and titania and surface composition.** ATR FTIR was used to characterize both bulk and surface vibrations of the materials, which allows to further understand how titania and carbon nitride interact at the nanoscale, and further support the presence of  $C_3N_4$  on the titania surface in the low loaded composites. Titania and carbon nitride are characterized by different vibration patterns. Full range FTIR spectra of titania nanotubes are characterized by 3 major absorption regions, regardless of the treatment, air or ammonia, they have been submitted to (Figure 4 a,b, green and brown - - - lines). The broadest and most intense absorption feature

between  $400$  and  $1000\text{ cm}^{-1}$  corresponds to Ti-O-Ti and Ti-O stretching vibrations from the titania framework. The large absorption band at  $3360\text{ cm}^{-1}$  corresponds to stretching vibrations of H-bonded terminal hydroxyl groups and physisorbed water, while the smaller feature at  $1630\text{ cm}^{-1}$  corresponds to the bending vibrations of adsorbed water. Full range FTIR spectra of carbon nitriles are characterized by 2 major absorption regions, regardless of the atmosphere, air or ammonia, they have been synthesized in (Figure 4 a, b, blue and orange ··· lines). The most prominent multi-peak feature between  $750$  and  $1750\text{ cm}^{-1}$  (Figure 4 d, f) corresponds to skeletal and in-plane vibrations

of polyaromatic units, namely C=N skeletal stretching modes of heterocycles at  $1623\text{ cm}^{-1}$ , to side-chain asymmetric C-N stretching vibrations at  $1534$  and  $1561\text{ cm}^{-1}$ , to C-N skeletal stretching modes of aromatic rings at  $1456$ ,  $1397$  and  $1312\text{ cm}^{-1}$ , to C-NH-C bridges *via* NH linear linkage of heptazine units at  $1227$  and  $1201\text{ cm}^{-1}$  and to the breathing mode of triazine units at  $803\text{ cm}^{-1}$ .<sup>57</sup> On the other hand, the broad band centered at about  $3150\text{ cm}^{-1}$  is composed of 3 components at  $3080$ ,  $3160$  and  $3260\text{ cm}^{-1}$ , due to vibrations of out of plane terminal NH and  $-\text{NH}_2$  functions (uncondensed amine groups) and physisorbed water (Figure 4 c, e), which are characteristic of the  $\text{C}_3\text{N}_4$  outer surface.

Interestingly, the vibration pattern of titania is significantly modified in the low loaded composite. Comparing the green dotted - - - and plain lines in Figure 4a or the brown dotted - - - and plain lines in Figure 4b, it appears that the addition of only a minor amount of  $\text{C}_3\text{N}_4$  to  $\text{TiO}_2$  NTs induces major inhibition of both the terminal and framework vibrations of  $\text{TiO}_2$  NTs. The band related to terminal hydroxyl groups ( $3360\text{ cm}^{-1}$ ) and the bands related to bulk Ti-O stretching vibrations ( $400$ - $1000\text{ cm}^{-1}$ ) indeed all markedly decrease. On the other hand, skeletal and terminal vibrations characteristic of the  $\text{C}_3\text{N}_4$  framework appear quite clearly between  $1200$  and  $1650\text{ cm}^{-1}$  and at  $3150\text{ cm}^{-1}$ , respectively. The fact that titania vibrations are inhibited in this composite suggests extensive coverage of the titania surface by  $\text{C}_3\text{N}_4$ , in agreement with  $\text{N}_2$  physisorption results (Figure 1), and strong interaction between  $\text{C}_3\text{N}_4$  and  $\text{TiO}_2$ .<sup>58</sup> When the  $\text{C}_3\text{N}_4$  content is further increased to 72 wt.%, the FTIR spectrum becomes very similar to that of pure  $\text{C}_3\text{N}_4$  (compare - · - · - · - and · · · lines) regardless of the polycondensation atmosphere (air or ammonia). This shows that the polycondensation of  $\text{C}_3\text{N}_4$  precursors on top of titania nanotubes drastically modifies the surface chemical composition of titania and that the surface chemistry of all composites is dominated and controlled by  $\text{C}_3\text{N}_4$ .

