Effective Inclusion of Sizable Amounts of Mo within TiO2 Nanoparticles Can Be Obtained by Reverse Micelle Sol-Gel Synthesis

Original
Effective Inclusion of Sizable Amounts of Mo within TiO2 Nanoparticles Can Be Obtained by Reverse Micelle Sol-Gel Synthesis / Esposito, Serena; Ditaranto, Nicoletta; Dell'Agli, Gianfranco; Nasi, Roberto; Rivolo, Paola; Bonelli, Barbara. - In: ACS OMEGA. - ISSN 2470-1343. - ELETTRONICO. - 6:8(2021), pp. 5379-5388.

Availability:
This version is available at: 11583/2874396 since: 2021-03-15T11:34:25Z

Publisher:
acs

Published
DOI:10.1021/acsomega.0c05552

Terms of use:
openAccess
This article is made available under terms and conditions as specified in the corresponding bibliographic description in the repository

(Article begins on next page)
Effective Inclusion of Sizable Amounts of Mo within TiO₂ Nanoparticles Can Be Obtained by Reverse Micelle Sol–Gel Synthesis

Serena Esposito, Nicoletta Ditaranto, Gianfranco Dell’Aglì, Roberto Nasi, Paola Rivolo, and Barbara Bonelli*

ABSTRACT: Six Mo/TiO₂ samples (with 0, 1.0, 2.5, 5.0, 7.5, and 10 wt % Mo nominal contents) were obtained by reverse micelle sol–gel synthesis, followed by calcination at 500 °C. The samples were characterized by means of powder X-ray Diffraction (PXRD), quantitative phase analysis as obtained by Rietveld refinement, field-emission scanning electron microscopy (FE-SEM) coupled with energy-dispersive X-ray analysis, N₂ adsorption/desorption at −196 °C, X-ray photoelectron spectroscopy, and diffuse reflectance (DR) UV–vis spectroscopy. As a whole, the adopted characterization techniques showed the inclusion of a sizeable Mo amount, without the segregation of any MoOₓ phase. Specifically, PXRD showed the occurrence of anatase and brookite with all the studied samples; notwithstanding the mild calcination temperature, the formation of rutile occurred at Mo wt % ≥ 2.5 likely due to the presence of brookite favoring, in turn, anatase to rutile transition. DR UV–vis and XP spectroscopies allowed determining the samples’ band gap energy (E𝑔) and valence band energy, respectively, from which the conduction band energy was calculated; and the observed E𝑔 value increase at 10 wt % Mo was ascribed to the Moss–Burstein effect.

INTRODUCTION

TiO₂ is one of the most studied oxides due to its unique physicochemical properties, including the low toxicity and its availability in several morphologies, polymorphic composition, and nanoparticle (NP) size. Such reasons, along with its chemical stability and light absorption properties, allow its use in various fields, namely pigments, food additives, PPCPs (pharmaceuticals and personal care products), DSSC (dye-sensitized solar cells), and heterogeneous catalysis, particularly photocatalysis.¹⁻⁵

Improving the ability to exploit solar light is particularly useful for photocatalytic applications because TiO₂ mostly absorbs in the UV range,⁶ and doping with heteroatoms (either metals or nonmetals) is a widely adopted strategy to shift the absorption edge toward the vis range.⁷⁻¹⁴ Doping may occur by different means leading to different results, and sometimes disappointing, i.e., when high dopant levels induce the formation of defects that, in turn, favor the electron/hole recombination, ultimately lowering the photocatalytic activity.¹⁵⁻¹⁷

Many literature methods that allow doping TiO₂, while simultaneously controlling the NP shape/size and type of polymorphic phase, imply the use of the sol–gel technique and the presence of a (soft or hard) template in order to induce (either intra- or interparticle) mesoporosity because the occurrence of mesopores is a desirable property, especially for catalytic and photocatalytic applications requiring a facile diffusion of reagents/products.¹⁸⁻²³

