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The influence of acids on tuning the pore size of mesoporous TiO_2 templated by non-ionic block copolymers

Stefano Loreto*[a], Hans Vanrompay[b] Myrjam Mertens[c], Sara Bals[b] and Vera Meynen[a]

Abstract: We show the possibility to tune the pore size of mesoporous TiO_2 templated by non-ionic block copolymers by adding different inorganic acids at well-chosen concentration. The effect of the inorganic anions on both the TiO_2 cluster formation and the non-ionic block copolymers micelles is investigated to explain the experimental results.

Tuning pore sizes and surface area of mesoporous TiO_2 is of great importance for its application as filters, adsorbents, catalysts, etc[1]. Nevertheless, controlling the pore size of mesoporous TiO_2 is a challenging step due to the fast hydrolysis of the precursors hampering an easy control over the mesopores diameter[2]. Therefore, the development of a facile route to obtain mesoporous TiO_2 with tailored pore size as easy as silica is required for its future applicability[3].

Similar to the synthesis of mesoporous silica, the most applied pathway for the synthesis of mesoporous TiO_2 is the soft-template approach[3]. This method usually undergoes a co-assembly process of the titanium precursor with the surfactant template. Non-ionic block copolymer templates have been increasingly used for this purpose as they lead to more robust structure, larger pores, easier control over the wall thickness and higher reproducibility than the ionic surfactants[4–8].

It is widely accepted that the pore size of mesoporous TiO_2 depends on the hydrophobic volume of the surfactant templates[3,9]. The strong effect of inorganic anions on the structure of porous materials template by non-ionic block copolymers has been already investigated[10–13]. However, the attention has been limited to the impact of such interaction on the order of the mesostructure of single crystal and polycrystalline silica materials.

In this study we demonstrate that different pores with narrow pore size distribution (PSD) can be achieved by simply using inorganic acids at well-chosen concentration in presence of the same block copolymers. In literature on block copolymer templated mesoporous TiO_2, the use of different inorganic acids to tune the pore sizes has not been reported before.

The mesoporous materials were synthetized by using $EO_{20}PO_{70}EO_{20}$ [denoted P123; EO is poly(ethylene oxide) and PO indicates poly(propylene oxide)] as template and tetrabutyl titanate (TBT) as inorganic precursor. The method was adapted from the reported dual template synthesis of mesoporous TiO_2[14]. The synthesis was altered by adding 1 ml of different concentrations (X = 1, 0.1 and 0.01M) of HCl (TiO_2HAX), $HClO_4$ (TiO_2PAX), HNO_3 (TiO_2NAX) or H_2SO_4 (TiO_2SAX) solution to the final mixed solution after 2h. For comparison, a material without adding acids (TiO_2) was also synthetized. Afterwards, the samples were transferred to autoclaves for hydrothermal treatment (120ºC for 48 h) and the precipitate was collected, washed with distilled water and dried at 80ºC. The as-prepared samples were calcined at 450ºC (1ºC/min) for 4 h in a Lenton chamber furnace under ambient atmosphere to remove the template.

Because of the strong influence of the pH on the crystal phase of TiO_2[15,16], wide angle (WAXRD) and small angle (SAXRD) XRD analysis were used to investigate the crystal phase and the mesostructural ordering of the calcined samples. The WAXRD patterns (Figure 1A) reveal that all samples are pure anatase, irrespective of the use of different acid. This shows that the crystal phase of the calcined samples is not influenced by the variation in pH in the acidic range examined in this work. Besides, the pure anatase phase suggests negligible effect of Cl^-, NO_3^- and ClO_4^- anions on the TiO_2 phase formation even though these species are known to stabilize rutile and brookite[16–18]. The SAXRD of TiO_2 and TiO_2HA1M (Figure 1B) shows a broad intense peak centered at 1.5º. Although the Bragg reflections of the space group are not resolved, the presence of a low angle diffraction peak suggests that the samples possess a semi-organized mesoporous structure with relative uniform pores, but without long range ordering[19,20]. The small shift, toward smaller value of 2θ, in TiO_2PA1M and TiO_2NA1M reveals an expansion of the unit cell[21]. Moreover, the diffraction peak of TiO_2NA1M is somewhat broader. The HAADF-STEM images (Figure S.I. 1) show the lattice fringes corresponding to (101)(d_{101}=0.35 nm) crystallographic planes of anatase, which confirm the high crystallinity of the pore walls and the crystal size of about 10 nm(Figure S.I. 1 and Table 1)

