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Correlation preparation parameters/activity for microTiO₂ decorated with SilverNPs for NO_x photodegradation under LED light

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Abstract

It well known that TiO₂ systems can be successfully employed as photocatalysts to abate environmental pollution, in either the gas or liquid phase, if properly exposed to UV radiation: in order to overcome such a limitation and possibly widen its applications under solar and/or LED light, TiO₂ surface decoration with noble metals could represent a powerful mean to achieve such a goal. In particular, the use of Ag species as decorating agent has been already demonstrated to improve TiO₂-based systems photoactivity even under LED light as well as exhibiting antibacterial properties even in the dark. Ample literature is available on the synthesis of silver nanoparticles (Ag NPs) but few are available on the interaction of such particles with micrometric samples, which pose less environmental and health concerns than the nano-sized powders widely adopted. The synthetic routes employed for Ag NPs decoration onto TiO₂ might deeply influence the final performances of the photocatalyst, in particular referring to both NPs shape and fine structure. Thus in the present contribution the attention was posed onto the preparation of Ag NPs by means of an electrochemical method followed by subsequent decoration onto a micrometric TiO₂ (Kronos 1077): different parameters, such as pH and the nature of physical nanoparticle dispersants were taken into account, in order to evaluate their effects on the resulting Ag NPs features. We evaluated the photocatalytic performances of the

various decorated materials we obtained towards the photodegradation of NO_x under LED light, concluding that the best output was obtained by means of photocatalysts synthesised at basic pH.

1. Introduction

Capturing renewable sunlight by permanently abducting photons into complex systems capable of storing them and, at the same time, realizing them or transforming them into reactive species would arguably be the Holy Grail of energy utilization of the current century.

Researchers are looking for more efficient ways to store and re-use solar energy. Photocatalysis, still far from being efficient, offers scientists the chance of embracing this challenge [1]. In particular, TiO₂ is now seen as an unforsaken vector to attain the objective of an affordable and efficient photocatalyst.

TiO₂ undoubtedly possesses alluring characteristics such as long-term mechanical and thermal stability, even under irradiation [2], availability, feasible synthesis and low cost [3]. However, its low efficiency ejects widespread commercial applications. The reason of its inadequacy lies in its wide band-gap (E_g), which limits the irradiation that can be absorbed. Indeed, an $E_g \approx 3.2$ eV requires $\lambda_{\text{irr}} < 385$ nm, which disqualifies 95 % of the solar spectrum. In addition, the high recombination rate of the photogenerated species results in a low production rate of secondary photo-generated reactive compounds [4,5]. Diverse approaches such as coupling TiO₂ with other semiconductors [6,7], dye sensitizing [8,9], ion implantation [10], noble metal [4] decoration, doping with heteroatoms [11] now account for several literature data. Among the noble metals Ag NPs have been a target since they also possess antibacterial properties [12]. However, besides this, AgNPs exhibit the surface plasmon band typical of noble metal NPs, which originates from the Mie absorption in the visible spectrum. When incorporated onto TiO₂, its band-gap decreases, opening up the light absorption over a wider light spectrum region. The fundamental mechanism of visible light absorption by TiO₂ decorated with Ag identifies with the injection of metal plasmonic electrons into the wide band-gap semiconductor. However, the plasmonic absorption, which is an optical property at the surface/bulk interface, only manifest for NPs bigger than 2 nm. Below this size, quantum effects prevails [13]. The most recent approaches focus on interposing a layer of conductive material between TiO₂ and Ag to provide a conductive

path for the electrons from the noble metal to the TiO₂ surface. For instance, Lang et al. intercalated graphene oxide (GO) nanosheets as bridges between Ag nanocubes and TiO₂ nanosheets to provide a conductive path for the electrons from the plasmonic Ag band to the semiconductor [14]. Asapu et al. fabricated core-shell super stable Ag-TiO₂-PAH where polyallylaminehydrochloride (PAH) constitute a polycation layer [15], whereas Jbeli et al. Intercalated a chitosan film that formed an AgCl layer between TiO₂ and Ag species [16].

Controlling the dispersion and size of the noble metal over TiO₂ is fundamental to both maximize photocatalytic activity by tackling the mass transfer of active primary and secondary photogenerated species, as well limiting the input of catalyst precursors' and solvents in an approach towards sustainability. For instance, Stucchi et al. doped micrometric (110 nm) TiO₂ with Ag nanoparticles (NPs) in the weight range from 1 to 20 % by means of ultrasound [17]. Zeng et al. synthesized Ag nanowires with TiO₂ NPS around them that were stable for several days and degraded acetaldehyde in few minutes in gas phase under fluorescent light [18].

AgNPs agglomerated electrochemically to control their size is an innovative and interesting approach because it is possible to precisely control the size of Ag. Starowicz et al. polarized a sacrificial anode of Ag and obtained AgNPs of about 20 nm [19]. With the same technique, Rodriguez-Sanchez et al. obtained nanoparticles in the range 2-7 nm in acetonitrile and tetrabutylammonium bromide as electrolyte and stabilizer [19]. TiO₂ particle size is another fundamental issue to tackle: . the benefits of nanotechnology dominate our thinking nowadays. The concerns regarding nano-particles (< 100 nm) deal with inhalation and skin contact of particles that are so small to be potentially not "recognizable" by the human body barriers, thus getting into contact with the organism cells. The number of papers on the subject "TiO₂ nanoparticles and toxicity", which raised from 57 (within 2008) to 985 in the last 10 years [Scopus.com source], is a proof of the increasing concern about the effects of nano-particles on living beings. Concurrently, major national and international agencies in Europe are promoting research on potential adverse effects of nanoparticles [20]. The effects of nano-sized TiO₂ on human health have not been fully demonstrated yet, but the first data on the adverse effect of nano-sized TiO₂ on animals just became available [21,22].

The authors recently confronted this issue by several papers published on increasing the photoactivity of micro-TiO₂ [23–25], whereby doping micro-sized TiO₂ the activity increased in the visible range.

As for the photocatalytic reactions that might be taken into account, NO_x abatement is one of the most frequently considered. A huge amount of papers were published in the last twenty years about this subject (Google Scholar source), most of them being focused onto the use of TiO₂: among them, an important contribution is represented by the paper by Folli et al [26] (A. Folli, J. Z. Bloh, M. Strøm, T. Pilegaard Madsen, T. Henriksen, D. E. Macphee “Efficiency of Solar-Light-Driven TiO₂ Photocatalysis at Different Latitudes and Seasons. Where and When Does TiO₂ Really Work?”, *J. Phys. Chem. Lett.*, 2014, 5 (5), pp 830–832, DOI: 10.1021/jz402704n) in which the authors reported a correlation between the maximum NO removal (minimum concentration) with the maximum UV irradiance. Another very recent review contribution by Schreck et al [27] (M. Schreck, M. Niederberger “Photocatalytic Gas Phase Reactions”, *Chem. Mater.*, Just Accepted Manuscript (2019), DOI: 10.1021/acs.chemmater.8b04444) reports about NO_x emissions, in particular from the transport sector, as they a significant impact on urban air quality. In the present research, the electrochemical synthesis of Ag NPs together with their subsequent deposit by incipient wetness on micrometric TiO₂ was reported. During the synthesis of the catalyst the pH was varied in the 4-12 range, observing exceptional catalytic performance (90 % NO_x conversion in 1 h) under LED light for the sample obtained at pH = 14 and PVP/Ag⁺ molar ratio = 3.

2. Experimental

2.1 Silver nanoparticles preparation

Ag NPs were prepared from an AgNO₃, polyvinyl pyrrolidone (PVP) and KNO₃ solution. KNO₃ (≥ 99.0 %) and PVP (average molecular weight = 40 000) are Sigma Aldrich and were employed them with no further purification. 100 mL of a 30 g/L AgNO₃ solution were placed into a becker containing 1 g of KNO₃ and a weighted amount of PVP. KNO₃ solution was added as supporting electrolyte. PVP acted as physical nanoparticle dispersant [26] and we varied its concentration to gauge the effect of PVP on the synthesis. We varied the dispersant to understand its influence on

the stabilization of Ag NPs. We selected polyvinyl alcohol (PVA) (average molecular weight = 9000-10000, 80% hydrolysed, Sigma Aldrich) [27] and poly acrylic acid (PAA, sodium salt, average molecular weight = 8000, Sigma Aldrich) [28]. The counter and working electrode were two platinum foils (40 mm x 20 mm), while the reference electrode was a saturated calomel electrode (SCE). To protect SCE from AgCl precipitation, we used double bridge filled up with a saturated KNO₃ solution, which acted as second electrolyte.