Other doping methods provided fair results as well, including spray pyrolysis and magnetron sputtering,²⁴,²⁵ laser ablation in solution,²⁶ hydrothermal synthesis,²⁷ etc. However, the availability of both diblock and triblock copolymers (acting as nonionic surfactants) and the EISA²⁸ (evaporation-induced self-assembly) technique (allowing the obtainment of uniform thin films) contributed to the widespread of template-assisted sol–gel techniques.²⁹ The use of a diblock copolymer in an organic solvent allows, indeed, the formation of reverse micelles having a hydrophobic shell and a hydrophilic core that acts as a nanoreactor, where NP nucleation and growth occur also in the presence of heteroatoms (here, Mo),
facilitating their effective inclusion in large(r) amounts and the size of NPs being determined by the micelle itself.30,31 It has been previously reported that reverse micelles provide an acidic environment, leading to the occurrence of brookite-containing Mo-doped NP TiO2;32 the occurrence of brookite was found to play a role in the stabilization of electron/hole pairs during the photodegradation of rhodamine B under simulated solar light. Furthermore, the positive photocatalytic effect of brookite was also demonstrated with a set of (undoped) TiO2 NPs toward the solar photodegradation of the emerging pollutant N-phenylurea.18

Concerning the doping mechanism(s), DFT (density functional theory) calculations have shown32 that Mo 4d orbitals form impurity levels below the conduction band (CB) of TiO2, whereas the Fermi level should not shift, finally improving the absorption of vis light in the resulting material. As mentioned before, the type of doping sites, i.e., substitu- tional versus interstitial ones, is crucial33,34 because the former has a prevailing role on the resulting TiO2 electronic structure, red shift, and light absorption abilities. Both Mo_6+ and Mo_5+ species have an ionic radius (0.59 and 0.61 Å, respectively) allowing the isomorphic substitution of Ti_4+ ions (0.605 Å).35 In order to balance the charge, the formation of Mo_5+ species usually occurs (although a Mo_6+ precursor is used), otherwise, oxygen vacancies and/or Ti_3+ species form.

In this work, a set of six samples with nominal Mo contents in the 0−10 wt % range was considered in order to provide an insight into the doping mechanism (interstitial vs substitu- tional); and the type of TiO2 polymorphs and how, in turn, such polymorphs may affect the Mo inclusion or vice versa. Indeed, according to the literature, the rutile structure may accommodate heteroatoms/defects more easily than anatase, while the ATR (anatase to rutile) transition may be favored by brookite, whereas high valence dopant cations (charge >+4) disfavor ATR.36

The aim of this work is to effectively introduce, by reverse micelle sol−gel technique, sizable amounts of Mo in TiO2 NPs in order to redshift their absorption onset and to lower the band gap energy. Furthermore, several complementary characterization techniques have been adopted in order to gain an insight into the type of Mo doping, the nature of Mo species and, consequently, the structural and surface properties of the obtained materials.

**RESULTS AND DISCUSSION**

**Textural Properties of the Samples.** Figure 1a shows the powder XRD patterns of the samples in the 20−90 2θ range. The TiO2 sample showed the peaks of anatase (labeled A) at the 2θ values of 25.2 (101), 37.8 (004), 47.9 (200), 53.8 (105), 54.9 (211), 62.6 (204), 68.7 (116), 70.1 (220), 74.9 (125), and 82.5 (224); and the same sample also showed a broad and weak signal centered at ca. 30.7 2θ (labeled B), readily ascribed to the (121) diffraction peak of brookite, and the formation of which is favored at pH values as low as 2.018,37 and, here, was likely favored by the adopted synthesis procedure, implying extremely acidic conditions in the reverse micelle core. The Mo_1 sample showed very similar XRD patterns, albeit the (121) diffraction peak of brookite, and the formation of which is favored at pH values as low as 2.018,37 and, here, was likely favored by the adopted synthesis procedure, implying extremely acidic conditions in the reverse micelle core. The Mo_1 sample showed very similar XRD patterns, albeit the (121) diffraction peak of brookite seemed less intense. At a higher Mo content (samples Mo_2.5, Mo_5, Mo_7.5, and Mo_10), two additional peaks (labeled R) were observed at 27.2 and 54.4 2θ values, respectively, assigned to the (110) and (211) diffraction peaks of rutile. Concerning the effect of Mo_5+/Mo_5+ doping, especially on the reticular plane of the various phases, a careful analysis of the 35−40 2θ range was carried out. The inset in Figure 1a shows a magnification of the 35−40 2θ range for the XRD patterns of the TiO2, Mo_5, and Mo_10 samples only, in order to highlight possibly
relevant strain/stress phenomena, as reported by the literature in similar TiO$_2$-based materials. After a careful analysis of the shape of the anatase (004) peak profiles, no relevant differences were, however, observed, likely due to the small difference in the cationic radii of octahedrally coordinated Ti$^{4+}$, Mo$^{5+}$, and Mo$^{6+}$ ions (0.605, 0.61, and 0.59 Å, respectively).