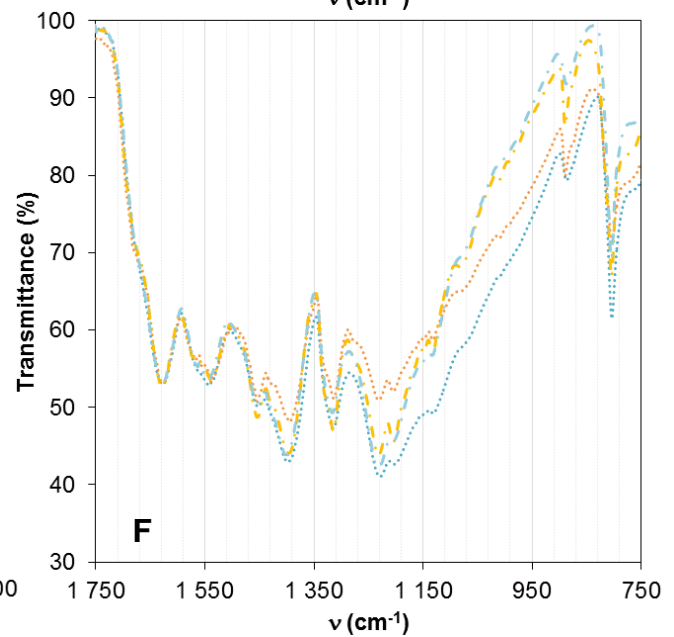
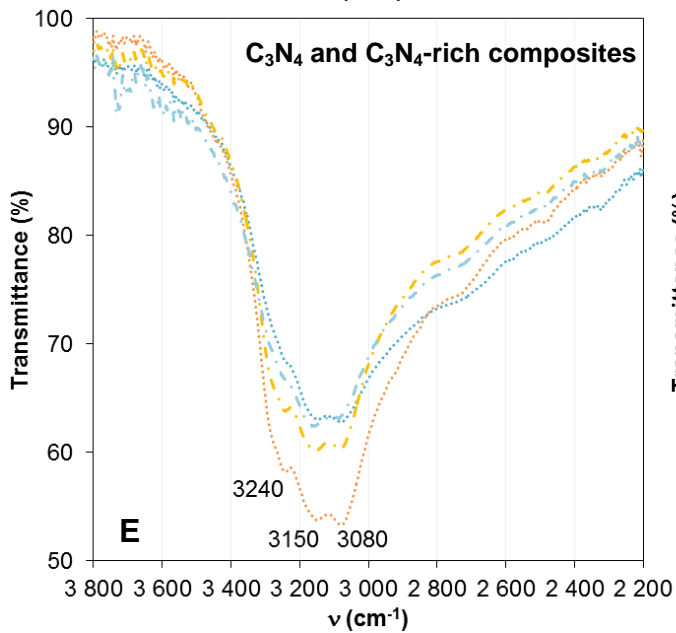
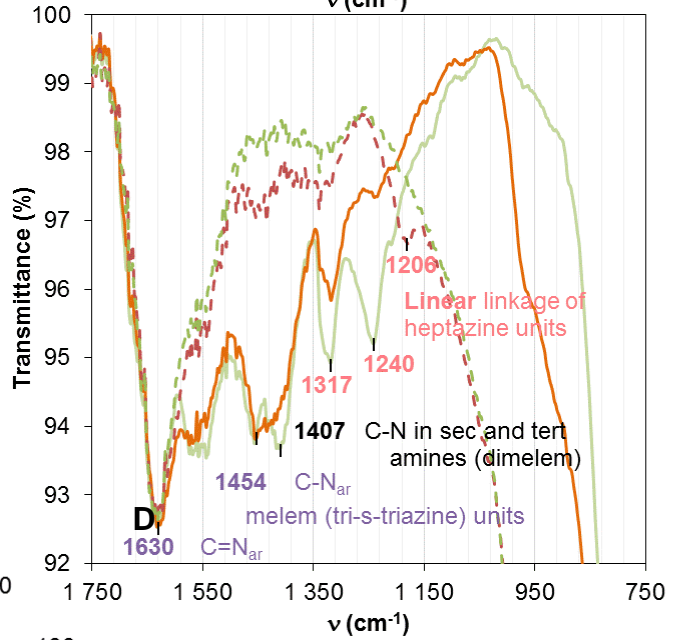
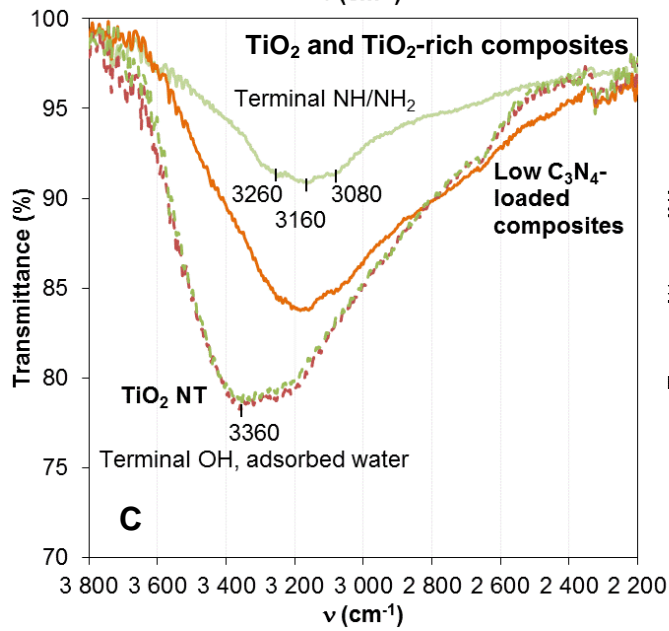
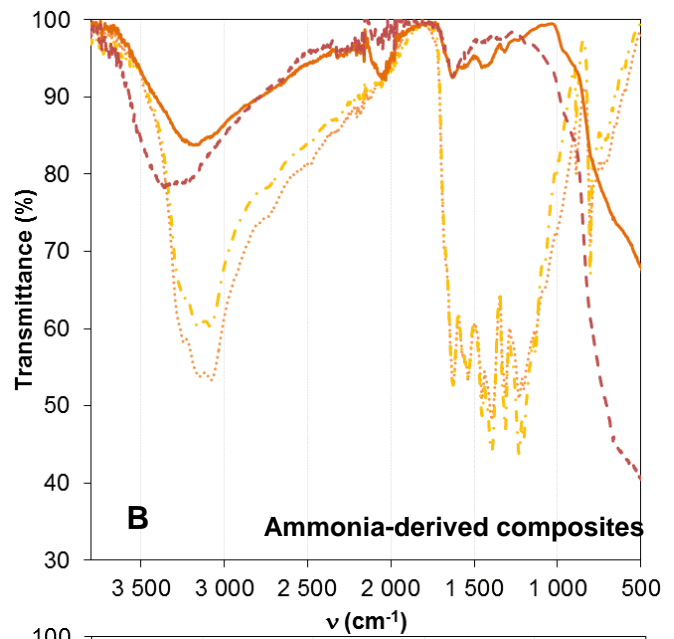
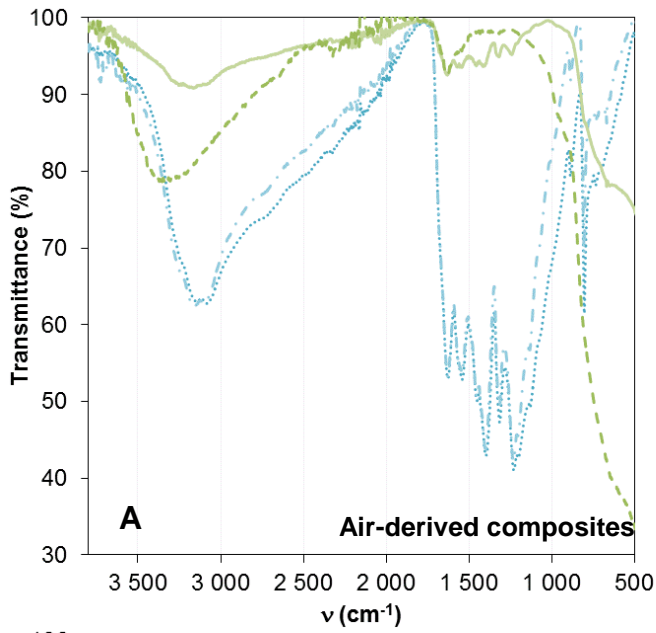
On the other hand, concerning the effect of the atmosphere, one can notice that the atmosphere of the post-synthesis treatment of titania NTs apparently does not affect the surface chemistry of titania as the water-normalized IR spectra of ammonia- and air-treated titania NTs are quasi-identical (Figures 4 c, d, - - - lines). However, the polycondensation atmosphere that is used for  $\text{C}_3\text{N}_4$  synthesis has a subtle impact on the surface chemistry of  $\text{C}_3\text{N}_4$  (Figure 4 e, f, · · · lines). In particular,  $\text{NH}_3$ -derived  $\text{C}_3\text{N}_4$  exhibits a more prominent feature at  $3150\text{ cm}^{-1}$  than air-derived  $\text{C}_3\text{N}_4$ , associated with decreased vibrations at  $1201$  and  $1227\text{ cm}^{-1}$ . This indicates that the  $\text{NH}_3$ -derived carbon nitride is much more functionalized with out of plane NH and  $\text{NH}_2$  functions and that the occurrence of linear linkages of heptazine units, such as dimelem and