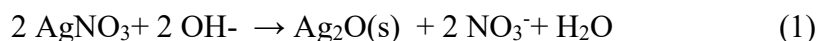
AUTOLAB potentiostat coupled with Nova software determined the reduction potential for each test through cyclic voltammetry (CV). The cyclic staircase started from 0.4 V, reached a lower potential -0.2 V, increased until 1.0 V, and returned to 0.4 V. The reductive current obtained from CVs was almost constant from + 0.3V to - 0.2V, therefore it was decided to synthesize Ag nanoparticles at +0.2 V, to maximize silver production and to avoid, at the same time, to deposit metallic silver on the electrode. We observed that in this condition, after 10 min, silver only deposited on the working electrode. Therefore, we set the duration of each synthesis to 10 min.

We also modified the pH of the solution after the electrochemical synthesis with either HNO₃ or NH₄OH, to study the influence of pH on the Ag nanoparticles structure/morphology and verify its possible influence of the final photocatalytic performance.

2.2 Catalyst synthesis

During the electrochemical synthesis, the colour of the mixture (not solution) gradually shifted from white to yellow and became cloudier, thus indicating the formation of nanoparticles. [3].

We then added NH₄OH to the silver nanoparticles (Ag NPs) solution to a pH of 12 to form NH₃. Ammonia stabilizes the dopant in the solution avoiding the formation of Ag₂O precipitate according to Tollens reaction (1-2):



We then suspended TiO₂ (Kronos 1077) in 6 mL of acetone (HPLC grade, Sigma Aldrich). We added the Ag NPs aqueous solution to the suspension to obtain an AgNPs mass loading of 8 % (value optimized in previous works). The solution was kept under stirring for 24 h, at a

temperature of 40 °C. After, we raised the temperature to 80 °C for 2 h. At the end of the impregnation, we removed water by evaporation, and heated the mixture to 100 °C. A furnace calcined the powder at 400 °C for 2 h under static atmosphere.

Here we compare 7 catalysts (Table 1) prepared with different conditions. Sample 7 was prepared in the same condition of sample 6 but with 5 times the reagents amount and the volumes (500 mL of AgNO₃ solution, 5 g of KNO₃ and 40 cm² of working electrode surface) so to verify a possible modification of the final result after a simple scale-up.

Table 1: Synthesis of the Ag-TiO₂ samples.

Sample	Ag NPs loading (% by weight)	mol PVP / mol Ag ⁺	pH
1	0	-	-
2	8	3:1	12
3	8	50:1	12
4	8	3:1	4
5	8	1:1	4
6	8	1:1	12
7	8	1:1	12

2.3 Characterization

A JEOL 3010-UHR Instrument fitted with a LaB6 filament (acceleration potential 300 kV) and equipped with an Oxford INCA Energy TEM 200 energy dispersive X-ray (EDX) detector (TEM-HRTEM) imaged the samples. Samples were dry dispersed onto Cu grids coated with “lacey” carbon film.

A PANalytical Xpert Multipurpose X-ray Diffractometer measured samples crystallinity. It is equipped with a Cu anode (K α radiation, $\lambda = 1.54060$ nm). The working potential was 45 kV while the working current was 40 mA. We analyzed our samples with a scan rate of 0.05° in a 2 θ range of 20°-80°.

An M-Probe (SSI) XPS instrument was used to analyze the samples surfaces detecting in particular Ti2p, O1s and Au4f regions. The instrument is equipped with a monochromatic Al k_{α} anode and is calibrated using C1s at 284.6 eV.

Specific surface area measurements were carried out by conventional N₂ adsorption/desorption (BET) at 77 K by means of a Sorptometer (Costech Mod. 1042) apparatus.

2.4 NO_x setup

We adopted a 20 L Pyrex glass batch reactor to degrade NO_x. The complete description of the setup is reported elsewhere [29]. We deposited a suspension of (0.050 ±0.001) mg of catalyst in isopropanol (technical grade, Sigma Aldrich) on a glass plate (200 mm x 20 mm). An ultrasonic bath suspended the powder in the alcohol before the deposition. After the evaporation of the solvent, we placed the plate with the catalyst on the top of it inside the reactor. The concentration of the model pollutant was 500 ppb of NO_x (initial bottle concentration 0.625 % of NO₂ and 0.125 % of NO, diluted with air). A LED lamp (MW mean well, 350 mA rated current, 9 V to 48 V DC voltage range, 16:8W rated power) with an emission from 400 nm to 700 nm was the photon source set at a distance to have 1000 lux on the sample surface. We set the relative humidity of the reactor at 50 %. Time 0 corresponded to the switching on of the lamp. An Ecotech Serinus 40NO_x directly connected to the reactor measured the concentration of both NO and NO₂ at 60, 180 and 360 min.

The calibration of the instrument was checked by sending the gas mixture directly from the NO_x cylinder to the instrument. The concentration of NO_x measured confirmed the one declared by the gas supplier. The sampling was realized by opening a valve to let the instrument automatically withdraw a gas aliquot from the reactor. The lower detection limit of the instrument is 0.4 ppb and a precision of 0.5 % [30]. Therefore, we calculated the error on the NO_x conversion using the formula for the error propagation.

3. Results and discussion

3.1 Selection of the capping agent

The electrochemical synthesis of AgNPs failed with PAA and PVA for different reasons. The carboxylic domains of PAA exchanged sodium ion with silver ion in the solution and formed an

insoluble complex that precipitated [31]. PVA did bring to the formation of an AgNPs solution, but that was in turn unstable. For all the concentrations tested, the NPs coagulated and aggregated within 3-4 hours. Literature reports stability for the Ag-PVA complex with increasing dispersant molecular weight and when other rheological additive are present [32]. We filed the synthesis with different concentration of PVA (from 10 to 30 g L⁻¹). We therefore selected PVP for all the synthesis.

3.2 Sample morphology and nanoparticle size distribution

All the samples object of the present research exhibit almost the same value ($\sim 12 \pm 2 \text{ m}^2 \text{ g}^{-1}$) of BET specific surface area, i.e. the value related to the bare TiO₂ (micrometric sample 1) despite the presence of Ag NPS.

TEM confirmed that the average dimensions for sample 1 (i.e., bare Kronos 1077) are around 110 nm. Its particles are well ordered, in most cases they are thin and not too much closed packed together. A detailed inspection at higher magnification (see Supporting Information Fig S1) indicates that all the particles are highly crystalline: the calculated distances (0.352 nm) among the fringes evidence that the most frequently exposed crystal planes belong to the (101) family of anatase [ICDD 21-1272]. This feature is also confirmed by the analysis of the electron diffraction.

The general morphology of the supporting material remains unchanged for Sample 2, despite the procedure followed to add silver species. Sample 2 exhibits the same external habit of the titania crystals reported for sample 1 and the same fringe patterns ascribable to anatase (see Figure 2b).