Table 1 reports the corresponding quantitative phase analysis (QPA) results, as obtained by the Rietveld refinement. Besides anatase, QPA showed the occurrence of brookite with all the samples, whereas the formation of rutile occurred at Mo wt % ≥ 2.5. Interestingly, no signals ascribable to any crystalline MoO$_3$ phase were detected, neither with the Mo$_{10}$ sample: on the one side, amorphous and/or extremely dispersed MoO$_3$ phases, if present, could escape the XRD detection, and on the other side, micro-Raman spectroscopy (Figure S1) shows the occurrence of the surface polimolbidate species (i.e., Mo$_3$O$_{24}$ and Mo$_5$O$_{26}$ species, where Mo was octahedrally coordinated) at a Mo content ≥ 5 wt %, without the MoO$_3$ segregation. Previous literature results concerning samples at a comparable Mo content that were obtained by a microemulsion method showed the formation of both Mo surface species and MoO$_3$ phases, indicating that the reverse micelle sol–gel synthesis described here was more effective toward the inclusion of Mo in the TiO$_2$ matrix, likely because of the adopted surfactant.

Interestingly, the trends are similar, i.e., both parameters increase with the increasing Mo content. The Mo content, instead, does not affect the anatase crystal size much, as shown by the corresponding values reported in Table 1. Unfortunately, the samples’ low crystallinity did not allow the calculation of brookite and the rutile cell volume and crystallite size and thus, we could not monitor the occurrence of Mo doping in the other (less abundant) phase(s), although we are aware that the rutile structure is able to accommodate defects more efficiently than anatase.

The morphological analysis, as carried out by FE-SEM, showed the occurrence of aggregated rounded particles (Figure S2). The corresponding particle size distributions and the NP average size values are reported in Figure 2a and in Table 1, respectively. As a whole, the TiO$_2$ sample shows smaller NPs than the Mo-doped ones; the NP size increases progressively with the Mo$_{1}$ and Mo$_{2.5}$ samples, and the latter having an average NP size very close to the Mo$_{5}$ sample. The Mo$_{5}$ sample, however, is characterized by a broader NP size distribution, as compared to the other samples. With both Mo$_{7.5}$ and Mo$_{10}$ samples, the NP average size decreases. The trend of NP average size as a function of the Mo nominal content is compared to that of the anatase cell volume (as obtained by the Rietveld refinement) in Figure 2b and, interestingly, the trends are similar, i.e., both parameters increase and, then, decrease with the Mo content, supporting the idea that Mo doping mainly occurs in the (most abundant) anatase phase.

Figure 3a shows the N$_2$ adsorption/desorption isotherms obtained at −196 °C on the studied samples, which showed type IV isotherms and type H2 hysteresis loop, typical of N$_2$ condensation within interparticle mesopores, and the corresponding BET SSA values are reported in Table 1. Figure 3b shows the corresponding PSD (pore size distribution) as obtained by applying the DFT method: as a whole, mesoporous samples were obtained, and their cumulative

Table 1. Textural Properties of the Studied Samples as Obtained by Powder XRD, FE-SEM, and EDX Analyses, N$_2$ Isotherms at −196 °C

<table>
<thead>
<tr>
<th>sample</th>
<th>Mo wt %$^{a}$</th>
<th>anatase wt %$^{b}$</th>
<th>crystal size (nm)$^{c}$</th>
<th>brookite wt %$^{b}$</th>
<th>rutile wt %$^{b}$</th>
<th>average NP size (nm)$^{d}$</th>
<th>BET SSA (m$^2$ g$^{-1}$)</th>
<th>total pore volume (cm$^3$ g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>0.83</td>
<td>91.00</td>
<td>16.3</td>
<td>9.00</td>
<td>10.7</td>
<td>71</td>
<td>0.084</td>
<td></td>
</tr>
<tr>
<td>Mo$_{1}$</td>
<td>0.83</td>
<td>90.00</td>
<td>18.7</td>
<td>10</td>
<td>20.6</td>
<td>42</td>
<td>0.064</td>
<td></td>
</tr>
<tr>
<td>Mo$_{2.5}$</td>
<td>3.2</td>
<td>87.56</td>
<td>17.1</td>
<td>6.04</td>
<td>6.40</td>
<td>25</td>
<td>0.161</td>
<td></td>
</tr>
<tr>
<td>Mo$_{5}$</td>
<td>5.8</td>
<td>85.46</td>
<td>18.5</td>
<td>7.96</td>
<td>6.58</td>
<td>25.1</td>
<td>0.133</td>
<td></td>
</tr>
<tr>
<td>Mo$_{7.5}$</td>
<td>7.7</td>
<td>90.30</td>
<td>22.1</td>
<td>5.41</td>
<td>4.27</td>
<td>19.7</td>
<td>0.122</td>
<td></td>
</tr>
<tr>
<td>Mo$_{10}$</td>
<td>9.75</td>
<td>93.47</td>
<td>18.6</td>
<td>3.06</td>
<td>3.47</td>
<td>16.1</td>
<td>0.127</td>
<td></td>
</tr>
</tbody>
</table>