melon, is significantly lower than in the air-derived composite. It is consistent with our previous XRD study of  $\text{C}_3\text{N}_4$  which showed that the air-derived materials is more linear (1D), while the  $\text{NH}_3$ -derived material is more crystallized (3D stacking of large planes).<sup>38</sup> It is interesting that these differences in the functionalization and morphology of  $\text{C}_3\text{N}_4$  are retained in the low loaded  $\text{C}_3\text{N}_4$ - $\text{TiO}_2$  composites (Figures 4 c, d, plain lines) and that the  $\text{NH}_3$ -derived material is the only composite that exhibits a distinct vibration band at  $2040\text{ cm}^{-1}$  corresponding to the  $=\text{C}=\text{N}$ - stretching vibration of ketimine derivatives ( $\text{R}_2\text{C}=\text{C}=\text{N}-\text{R}$ ).<sup>59-62</sup> On the contrary, in the  $\text{C}_3\text{N}_4$ -rich composites, the presence of titania masks differences in functionalization of the  $\text{C}_3\text{N}_4$  component obtained under different polycondensation atmospheres. No significant difference is indeed observed in the FTIR spectra of highly loaded  $\text{C}_3\text{N}_4$ - $\text{TiO}_2$  composites (Figures 4 e, f, - · - · - · - lines). This means that similar free terminal groups are present on the two quite different  $\text{C}_3\text{N}_4$  morphologies (Figure 1c, d, Figure 3). This suggests that carbon nitride strongly interacts with the titania surface, possibly via the functions corresponding to the diminished vibrations, blocking these vibrations upon immobilization.