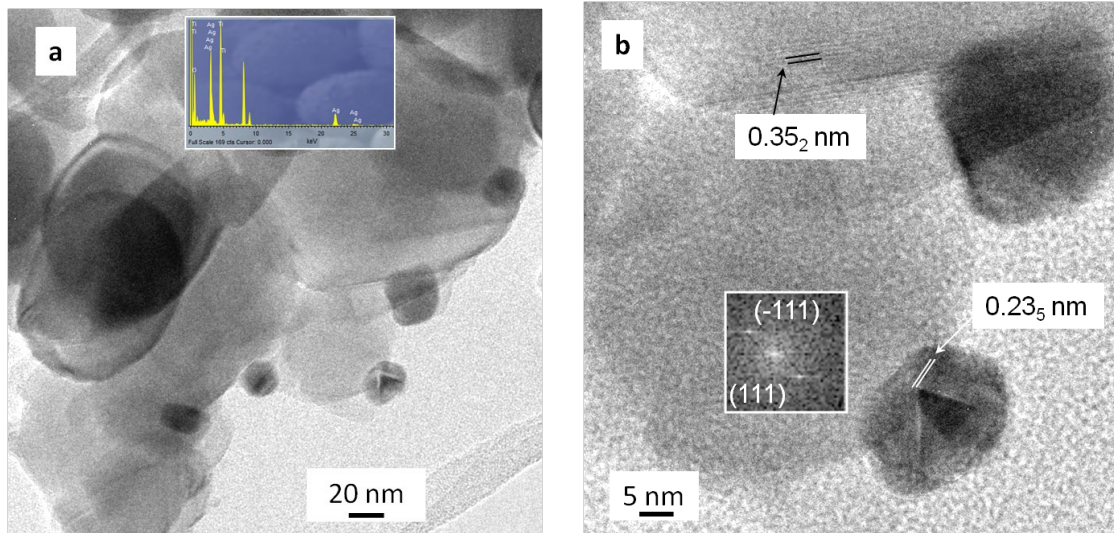


Figure 2. C-TEM (section a) and HR-TEM (section b) images referred to sample 2.

The extra particles present in Figure 2a, characterized by a much lower size and higher contrast as well, are made up of Ag. This is confirmed by different experimental evidences: (i) the EDX analysis, reported in the inset to Figure 2a, indicates the presence of metallic Ag, besides Ti and O; (ii) the inspection of the fringe patterns exhibited by the smaller particles (Figure 2b) puts into evidence that the calculated 0.23 nm distances are ascribable to metallic silver [ICDD 004-0783]. Sample 3 resembles sample 2 (Figure 3). Both samples have been synthesized in similar pH (basic) conditions but with different PVP.

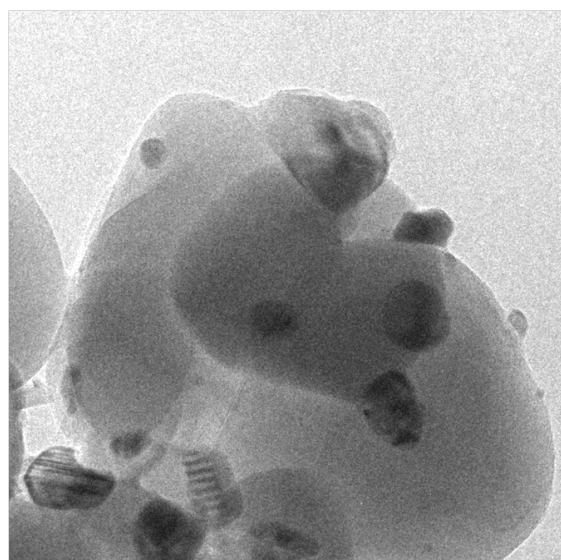


Figure 3. C-TEM image referred to sample 3

Samples 4 and 5 were synthesized in acidic conditions. Their morphology confirms to be unaltered for the titania support, but deeply different for what concerns the Ag NPs appearance (see Figure 4 and 5, respectively). In fact, their size is much smaller, being far beyond a half than in the case of the samples obtained at basic pH.

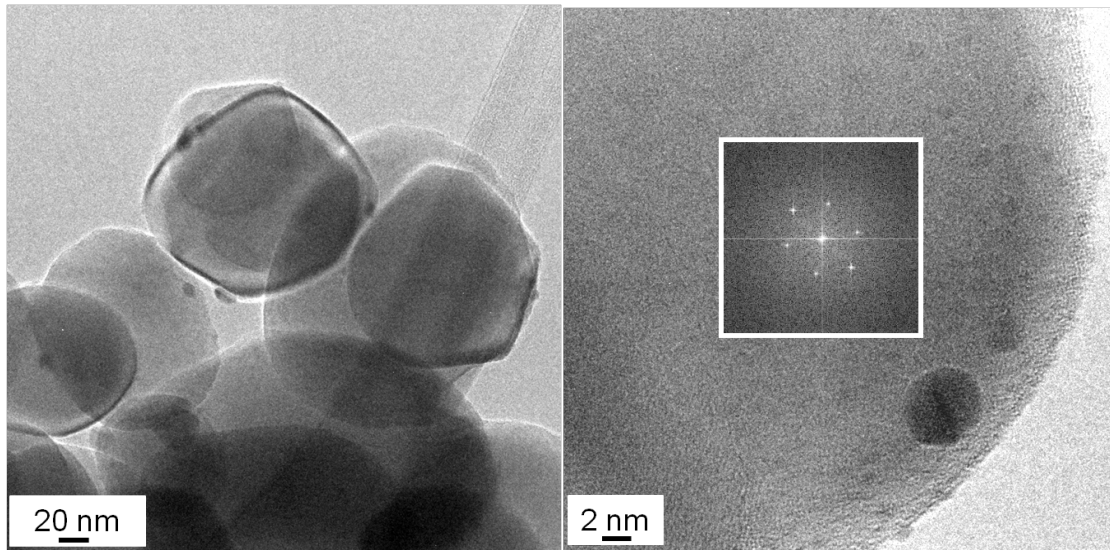


Figure 4. C-TEM (section a) and HR-TEM (section b) images referred to sample 4.

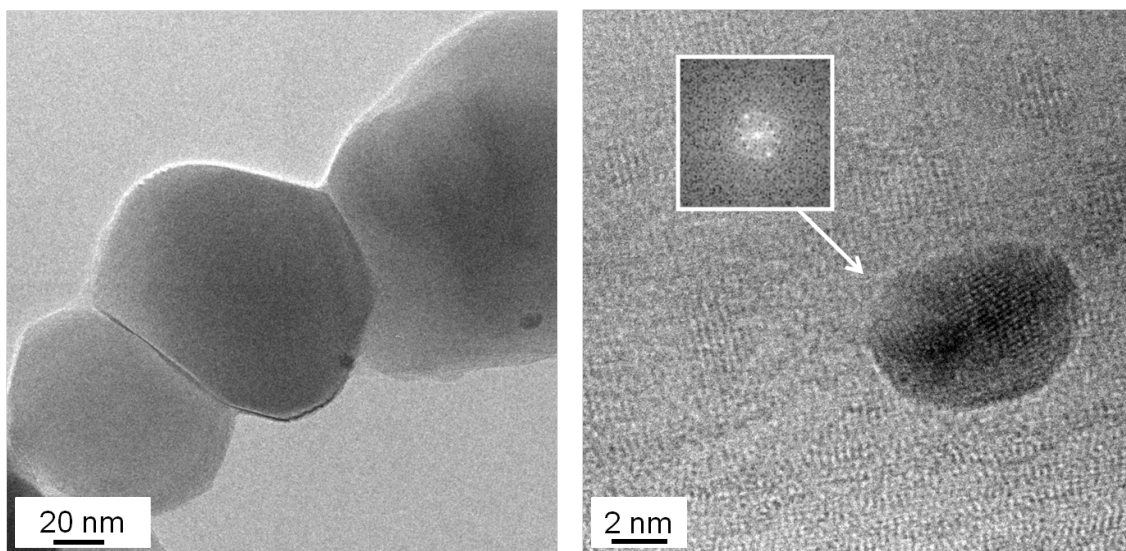


Figure 5. C-TEM (section a) and HR-TEM (section b) images referred to sample 5.

In the case of sample 6 the situation is intermediate between the two above described: see Figure 6. Sample 7 shows the same morphology of sample 6 confirming that the scale-up process does not alter the AgNPs features.