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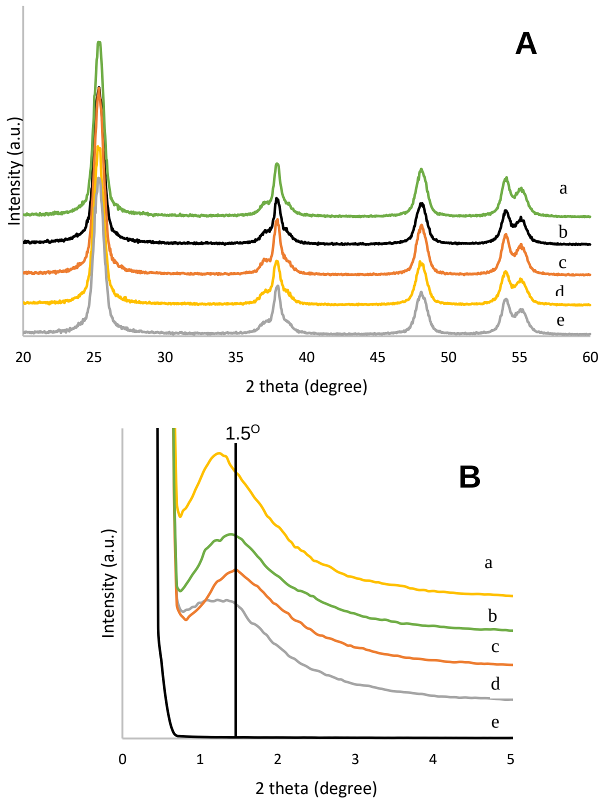

Figure 1. A) WAXRD pattern of TiO_2 (a), TiO_2SA1M (b), TiO_2HA1M (c), TiO_2PA1M (d) and TiO_2NA1M (e). B) SAXRD pattern of TiO_2PA1M (a), TiO_2 (b), TiO_2HA1M (c), TiO_2NA1M (d) and TiO_2SA1M (e). The XRD analysis was performed on samples after calcination at 450°C for 4h .

The absence of reflections in the SAXRD of TiO_2SA1M might indicate that the mesostructure semi-ordering is lost if H_2SO_4 is used, even though the large pore size of this sample (see Table 1) falls outside the measuring range. However, the SAXRD of $TiO_2SA0.1M$ and $TiO_2SA0.01M$ (Figure S.I. 2) seems to confirm the effect of the sulfate anions on the ordering of the mesostructure.

With regard to the mesoporous structure, the N_2 sorption analysis (Figure 2A) shows for all samples a type IV(a) isotherm with a H1 hysteresis loop, indicating mesoporous materials. There is one exception being TiO_2PA1M with ink bottle type pores (H2 hysteresis, see Figure 2A) with a large bulk pore size and a narrower pore opening[22]. Similar surface areas and pore volumes are observed for all samples except for TiO_2PA1M that has a slightly lower surface area and half of the pore volume of the other TiO_2 materials (Table 1). This difference fully correlates to the smaller bulk pores (8.4 nm) and pore openings (6.5 nm) of TiO_2PA1M. On the other hand, TiO_2SA1M has a much higher pore volume induced by the much larger pore sizes. Although the porous structure seems to be quite uniform in surface area, the use of different inorganic acids has a strong impact on the size of both the bulk pores and the pore openings(Figure 2B and 2C). In particular, except for H_2SO_4, the use of inorganic acids leads to sharper PSD (Figure 2B, C and Table S.I. 1), meaning more uniform pores. This is enhanced for TiO_2PA1M and is even visible at concentrations as low as 0.01M.The existence of a porous matrix is further confirmed by the TEM analysis (Figure S.I. 3). Additionally, the TEM confirm that only local order of relatively uniform mesopores is present and no long range ordering can be observed, as indicated by the broad reflection peak in the SAXRD analysis (see Figure 1 B).