### Gold deposition.

Gold was deposited onto  $\text{C}_3\text{N}_4$ ,  $\text{TiO}_2$  and  $\text{C}_3\text{N}_4$ - $\text{TiO}_2$  composites using a sonicated-assisted chemical reduction method performed in the presence of the support. Deposition yields of 60 to 90% are achieved (Table 1). They are minimal over pure titania NTs despite their larger surface areas (60-70%), indicating a poorer affinity of the titania surface for chloroauric anions and gold nanoparticles, as compared with the  $\text{C}_3\text{N}_4$  surface (80%). They are higher (83-90%) on all  $\text{C}_3\text{N}_4$ - $\text{TiO}_2$  composites, except  $\text{C}_3\text{N}_4$ (2%)- $\text{TiO}_2$  (air), and maximal for the  $\text{C}_3\text{N}_4$ (75%)- $\text{TiO}_2$  composition. The similarities in deposition yields for 3 out of the 4 composites (entries 4-6) are attributed to their similar surface chemistries, as shown by FTIR.

Average Au NPs sizes have been statistically determined by measuring their diameters on TEM images. Although they are obtained on differently-sized populations (due to lower contrast, associated with lower loading, of the titania-rich samples), they are found representative of the population of each composite. They essentially vary between 3.1 and 4.2 nm (Table 1). A lower average size (2.3 nm) is found for the  $\text{NH}_3$ -derived  $\text{C}_3\text{N}_4$ -rich composite, suggesting a particularly strong affinity between gold precursors and the support surface. The larger size (5.1 nm) found for air-derived pure  $\text{C}_3\text{N}_4$  is attributed to the particularly low surface area and porous volume of the composite support ( $10\text{ m}^2\text{ g}^{-1}$  and  $0.05\text{ cm}^3\text{ g}^{-1}$ , the lowest of the series).





5a, Figure S2). On the other hand, performances of the ammonia series are much more dependent on the  $C_3N_4$  content (Figure 5f), with  $O_2$  TOF at 250°C ranging from 0.58 to 2.72  $s^{-1}$  (Table 1, Figure S2), and apparently controlled by the porosity of the support. Indeed, the catalyst with a higher average pore size (40 nm) than the titania-supported catalyst (21 nm), i.e. the  $C_3N_4$ -supported catalyst, performs better, while the catalyst with a lower average pore size (8 nm), namely the titania-rich composite, performs worse. The  $C_3N_4$ -rich composite performs similarly to Au/TiO<sub>2</sub>-550 (NH<sub>3</sub>) due to the presence of smaller pores (8 nm), in addition to the larger pores (40 nm), which may confine part of gold nanoparticles and limit their access, so that not all the catalytic surface is easily available.