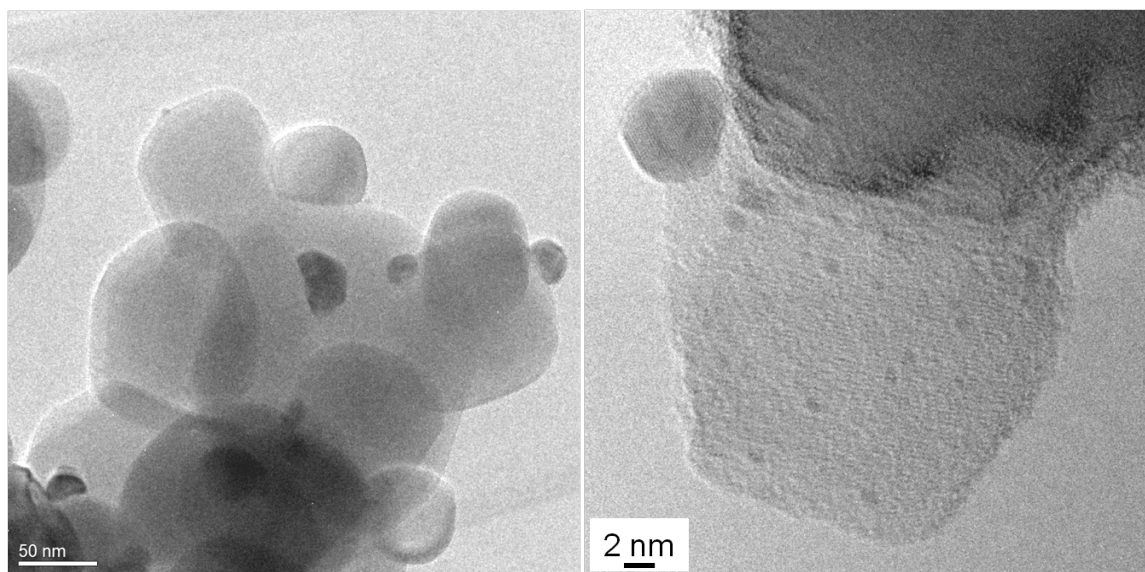


Figure 6. C-TEM (section a) and HR-TEM (section b) images referred to sample 6.

For samples 2, 3 and 6 (and 7) there is a broader spread of Ag NPs dimensions, ranging in the 5-25 nm (with dominating dimensions in the 15-20 nm range, Supporting Information Figure S2) with respect to samples 4 and 5, for which the distribution is much narrower and whose mean size is located in the 1-5 nm range.

The amount of silver in the various preparations (Table 1) was constant (8%_{w/v}), whereas the parameters that have been changed are either the amount of the PVP dispersing agent or the pH of the solutions before the electrochemical synthesis.

In the condition of constant pH (no matter acidic or basic), the effect of a different amount of PVP is almost negligible, as the relevant AgNPs distribution are similar for the two pH values. Our results hold also considering diverse AgNPs preparation methods. Malina et al. [33] reduced AgNO₃ with NaBH₄ varying the concentration of PVP. They did not see a significant change in

AgNPs size below a concentration of 10 % of PVP. Moreover, changing PVP concentration leads to similar NPs distribution during the laser ablation preparation method [34].

On the other hand, the different pH values have a great influence in the Ag NPs distributions. In fact, changing pH from 11.5 to 12.5 leads to bigger nanoparticles when the reducing agent is a sugar [35]. Therefore, pH possesses a leading role in determining the ultimate size(s) of the AgNPs, during the direct electrochemical reduction of AgNO_3 .

The crystallographic phase composition of the various samples has been assessed also based on the X-Ray diffraction investigation: Figure 7 summarizes the relevant results for the 2 to 5 powders.

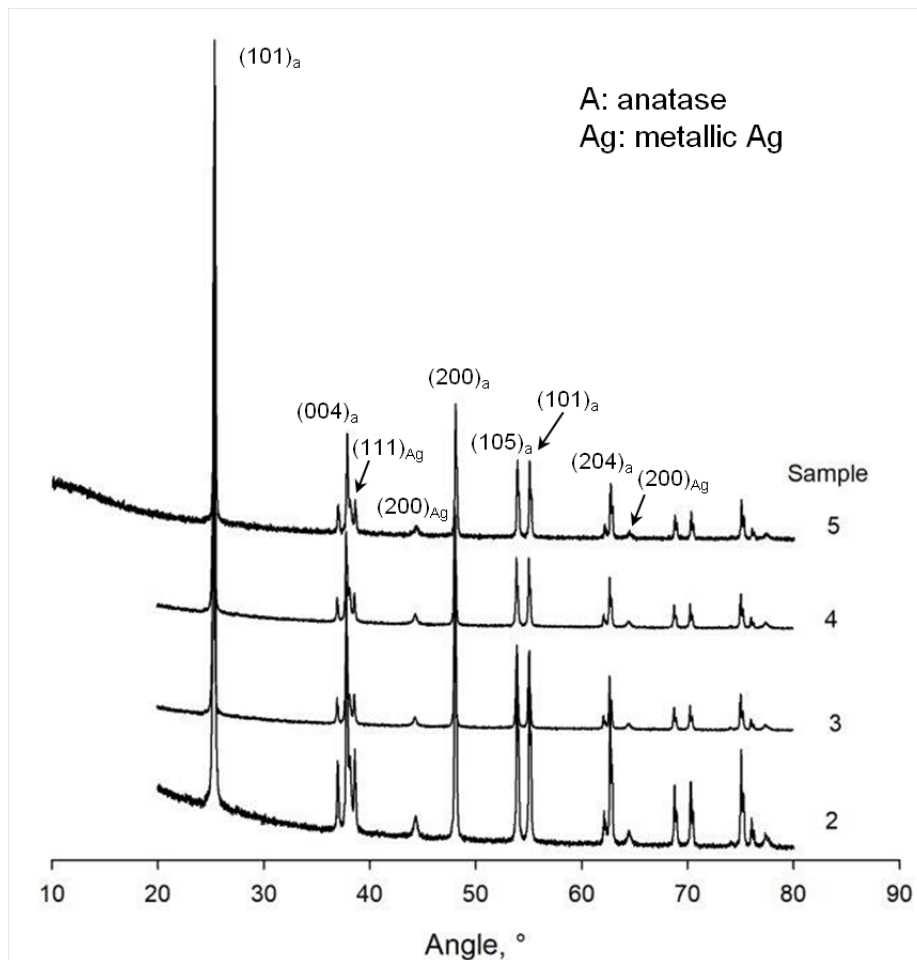


Figure 7: XRD of samples 2-5.

It is well evident that the main features are ascribable to the anatase TiO_2 polymorph, as expected also on the basis of the morphological characterization carried out by means of HR-TEM investigation. In all the diffractograms, the main peak at $2\theta \sim 25^\circ$ can be ascribed to the

most intense (101) peak due to anatase [ICDD card n. 21-1272], as well as many other reflexes: a few differences in intensity for the minor peaks is observable, but this is the only peculiarity that can be evidences in particular for sample 4 and 5, synthesized in acidic conditions. Besides these peaks, a clear indication of the presence of metallic Ag comes from the three reflexes located at $2\theta \sim 38^\circ$, 44° and 65° , respectively ascribable to (111), (200) and (200) crystal planes [on the basis of metallic Ag ICDD card n. 4-0783]. No extra peaks are observable that can indicate the presence of oxidated Ag species: this fact may be due to the very low amount of these species (if present most likely due to passivation effects), lying then under the detection power of the XRD technique. For this reason, we resorted the XPS analysis in order to shed some light onto this feature.

High resolution XPS for O 1s region (sample 6) is the sum of three contributions: a main peak centred at 530 eV, representing the lattice oxygen of TiO_2 , a less intense shoulder peak with binding energy at 531 eV, corresponding to the lattice oxygen of Ag_xO , and a third shoulder peak at 532 eV, related to OH species [36] (Figure 8 right).

Ti 2p spectrum (Supporting Information, Figure S3) only highlights the presence of a single doublet typical of Ti^{4+} in TiO_2 .