$^{a}$As obtained by the EDX analysis. $^{b}$As obtained by the Rietveld refinement. $^{c}$As obtained by the FE-SEM analysis.
pore volume values are reported in Table 1. The Mo_2.5, Mo_5, and Mo_7.5 samples show broader PSD curves, in agreement with the fact that we are dealing with interparticle mesoporosity, and the same samples also showed broader NP size distributions (Figure 2a).

Bulk and Surface Composition. Table 2 reports, inter alia, the samples’ bulk and surface composition, as determined by EDX and XPS analyses, respectively. As mentioned before, the EDX values were in fair agreement with the nominal ones, and the EDX maps (Figure S3) showed a uniform Mo distribution also with the Mo_10 sample. Although EDX is a semiquantitative technique, the adopted synthesis technique allows an effective inclusion of Mo, without the segregation of other phases, likely due to an optimized mixing of the Mo precursor and the Ti precursor within the reverse micelle core.

The XPS analysis was used to determine the samples’ surface composition and allows us inferring possible differences between the surface and bulk composition. The XPS determined (surface) Mo/Ti at. % as a function of the EDX determined (bulk) Mo/Ti at. % (Figure 4) does not show a linear trend, but the tendency of Mo to sit at the NP surface and with the Mo_10 sample, the surface Mo/Ti at. % seems to reach a plateau. Such a “surface enrichment” is in agreement with micro-Raman spectroscopy (Figure S1 in the Supporting Information) showing the formation of surface polymolibdates at a higher Mo loading. Such a phenomenon could also affect the surface acidity, which was studied by measuring the samples’ electrophoretic mobility in water, with the determination of their ζ potential (Figure 5) and pH at isoelectric point (pHIEP, Table 2). The inspection of the curves in Figure 5 allows some considerations to be drawn: first of all, the TiO2 sample shows a lower pHIEP value as compared to the reported literature values for P25 (6.2 − 6.9)49 and other types of TiO2.50−52 Such a phenomenon in the TiO2 sample can be ascribed to the peculiar synthesis, which leads to the formation of an acidic surface, as already reported in the literature.18,51 The (XPS determined) Mo enrichment of the samples’ surface brings about a further increase in surface acidity, with progressive lowering of the pHIEP values, as the amount of Mo increases. Another point of interest is the measured value of ζ potential, which can be used to evaluate the stability of the suspension: usually, NP suspensions in water are stable with ζ potential values above +30 mV or below −30 mV.53 In the examined pH range, stability is reached at basic pH with TiO2 NPs and, to a minor extent, with Mo_2.5 NPs, indicating a tendency of the NPs to aggregate in water as the Mo content increases, indicating a modification of the NP surface. In Figure 5b, the measured pHIEP has been plotted as a function of the (XPS determined) surface Mo/Ti at. %: indeed, the pHIEP does not change sizably from sample Mo_1 to sample Mo_5, notwithstanding the progressive Mo surface enrichment. This likely means that the Mo is forming highly coordinated polymolibdate units, whereas at higher Mo...
The oxidation state of the surface Mo species was also studied by XPS by applying a curve-fitting procedure to the Mo3d doublet of all the studied samples. Figure 6a shows the comparison of the Mo3d spectral regions, whereas Figure 6b shows a typical curve-fitting procedure for the Mo_2.5 sample. In all the studied cases, two doublets were used to properly interpret the spectral lines: the obtained binding energy (BE) values were compatible with the presence of both Mo6+ and Mo5+ surface species (BE Mo3d5/2 = 231.3 ± 0.3 eV and BE Mo3d5/2 = 232.5 ± 0.2 eV, respectively). After the curve-fitting procedure, the relative abundance of Mo6+/Mo5+ species was obtained, and the corresponding values are reported in Table 2. The occurrence of surface Mo5+ species is not surprising because when isomorphic substitution occurs, the positive extra charges induced by the Mo6+ species have to be balanced by different means, namely the formation of oxygen vacancies, formation of (reduced) Mo5+ species, and reduction of Ti4+ to Ti3+ species. If those phenomena occur at the surface, they can be studied by XPS. Concerning the formation of reduced Ti3+ species, Figure 6c reports the position of the Ti2p1/2 peak component as the surface Mo content (Mo/Ti at. %) increases: the Ti4+ peak position is seen to shift with progressive doping, but the observed Ti2p spin–orbit splitting is constant, indicating the unlikely formation of Ti3+ species at the surface. To evaluate the occurrence of oxygen vacancies, the O1s spectral region was investigated and subjected to a curve-fitting procedure (Figure 6d shows, as an example, the results obtained with the Mo_7.5 sample). With all the samples, two peak components were found at BE = 529.8 ± 0.2 eV and BE = 530.8 ± 0.2 eV, ascribable to the lattice oxide species (M–O) and to oxygen species in the oxygen-deficient region, respectively. The relative abundance of the oxygen vacancy component amounts to 15 ± 2% and is almost constant with the Mo content, with the exception of the Mo_5 sample in which the peak is less intense, and the amount of oxygen vacancies is equal to 9 ± 1%. The same sample also showed a lower amount of surface Mo5+ species; because XPS allows the study of surface species, (further) oxygen vacancies and/or Mo5+ species could be located in the bulk of Mo_5 NPs, finally escaping XPS detection.