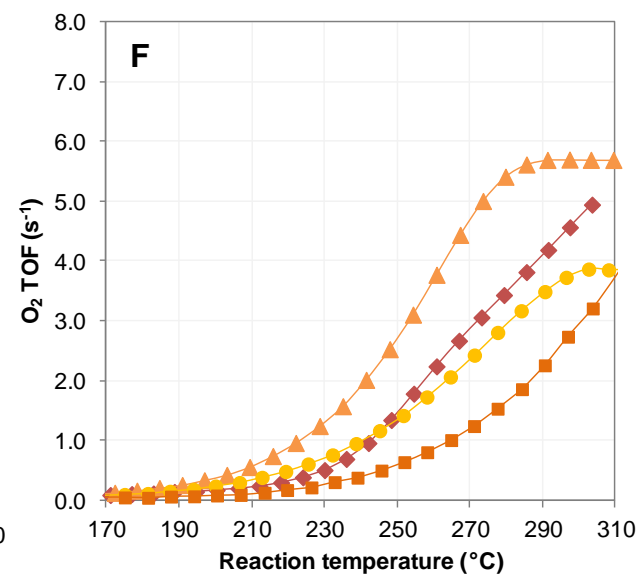
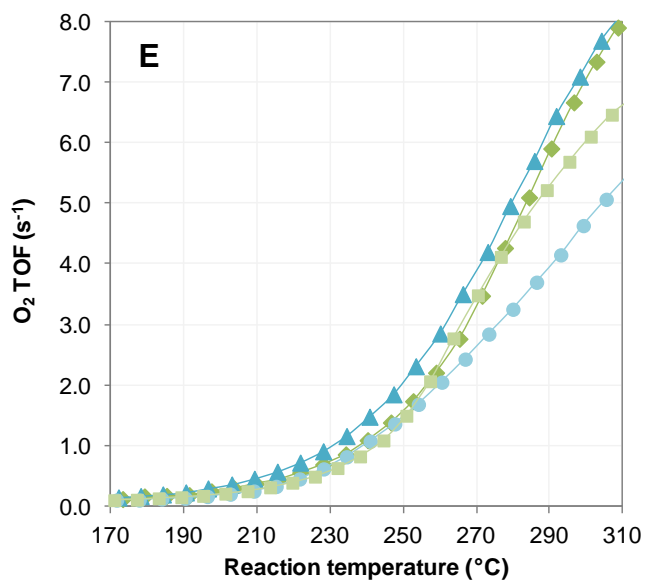
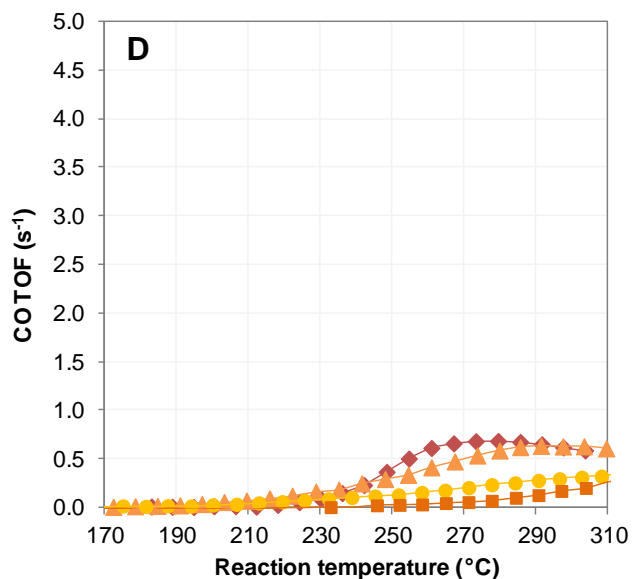
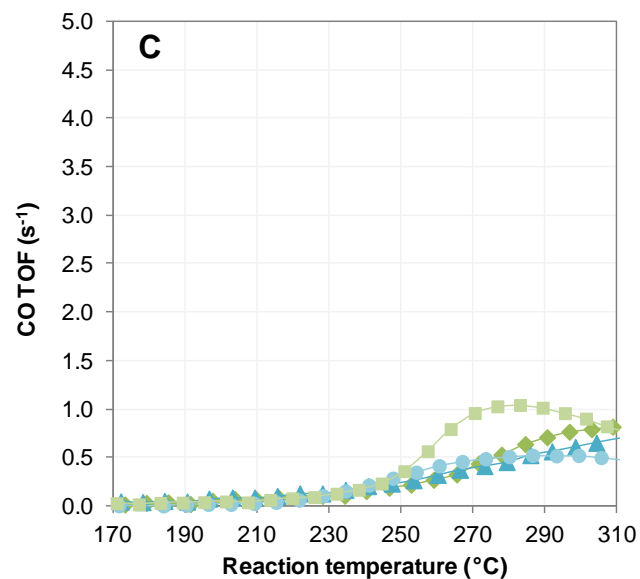
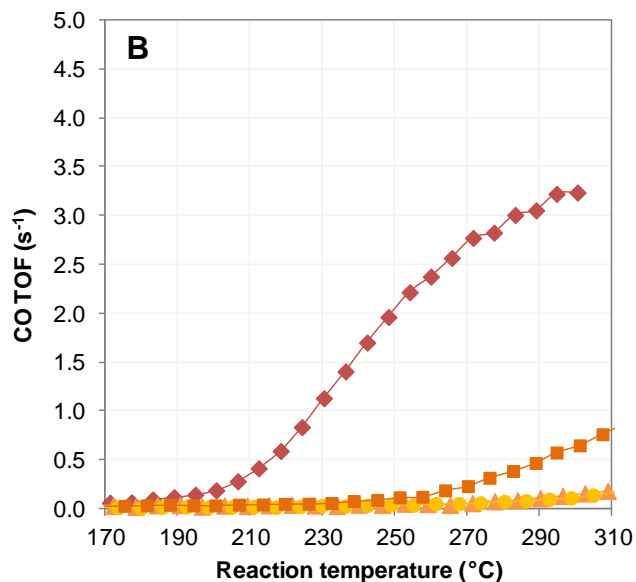
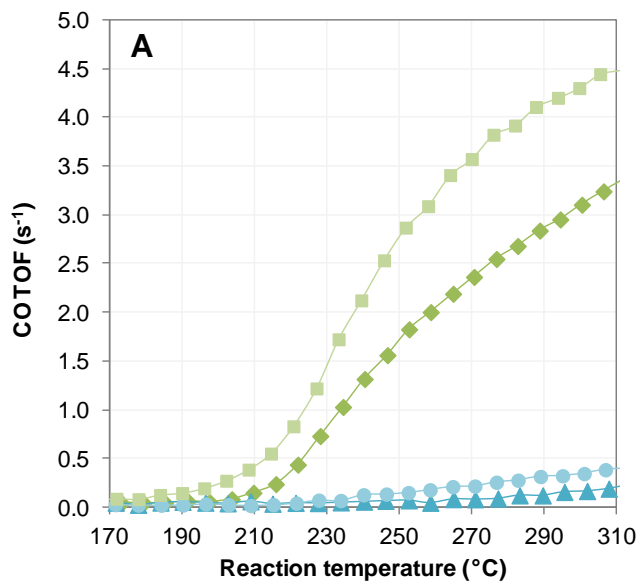
By comparison, the air series (Figure 5e) performs similarly to the ammonia-derived TiO<sub>2</sub>-supported catalyst (Figure 5f, Figure S2). Hence, titania-based catalysts, with similar pore size distributions whether treated in air or in ammonia, perform similarly. The air-derived titania-rich composite shows a similar activity as well, and similar average pore size (21 nm). It markedly contrasts with its ammonia counterpart, which exhibits the lowest activity of all and also the smallest average pore size. Finally, for the  $C_3N_4$  and  $C_3N_4$ -rich catalysts, a smaller difference in activities is found between the two series. The ammonia-derived  $C_3N_4$  catalyst, which shows the largest average pore sizes (40 nm) and the absence of any small pores, performs only slightly better than its essentially non-porous air-derived counterpart.