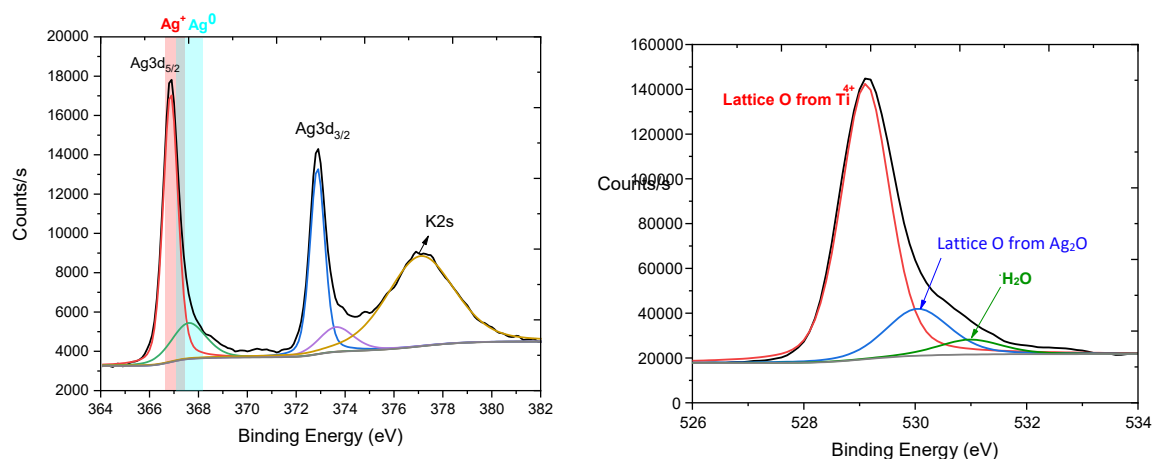


Figure 8: XPS High-resolution spectrum of O1s (right) and Ag3d (left) for sample 6

The ratio between the areas of the peaks located at 529 and 532 eV, respectively, gives useful information about the hydroxyl species (OH) located at the surface of the photocatalyst. In

particular, if we compare the $\text{OH}/\text{O}_{\text{tot}}$ ratio calculated for samples 6 and 1 (bare TiO_2), we obtain 0.06 and 0.32 [36], respectively: on the basis of this evidence, we can preliminary conclude sample 6 activity is related to the creation of oxyradicals in situ, favoured because of controlled humidity (50 %) (see the NO_x degradation section).

The $\text{Ag}3d$ XPS spectrum of sample 6 (Figure 8 left) fits into two separated peaks, one referring to Ag^0 and the other one to its higher valence state $\text{Ag}^+/\text{Ag}_x\text{O}$ [31]. The presence of higher valence state Ag confirms the deduction made discussing the $\text{O}1s$ XPS spectrum, due to the presence of a fitted peak at ~ 531 eV. Due to the calcination in air during the final preparation step, a mix of metal and oxidized Ag nanoparticles are present on the surface of the TiO_2 micro-particles. This morphological feature has not been evidenced by the HR-TEM inspection, as the fraction of oxidized AgNPs is most likely so low that lies under the detection power of this experimental technique.

3.3 NO_x degradation

Bare 1077 micro TiO_2 (sample 1) is ineffective towards NO_x degradation under visible light. Our result is comparable to literature and confirms that this material is only active under UV light [29].

Sample 2 exhibits exceptional activity. It converts 90 % of NO_x after 1 h of irradiation. Sample 3, 5 and 6 have similar kinetics, while sample 4 is the least active among the series (Figure 9 a). Sample 7 shows the same result of sample 6 even if it was prepared with 5 times the volumes of reactant. Therefore, the properties of this catalyst is unaffected by the volume of the synthesis.

All the catalysts tend to deactivate after 6 h due to the formation of nitrate species (NO_3^-), which we already detected in previous works employing photocatalytic tiles [29,37].

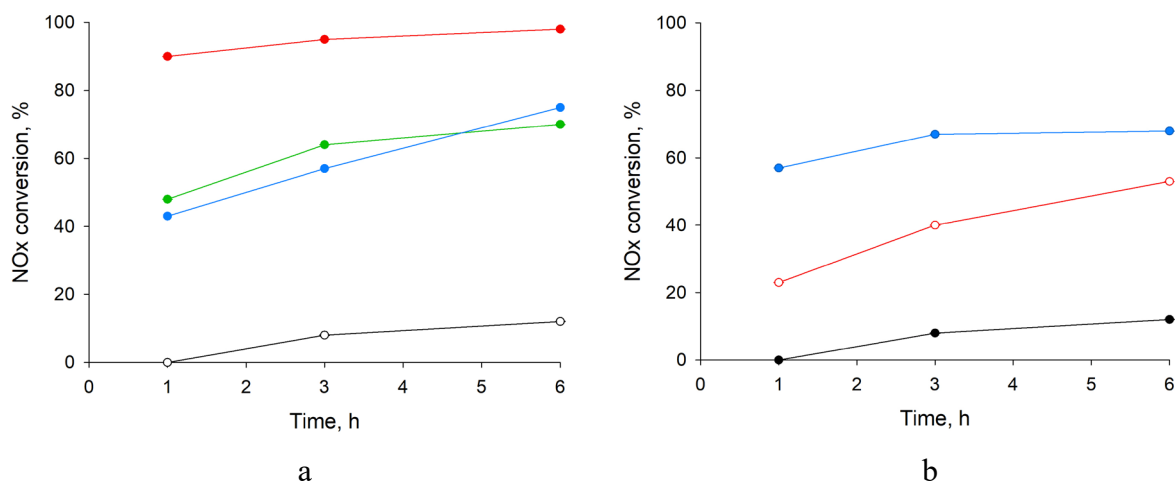


Figure 9 : NOx conversion versus time for catalysts prepared at basic (a) and acid (b) pH. Black line is Kronos 1077 while blue, red and green lines represent a PVP/Ag molar ratio of 1, 3 and 50, respectively.

Ag NPs, as well as gold NPs, degrade VOC through different mechanisms [38]. Here, we adopted LED light, whose energy is insufficient to directly promote electrons to the valence band of TiO₂. Localized surface plasmon resonance (LSPR) absorption in Ag NPs is the main effect that makes the samples active. Sarina et al. correlated the conversion of a photocatalytic reaction (ethylene oxidation) to the plasmon intensity [38]. In another work, Amendola et al. calculated the LSPR of different AgNPs, varying their shapes and assemblies [39]. A single spherical AgNP (radius = 10 nm) absorbs light whose wavelength is between 350 and 450 nm. However, when nanoparticles cluster, the absorption is broader and covers a wavelength range of 350 – 500, a range that falls in the emission of the LED lamp employed in our study.

The same authors also demonstrated that AgNPs smaller than 5 nm, like the ones we obtained in the synthesis with pH = 4, broaden the absorption band, which correlates with their lower performances compared to catalyst prepared at basic pH.

Optimal PVP/Ag⁺ molar ratio at pH = 4 resulted to be 1, while at pH = 12 it becomes 3 (Figure 10). This might be connected to the particle dimensions. At acid pH, smaller particles form (1-5

nm), therefore less PVP is needed to stabilize them, even though their number is higher, and as a matter of fact, an AgNP size smaller than 5 nm leads to lower NO_x conversions.