Furthermore, by XPS it was also possible to measure the position of the valence band (VB) energy (the corresponding
values being reported in Table 2) that, in turn, was used to determine the CB position, by considering the \( E_g \) values determined by DR UV–vis spectroscopy (vide infra).

DR UV–vis spectra (Figure 7a) show a redshift of the onset of absorption with Mo doping, along with a broad absorption band in the d-d transition range. As expected, the TiO\(_2\) sample absorbed below 400 nm, whereas the introduction of Mo brought about two effects: a slight redshift of the absorption edge and the appearance of a broad absorption centered at ca. 550 nm, readily assigned to the sub-band transitions related to midband gaps formed by Mo doping. The redshift of the absorption edge shows that Mo doping is modifying the materials’ \( E_g \) values that were here calculated by the Tauc’s plot method (not shown) for the indirect semiconductor, anatase being the most abundant polymorph (Table 2). The smallest \( E_g \) value was obtained with the Mo_7.5 sample, then an \( E_g \) increase occurred at a higher Mo content. Figure 7b shows the \( E_g \) values along with the position of VB samples, as determined by the XPS analysis and CB values calculated as (VB + \( E_g \)). Interestingly, when a template-free sol–gel method was adopted to obtain Mo-doped TiO\(_2\) with a similar composition, the effect on the \( E_g \) was ca. 10% smaller, especially at higher Mo contents, showing that here the reported reverse micelle sol–gel synthesis may lead to a remarkable decrease in \( E_g \). The figure also shows that the Mo introduction modifies the position of both the VB and the CB and that at a higher Mo content, an increase in \( E_g \) is observed. The latter phenomenon can be due to the occurrence of the Moss–Burstein (or Burstein–Moss) effect, i.e., the apparent increase of a semiconductor band gap, due to the fact that at high doping levels, some states close to the CB are being populated. When the electron carrier concentration exceeds the CB edge density of the states, degenerate doping in semiconductors occurs: here, it shows that the adopted synthesis method allowed such an effective inclusion of Mo in the TiO\(_2\) matrix that the Moss–Burstein effect was observed.

Indeed, such an effect, i.e., an (unexpected) increase in the \( E_g \) at a higher amount of dopant had been already observed in Mo-doped TiO\(_2\) NPs which, at an intermediate Mo content, were active toward the photocatalytic degradation of rhodamine B (a model water pollutant) under simulated solar light, showing that this type of doped TiO\(_2\) has indeed appealing photocatalytic properties, in agreement with the literature in the field. In perspective, such an effective doping procedure could be applied not only to introduce other types of doping elements within TiO\(_2\) matrices but also to synthesize other types of materials, like doped ZnO, which is along with TiO\(_2\), the most studied semiconductors with many and diverse applications in photocatalysis and biology as an antibacterial, etc., as acknowledged by the literature.