Hence, the impact of the porosity on the overall catalytic oxidation performance of these Au/ $C_3N_4$ -TiO<sub>2</sub> composites in PROX can be described in terms of ease of oxygen diffusion towards the catalytic gold nanoparticles. The most active catalyst is that with the largest pores (40 nm) and no small pores, closely followed by those with no pores in which the slightly less dispersed Au NPs are located on the outer surface and thus easily accessible. The least active catalyst is the one with the lowest average pore size, which contains no large pores.

Hence, the ammonia-derived  $C_3N_4$  gold catalyst, which is inactive for CO oxidation due to the inadequate support surface chemistry (Figure 5b), exhibits the highest overall PROX activity amongst all supports studied here (Figure 5f, Figure S2), due to its large pore size distribution rang-

ing from 10 to 90 nm. This is much larger than the size of the reactant and product molecules involved in the process (CO, O<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>, H<sub>2</sub>O). The need for a pore size  $\gg$  10 nm suggests that cumbersome molecular intermediates may be involved in gold-catalyzed PROX over inert supports, i.e. that intermediates larger than the usually postulated OOH-type species<sup>16,17</sup> may be needed to activate oxygen *via* hydrogen- and water-mediated pathways.

The selectivity of the PROX reaction at 250°C (Table 1, Figure S2) is quite low for all the catalysts, i.e. below 15%. It is attributed to the high light-off temperatures for CO oxidation, which makes it detectable in a temperature range where hydrogen oxidation severely competes.<sup>66,67</sup> Nevertheless, it is interesting that the selectivity of the PROX reaction varies with the  $C_3N_4$  content of the support in a similar manner as that observed for CO TOF, with a stronger dependence however on the  $C_3N_4$  content (Figure S2). The ammonia series contains the most selective (Au/TiO<sub>2</sub>, 14%) and least selective (Au/ $C_3N_4$ (2%)-TiO<sub>2</sub>, 2%) catalysts. Hence introducing only 2% of  $C_3N_4$  on the titania support prior to gold deposition drastically lowers the selectivity of the catalyst. This could be attributed to the drastic reduction in pore size from 20 to 8 nm, which likely has more impact on the oxidation of CO than on the oxidation of the smaller, labile hydrogen molecule. The  $C_3N_4$ -rich and  $C_3N_4$  materials with larger pores exhibit a little higher selectivities of 5 and 6%, respectively. Hence, for the ammonia series, the selectivities of the composites are lower than the selectivities of the single components. On the contrary, for the air series, the growth of  $C_3N_4$  over titania NTs is beneficial to the selectivity, which reaches 12% over  $C_3N_4$ (2%)-TiO<sub>2</sub> and 11% over  $C_3N_4$ (75%)-TiO<sub>2</sub> vs. 6-7% for the single components. This synergy can be attributed to partial masking of unselective sites of the titania surface, i.e. OH groups which, under PROX conditions have been shown to promote hydrogen oxidation.<sup>17,23</sup> All in all, air-derived composites are significantly more selective (11-12%) than their ammonia counter-parts (2-5%), which highlights the more suitable interfacing between titania and carbon nitride obtained by polycondensation of  $C_3N_4$  precursors in air for the PROX reaction.