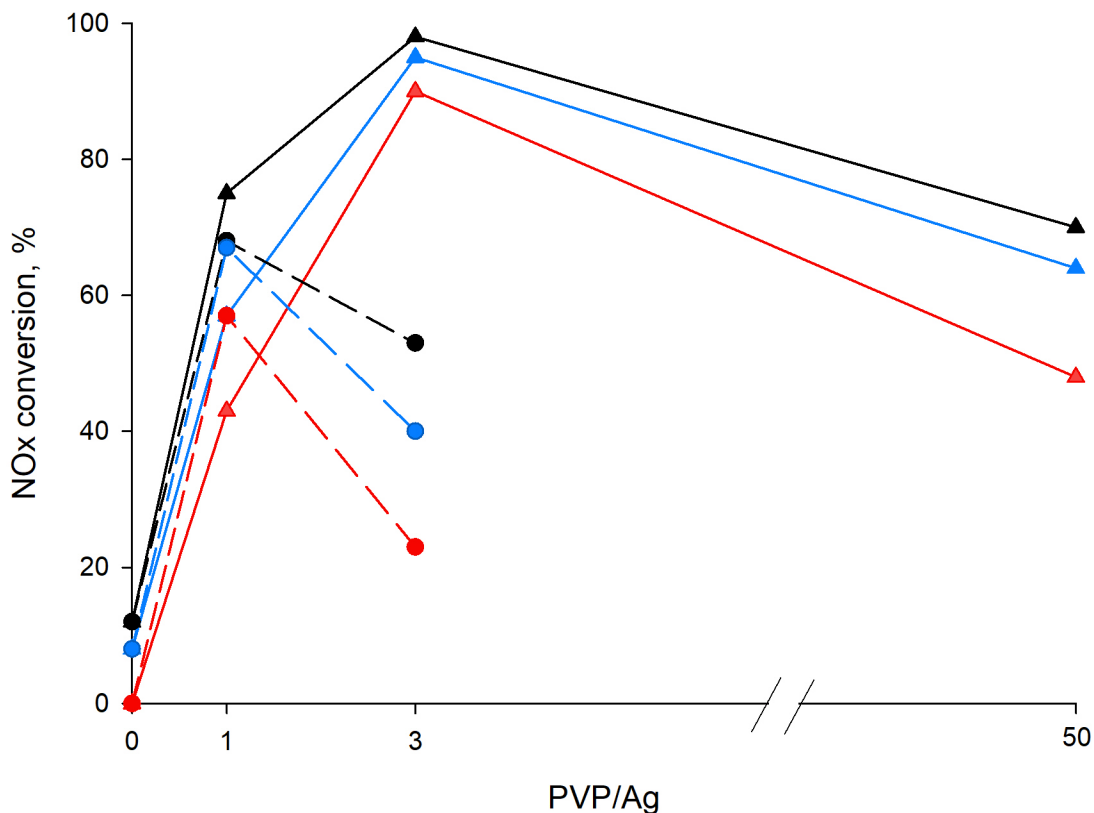


Figure 10: PVP/Ag molar ratio versus NO_x conversion for acid pH (dotted lines and points) and basic pH (full line and triangles). Red, blue and black lines represent conversion at time 1 h, 3 h, and 6 h, respectively.

4. Conclusion

In the present contribution we synthesized AgNPs reducing silver nitrate in solution by an electrochemical method. The pH of the solution tailors the dimension of the nanoparticles. At pH = 4 we obtained a NPs distribution 1-5 nm, whereas at pH = 12 this figure becomes 5-25 nm. pH and polyvinyl pyrrolidone has no influence on the crystallinity of samples and the calcination procedure we propose (400 °C for 2 h in air) yield stable nanoparticles.

As for the titania photocatalyst support, we decided to employ a micrometric commercial system (1077 by Kronos) rather than a nanometric powder, in order to avoid all the possible drawbacks typical of the interaction of NPs with human tissues by either inhalation or skin contact. The photocatalysts we obtained retain all the positive properties due to the micrometric support, such as SSA, crystallographic phase composition, being thus positively influenced in their photocatalytic performances by the promotion by AgNPs, even though a different photodegradation behaviour, as a function of the different AgNPs preparation route, has been put into evidence.

In particular, photocatalytic degradation of NO_x under LED light evidenced that the samples prepared at basic conditions exhibit better performances rather than those prepared at acid conditions: AgNPs with diameters of 1-5 nm are less active under LED light because of the broadening of the surface plasmon band. Moreover, the synthesis was scaled up to 500 mL volume, without affecting the final catalysts performances.

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References

- [1] G. Mamba, J. Kiwi, C. Pulgarin, R. Sanjines, S. Giannakis, S. Rtimi, Evidence for the degradation of an emerging pollutant by a mechanism involving iso-energetic charge transfer under visible light, *Appl. Catal. B Environ.* 233 (2018) 175–183. doi:10.1016/j.apcatb.2018.03.109.
- [2] C. Pirola, D.C. Boffito, S. Vitali, C.L. Bianchi, Photocatalytic coatings for building industry: study of 1 year of activity in the NO_x degradation, *J. Coatings Technol. Res.* 9 (2012) 453–458. doi:10.1007/s11998-011-9381-7.
- [3] M. Hosseini-Sarvari, F. Jafari, A. Mohajeri, N. Hassani, Cu₂O/TiO₂ nanoparticles as visible light photocatalysts concerning C(sp²)-P bond formation, *Catal. Sci. Technol.* 8

- (2018) 4044–4051. doi:10.1039/C8CY00822A.
- [4] Z. Wei, M. Janczarek, M. Endo, K. Wang, A. Balčytis, A. Nitta, M.G. Méndez-Medrano, C. Colbeau-Justin, S. Juodkazis, B. Ohtani, E. Kowalska, Noble metal-modified faceted anatase titania photocatalysts: Octahedron versus decahedron, *Appl. Catal. B Environ.* 237 (2018) 574–587. doi:10.1016/j.apcatb.2018.06.027.
- [5] Z. Song, B. Hong, X. Zhu, F. Zhang, S. Li, J. Ding, X. Jiang, J. Bao, C. Gao, S. Sun, CdS/Au/Ti/Pb(Mg $_{1/3}$ Nb $_{2/3}$) $_{0.7}$ Ti $_{0.3}$ O $_3$ photocatalysts and biphotocatalysts with ferroelectric polarization in single domain for efficient water splitting, *Appl. Catal. B Environ.* 238 (2018) 248–254. doi:https://doi.org/10.1016/j.apcatb.2018.07.033.
- [6] N. Saadatkhan, M.G. Rigamonti, D.C. Boffito, H. Li, G.S. Patience, Spray dried SiO $_2$ /WO $_3$ /TiO $_2$ and SiO $_2$ vanadium pyrophosphate core-shell catalysts, *Powder Technol.* 316 (2017) 434–440. doi:10.1016/j.powtec.2016.10.056.
- [7] H. Khan, M.G. Rigamonti, G.S. Patience, D.C. Boffito, Spray dried TiO $_2$ /WO $_3$ heterostructure for photocatalytic applications with residual activity in the dark, *Appl. Catal. B Environ.* 226 (2018) 311–323. doi:10.1016/j.apcatb.2017.12.049.
- [8] Z. Wang, X. Lang, Visible light photocatalysis of dye-sensitized TiO $_2$: The selective aerobic oxidation of amines to imines, *Appl. Catal. B Environ.* 224 (2018) 404–409. doi:10.1016/j.apcatb.2017.10.002.
- [9] X. Li, J.-L. Shi, H. Hao, X. Lang, Visible light-induced selective oxidation of alcohols with air by dye-sensitized TiO $_2$ photocatalysis, *Appl. Catal. B Environ.* 232 (2018) 260–267. doi:10.1016/j.apcatb.2018.03.043.
- [10] A. Utsunomiya, A. Okemoto, Y. Nishino, K. Kitagawa, H. Kobayashi, K. Taniya, Y. Ichihashi, S. Nishiyama, Mechanistic study of reaction mechanism on ammonia photodecomposition over Ni/TiO $_2$ photocatalysts, *Appl. Catal. B Environ.* 206 (2017) 378–383. doi:10.1016/j.apcatb.2017.01.045.
- [11] I. Milošević, S. Rtimi, A. Jayaprakash, B. van Driel, B. Greenwood, A. Aimable, M. Senna, P. Bowen, Synthesis and characterization of fluorinated anatase nanoparticles and subsequent N-doping for efficient visible light activated photocatalysis, *Colloids Surfaces*