CONCLUSIONS

The obtained results allowed inferring a prominent role of the adopted synthesis technique on the samples’ physicochemical properties in that reverse micelle sol–gel synthesis allowed the inclusion of a sizeable amount of Mo in the bulk, with a consequent modification of the VB and CB of the final material. The type of synthesis also affected the kind of mixed phases occurring in the final product (anatase, brookite, and rutile, the last one at Mo wt % \( \geq 2.5 \)) as well as the surface...
species in the samples’ surface is extremely acidic especially when Mo doping occurs.

The surface species were also studied by the XPS analysis, showing the occurrence of both Mo$^{6+}$ and Mo$^{5+}$ species, the latter forming, along with oxygen vacancies, in order to balance the extra positive charge induced by doping.

The energies of both the VB and CB were determined by the density functional theory (DFT) method; pore total volume was measured at $\theta = 0.026$°, time per step: 2 s).

The samples’ phase composition and structural parameters were determined by the Rietveld analysis as implemented in the MAUD software.$^{60}$ Instrumental broadening was characterized by the NIST standard 660a (LaB$_6$).

The Raman spectra were taken by a Renishaw InVia Reflex micro-Raman spectrometer equipped with a cooled charge-coupled device (CCD) camera; the source was a diode laser ($\lambda_{ex} = 514$ nm); and powders were pressed into self-supporting wafers to ensure the inspection of a flat surface by means of a microscope objective (100X) in a backscattering light collection mode (laser power: 0.5 mW; exposure time: 10 s; 1 accumulation).

The diffuse reflectance (DR) UV–visible spectra were recorded by a UV–visible Varian Cary 5000 spectrophotometer equipped with an integration sphere for the DR measurements. The samples’ band gap energy ($E_g$) was then calculated by applying the Tauc’s plot method for the indirect semiconductors.

The surface chemical composition and speciation were investigated by X-ray photoelectron spectroscopy (XPS) using a Versa Probe II scanning XPS microprobe spectrometer (Physical Electronics GmbH), equipped with a monochromatized Al Kα source (X-ray spot = 100 μm) at a power of 26.7 W. Both wide scans and high-resolution XP spectra were acquired using a fixed analyzer transmission (FAT) mode with pass energies of 117.40 and 29.35 eV, respectively. An electron gun was used for the charge compensation (1.0 V 20.0 μA).

The data processing was performed by using MultiPak software version 9.9.0.8.

The samples’ electrophoretic mobility was measured using a Zetasizer Nano ZSP instrument (Malvern Instruments Ltd.,

![Figure 7.](https://pubs.acs.org/doi/10.1021/acsomega.0c05552)
GB) on mixtures prepared by adding ca. 5 mg of powder to 10 mL of bi-distilled water and then sonicating for 5 min; during the measurements, pH was adjusted by the addition of either HCl or NH₄OH aqueous solutions. The samples’ ζ potential was obtained from the electrophoretic mobility by applying the Smoluchowski’s approximation.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c05552.

- Micro-Raman spectra (Figure S1); FE-SEM micrographs (Figure S2); and EDX elemental maps (Figure S3) (PDF)

AUTHOR INFORMATION

Corresponding Author
Barbara Bonelli – Department of Applied Science and Technology, Politecnico di Torino, Torino I-10129, Italy; INSTM Unit of Torino-Politecnico, Torino I-10129, Italy; orcid.org/0000-0002-4716-864X; Email: barbara.bonelli@polito.it

Authors
Serena Esposito – Department of Applied Science and Technology, Politecnico di Torino, Torino I-10129, Italy; INSTM Unit of Torino-Politecnico, Torino I-10129, Italy; orcid.org/0000-0001-9159-0541
Nicoleta Ditaranto – Dipartimento di Chimica, Università degli Studi di Bari “Aldo Moro”, Bari 70125, Italy
Gianfranco Dell’Agli – Dipartimento di Ingegneria Civile e Meccanica, Università degli Studi di Cattolica del Lazio Meridionale, Cattolica (FR) I-60034, Italy
Roberto Nasi – Department of Applied Science and Technology, Politecnico di Torino, Torino I-10129, Italy
Paola Rivolo – Department of Applied Science and Technology, Politecnico di Torino, Torino I-10129, Italy; orcid.org/0000-0003-0672-5793

Complete contact information is available at: https://pubs.acs.org/doi/10.1021/acsomega.0c05552

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank Prof. Marco Armandi (Department of Applied Science and Technology, Politecnico di Torino) for the assistance during the N₂ adsorption/desorption measurements and Mauro Raimondo (Department of Applied Science and Technology, Politecnico di Torino) for the assistance during the FE-SEM and EDX measurements.

REFERENCES