**Figure 5. Catalytic properties of Au/C<sub>3</sub>N<sub>4</sub>-TiO<sub>2</sub> composites.** CO conversions obtained in the CO oxidation (a, b) and PROX (c, d) reaction over composites of the air (a, c) and ammonia (b, d) series. Oxygen conversions in PROX (e, f). C<sub>3</sub>N<sub>4</sub> (▲), C<sub>3</sub>N<sub>4</sub>(75%)-TiO<sub>2</sub> (●), C<sub>3</sub>N<sub>4</sub>(2%)-TiO<sub>2</sub> (■), TiO<sub>2</sub>-550 (◆).

## CONCLUSION

Successful control of the surface chemistry and mesoporosity of C<sub>3</sub>N<sub>4</sub>-TiO<sub>2</sub> composites was achieved at low C<sub>3</sub>N<sub>4</sub> contents by tuning the growth of C<sub>3</sub>N<sub>4</sub> over pre-formed anatase titania nanotubes with two different polycondensation atmospheres (air and ammonia). Air hardly affects the mesoporosity of the intertube space (centered at 20 nm and extending over 55 nm), due to the growth of thin C<sub>3</sub>N<sub>4</sub> layers partially covering titania crystallites surface. On the contrary, a quite narrow size distribution of small pores centered at 8 nm is created under ammonia, due to partial filling of the intertube space by short, stacked C<sub>3</sub>N<sub>4</sub> layers. After deposition of similarly sized Au NPs on the composites, it is found that:

- (1) gold-catalyzed CO oxidation is critically dependent on the surface chemistry of the mixed support and requires the presence of oxygenated surface functions
- (2) the presence of only a small amount of uncovered titania surface is enough to warrant oxygen activation and activity in CO oxidation
- (3) Au/C<sub>3</sub>N<sub>4</sub> is active for PROX, i.e. hydrogen/water-mediated CO oxidation pathways are active on otherwise “inert” non-hydroxylated, NH<sub>2</sub>-terminated C<sub>3</sub>N<sub>4</sub> supports
- (4) activity in PROX is controlled by the porosity of these intricate composite supports, regardless of their surface chemistry, i.e. by the diffusion of activated oxygen species towards the confined Au NPs; large pores (40 nm) are needed, suggesting that rather large multi-molecule intermediate scaffolds are involved
- (5) selectivity in PROX, although low, benefits from the favorable interfacing between C<sub>3</sub>N<sub>4</sub> and TiO<sub>2</sub> obtained by polycondensation in air
- (6) modification of titania by a low amount of C<sub>3</sub>N<sub>4</sub> (2wt.%) leads to the best catalytic performances

This study highlights the often overlooked pore size domain that should be targeted when designing gold PROX catalysts and, more generally, the relevance of compositions at the very edge of the range for binary composites.

## ASSOCIATED CONTENT

### Supporting information

Characterization of morphology and stability of titania nanotubes (TEM, XRD) and additional catalytic graphs.

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The manuscript was written through contributions of all authors.

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## Notes

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## ABBREVIATIONS

NPs, nanoparticles; NTs, nanotubes; FTIR, Fourier Transform Infra Red; TEM, transmission electron microscopy; BET, Brunauer Emmett Teller; XRD, X-ray diffraction.

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