- B *Biointerfaces*. 171 (2018) 445–450. doi:10.1016/j.colsurfb.2018.07.035.
- [12] S. Rtimi, D.D. Dionysiou, S.C. Pillai, J. Kiwi, Advances in catalytic/photocatalytic bacterial inactivation by nano Ag and Cu coated surfaces and medical devices, *Appl. Catal. B Environ.* 240 (2019) 291–318. doi:10.1016/j.apcatb.2018.07.025.
- [13] A. Moores, F. Goettmann, The plasmon band in noble metal nanoparticles: an introduction to theory and applications, *New J. Chem.* 30 (2006) 1121. doi:10.1039/b604038c.
- [14] Q. Lang, Y. Chen, T. Huang, L. Yang, S. Zhong, L. Wu, J. Chen, S. Bai, Graphene “bridge” in transferring hot electrons from plasmonic Ag nanocubes to TiO₂ nanosheets for enhanced visible light photocatalytic hydrogen evolution, *Appl. Catal. B Environ.* 220 (2018) 182–190. doi:10.1016/j.apcatb.2017.08.045.
- [15] R. Asapu, N. Claes, S. Bals, S. Denys, C. Detavernier, S. Lenaerts, S.W. Verbruggen, Silver-polymer core-shell nanoparticles for ultrastable plasmon-enhanced photocatalysis, *Appl. Catal. B Environ.* 200 (2017) 31–38. doi:10.1016/j.apcatb.2016.06.062.
- [16] A. Jbeli, Z. Hamden, S. Bouattour, A.M. Ferraria, D.S. Conceição, L.F.V. Ferreira, M.M. Chehimi, A.M.B. do Rego, M. Rei Vilar, S. Boufi, Chitosan-Ag-TiO₂ films: An effective photocatalyst under visible light, *Carbohydr. Polym.* 199 (2018) 31–40. doi:10.1016/j.carbpol.2018.06.122.
- [17] M. Stucchi, C.L. Bianchi, C. Argiris, V. Pifferi, B. Neppolian, G. Cerrato, D.C. Boffito, Ultrasound assisted synthesis of Ag-decorated TiO₂ active in visible light, *Ultrason. Sonochem.* 40 (2018) 282–288. doi:10.1016/j.ultsonch.2017.07.016.
- [18] Q. Zeng, X. Xie, X. Wang, Y. Wang, G. Lu, D.Y.H. Pui, J. Sun, Enhanced photocatalytic performance of Ag@TiO₂ for the gaseous acetaldehyde photodegradation under fluorescent lamp, *Chem. Eng. J.* 341 (2018) 83–92. doi:10.1016/j.cej.2018.02.015.
- [19] M. Starowicz, B. Stypuła, J. Banaś, Electrochemical synthesis of silver nanoparticles, *Electrochem. Commun.* 8 (2006) 227–230. doi:10.1016/j.elecom.2005.11.018.
- [20] K. Ozawa, M. Emori, S. Yamamoto, R. Yukawa, S. Yamamoto, R. Hobara, K. Fujikawa, H. Sakama, I. Matsuda, Electron–Hole Recombination Time at TiO₂ Single-Crystal Surfaces: Influence of Surface Band Bending, *J. Phys. Chem. Lett.* 5 (2014) 1953–1957.

doi:10.1021/jz500770c.

- [21] F. Hong, L. Wang, Nanosized titanium dioxide-induced premature ovarian failure is associated with abnormalities in serum parameters in female mice, *Int. J. Nanomedicine*. Volume 13 (2018) 2543–2549. doi:10.2147/IJN.S151215.
- [22] P. Sá-Pereira, M.S. Diniz, L. Moita, T. Pinheiro, E. Mendonça, S.M. Paixão, A. Picado, Protein profiling as early detection biomarkers for TiO₂ nanoparticle toxicity in *Daphnia magna*, *Ecotoxicology*. 27 (2018) 430–439. doi:10.1007/s10646-018-1907-7.
- [23] M. Stucchi, D. Boffito, E. Pargoletti, G. Cerrato, C. Bianchi, G. Cappelletti, Nano-MnO₂ Decoration of TiO₂ Microparticles to Promote Gaseous Ethanol Visible Photoremoval, *Nanomaterials*. 8 (2018) 686. doi:10.3390/nano8090686.
- [24] G. Cerrato, C.L. Bianchi, F. Galli, C. Pirola, S. Morandi, V. Capucci, Micro-TiO₂ coated glass surfaces safely abate drugs in surface water, *J. Hazard. Mater.* 363 (2019) 328–334. doi:10.1016/j.jhazmat.2018.09.057.
- [25] M. Stucchi, C.L. Bianchi, C. Pirola, S. Vitali, G. Cerrato, S. Morandi, C. Argiris, G. Sourkouni, P.M. Sakkas, V. Capucci, Surface decoration of commercial micro-sized TiO₂ by means of high energy ultrasound: A way to enhance its photocatalytic activity under visible light, *Appl. Catal. B Environ.* 178 (2015) 124–132. doi:10.1016/j.apcatb.2014.10.004.
- [26] B. Yin, H. Ma, S. Wang, S. Chen, Electrochemical Synthesis of Silver Nanoparticles under Protection of Poly(N-vinylpyrrolidone), *J. Phys. Chem. B*. 107 (2003) 8898–8904. doi:10.1021/jp0349031.
- [27] R. Surudzic, Z. Jovanovic, N. Bibic, B. Nikolic, V. Miskovic-Stankovic, Electrochemical synthesis of silver nanoparticles in poly(vinyl alcohol) solution, *J. Serbian Chem. Soc.* 78 (2013) 2087–2098. doi:10.2298/JSC131017124S.
- [28] S. Magdassi, M. Grouchko, O. Berezin, A. Kamyshny, Triggering the Sintering of Silver Nanoparticles at Room Temperature, *ACS Nano*. 4 (2010) 1943–1948. doi:10.1021/nn901868t.
- [29] C.L. Bianchi, C. Pirola, F. Galli, G. Cerrato, S. Morandi, V. Capucci, Pigmentary TiO₂: A

- challenge for its use as photocatalyst in NO_x air purification, *Chem. Eng. J.* 261 (2015) 76–82. doi:10.1016/j.cej.2014.03.078.
- [30] Ecotech, Serinus 40 brochure, (2018) 2. <https://www.ecotech.com/wp-content/uploads/2015/03/ECOTECH-Serinus-40-NOx-Gas-Analyser-spec-sheet-20181202.pdf> (accessed January 21, 2019).
- [31] J.A. Dean, *Lange's Handbook Of Chemistry*, 15th ed., 1999.
- [32] K.A. Juby, C. Dwivedi, M. Kumar, S. Kota, H.S. Misra, P.N. Bajaj, Silver nanoparticle-loaded PVA/gum acacia hydrogel: Synthesis, characterization and antibacterial study, *Carbohydr. Polym.* 89 (2012) 906–913. doi:10.1016/j.carbpol.2012.04.033.
- [33] D. Malina, A. Sobczak-Kupiec, Z. Wzorek, Z. Kowalski, Silver nanoparticles synthesis with different concentrations of Polyvinylpyrrolidone, *Dig. J. Nanomater. Biostructures.* 7 (2012) 1527–1534.
- [34] T. Tsuji, D.-H. Thang, Y. Okazaki, M. Nakanishi, Y. Tsuboi, M. Tsuji, Preparation of silver nanoparticles by laser ablation in polyvinylpyrrolidone solutions, *Appl. Surf. Sci.* 254 (2008) 5224–5230. doi:10.1016/j.apsusc.2008.02.048.
- [35] A. Panáček, L. Kvítek, R. Prucek, M. Kolář, R. Večeřová, N. Pizúrová, V.K. Sharma, T. Nevěčná, R. Zbořil, Silver Colloid Nanoparticles: Synthesis, Characterization, and Their Antibacterial Activity, *J. Phys. Chem. B.* 110 (2006) 16248–16253. doi:10.1021/jp063826h.
- [36] H. Ren, P. Koshy, F. Cao, C.C. Sorrell, Multivalence Charge Transfer in Doped and Codoped Photocatalytic TiO₂, *Inorg. Chem.* 55 (2016) 8071–8081. doi:10.1021/acs.inorgchem.6b01200.
- [37] C.L. Bianchi, C. Pirola, F. Galli, S. Vitali, A. Minguzzi, M. Stucchi, F. Manenti, V. Capucci, NO_x degradation in a continuous large-scale reactor using full-size industrial photocatalytic tiles, *Catal. Sci. Technol.* 6 (2016) 2261–2267. doi:10.1039/C5CY01627D.
- [38] S. Sarina, E.R. Waclawik, H. Zhu, Photocatalysis on supported gold and silver nanoparticles under ultraviolet and visible light irradiation, *Green Chem.* 15 (2013) 1814. doi:10.1039/c3gc40450a.

- [39] V. Amendola, O.M. Bakr, F. Stellacci, A Study of the Surface Plasmon Resonance of Silver Nanoparticles by the Discrete Dipole Approximation Method: Effect of Shape, Size, Structure, and Assembly, *Plasmonics*. 5 (2010) 85–97. doi:10.1007/s11468-009-9120-4.

Supporting Information

Correlation preparation parameters/activity for microTiO₂ decorated with SilverNPs

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Figure S1: TEM images of Kronos 1077

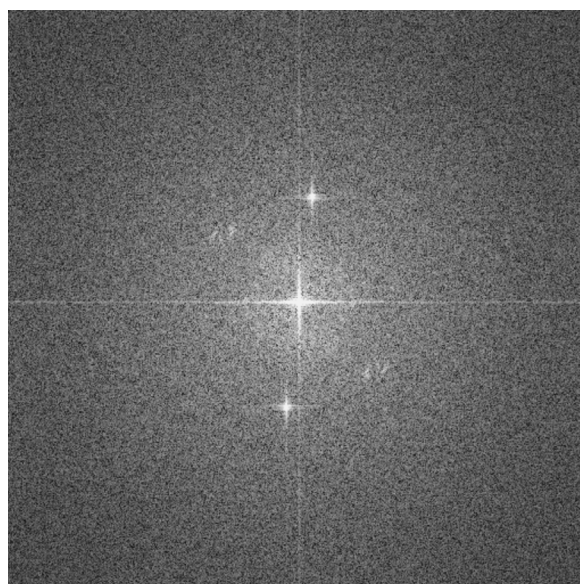
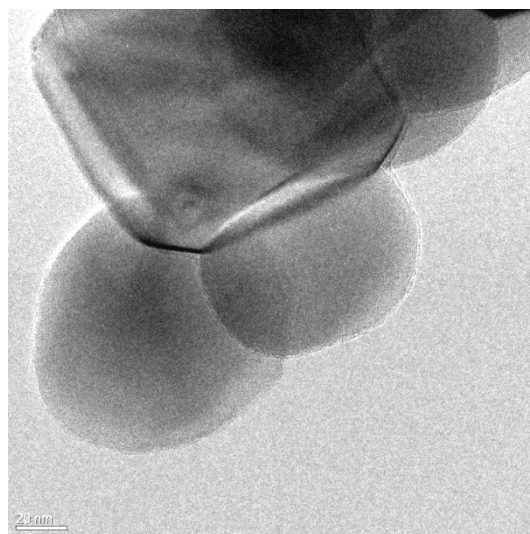
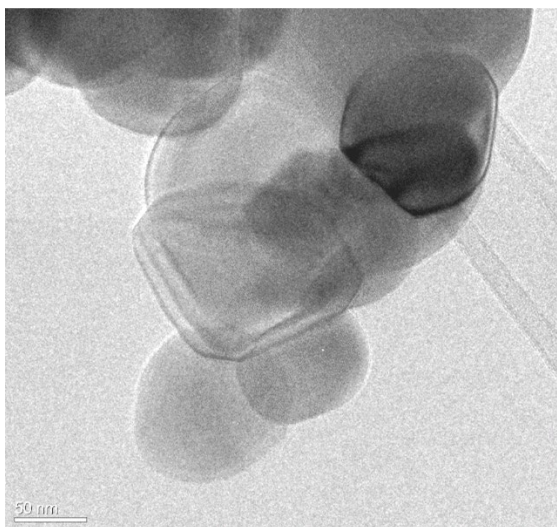


Figure S2: Ag particle size distribution based on HR-TEM images for samples 2-6.

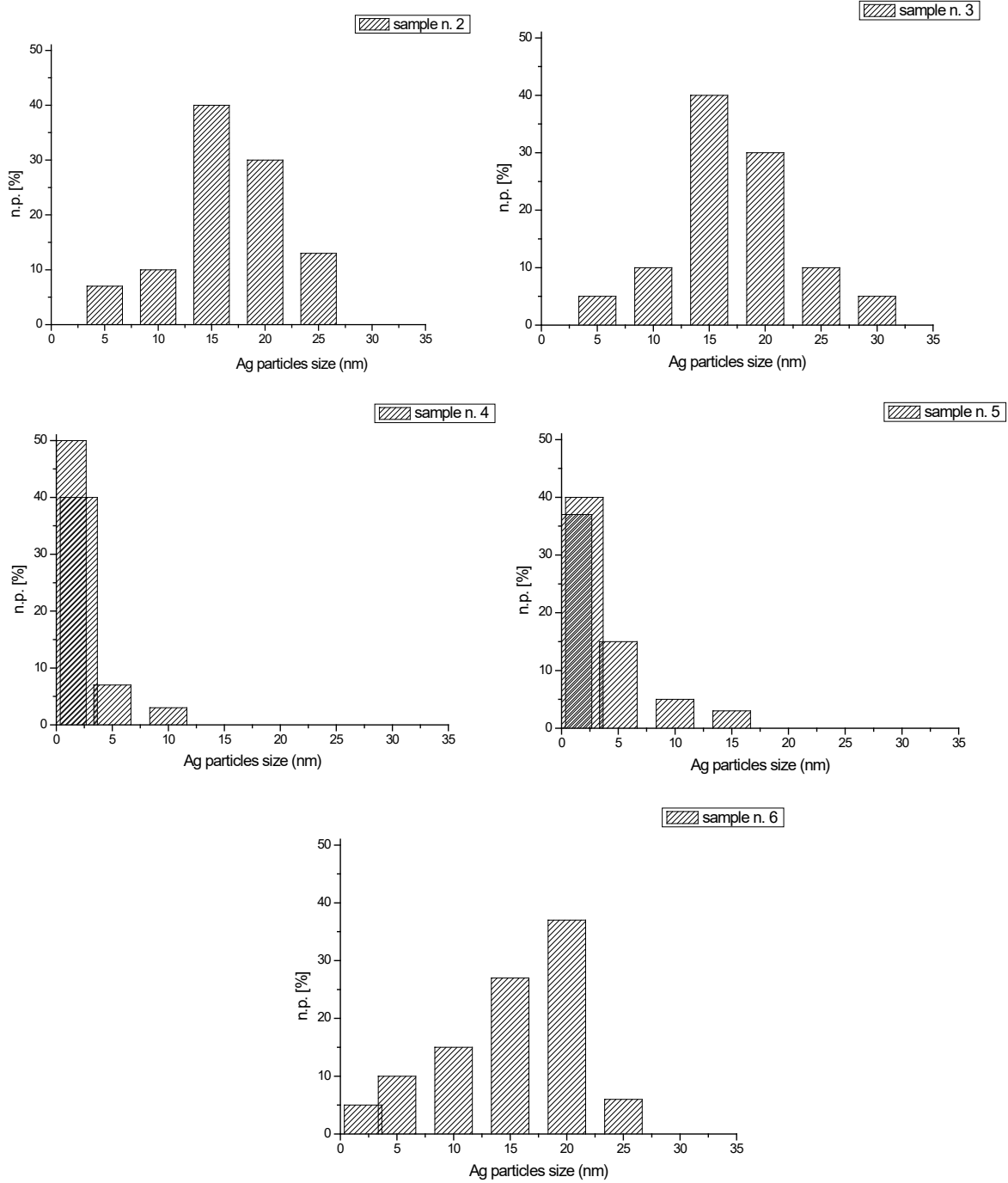


Figure S3: XPS High-resolution spectrum of Ti2p for sample 6

Ti2p3

Figure S4: scheme of the reactor setup. 1: NOx cylinder, 2: air cylinder, 3: glass reactor, 4: LED lamp and 5: NOx analyzer

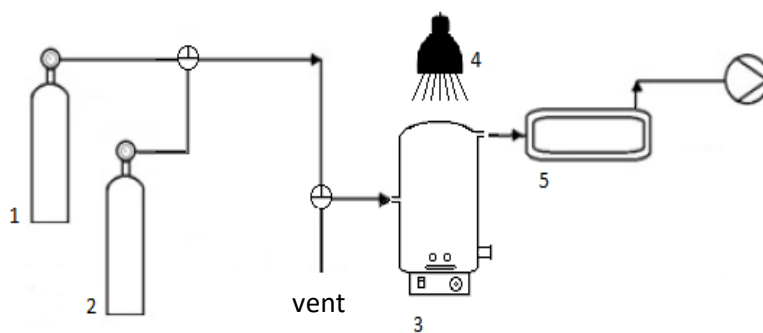


Figure S5: UV-Vis spectra

Numbering of samples name in the spectra:

n.2 sample 2

n.3 sample 3

n.10 sample 4

n.11 sample 5

n.12 sample 6

n.13 sample 7