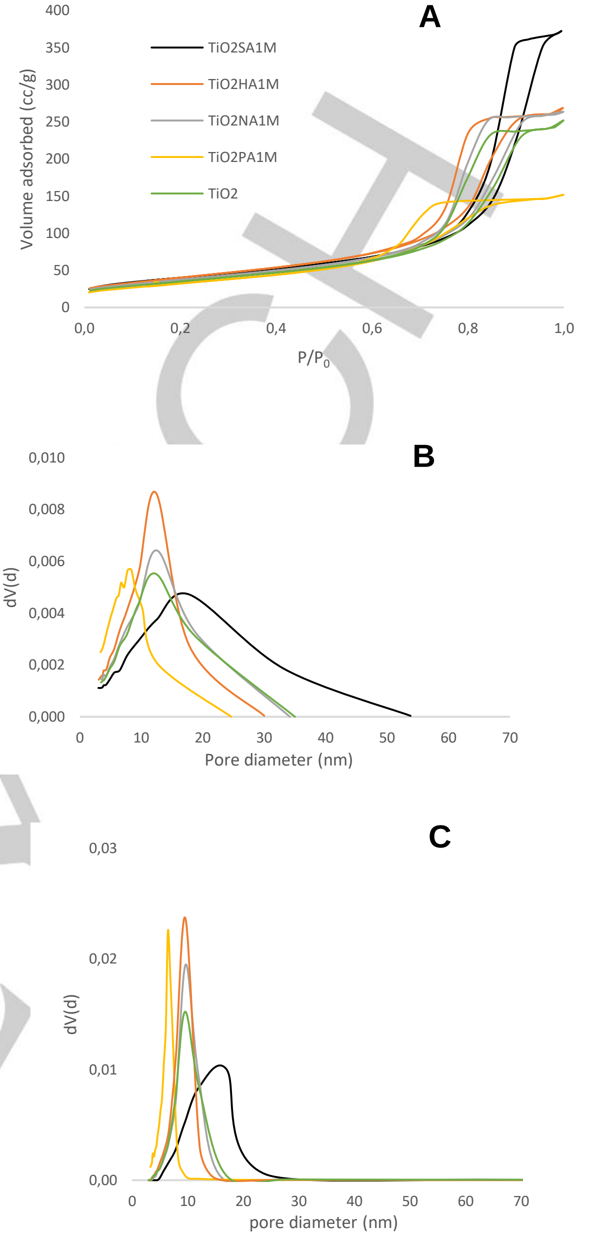

Figure 2. A) nitrogen desorption-adsorption isotherms of TiO_2 (green), TiO_2HA1M (orange), TiO_2NA1M (grey), TiO_2PA1M (yellow) and TiO_2SA1M (black). B) PSD (BJH adsorption branch). C) PSD (BJH desorption branch). The analysis was performed on samples after calcination at 450°C for 4h. All samples were degassed for 16h at 150°C before the analysis.

Table 1. Summary of XRD and N_2 sorption analysis of mesoporous TiO_2 synthetized with different inorganic acids after calcination at 450°C for 4h.

	S_{BET} (m²/g)	Total V_P (cc/g)	D_P BJH des (nm)	D_P BJH ads (nm)	Crystal phase	Crystallite size (nm)[a]
TiO_2	127	0.4	9.6	12.2	anatase	10.4
TiO_2SA1M	142	0.6	16.8	17.8	anatase	10.7
TiO_2NA1M	136	0.4	9.6	12.6	anatase	9.4
TiO_2HA1M	146	0.4	9.6	12.6	anatase	10.3
TiO_2PA1M	118	0.2	6.5	8.4	anatase	10.1

[a] Calculated using the Sherrer equation.

The strong influence of the pH on the micelle diameter of the triblock copolymer P123 has already been shown[23]. However, because the pH is the same for all of the synthesis solutions (TiO_2HA1M, TiO_2NA1M, TiO_2PA1M and TiO_2SA1M), the role of the inorganic anions has to be considered to explain the observed differences in the PSD.

Interactions between inorganic anions and non-ionic[10,11] and ionic[24] surfactants have been already described. The inorganic anions show peculiar interactions with the different surfactants leading to divergent effect on the surfactant micelles; various series of anions inducing structural changes in silica materials have been reported[11,24].

The N_2 sorption analysis of mesoporous TiO_2 synthetized by varying the concentration of the inorganic acids (Figure S.I. 4 A, B) shows different effect on the pores (Figure S.I. 5 A, B, Figure S.I. 6 A, B and Tab. 2) depending on the concentration and the acid used. TiO_2NA0.1M and TiO_2SA0.1M present smaller pore size than TiO_2NA1M and TiO_2SA1M. On the contrary, a larger pore size is observed for TiO_2PA0.1M than for TiO_2PA1M. The N_2 sorption analysis shows only weak differences between TiO_2HA0.1M and TiO_2HA1M. It has to be noticed that the effect of the acid concentration discussed above is observed for both the bulk pores and the pore openings. As the pH variation due to the different acid concentrations is the same for all the solution, the divergent effect on the pores further confirm the important role of the inorganic anions.

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Table 2. Summary of the N_2 sorption analysis of mesoporous TiO_2 synthetized using different inorganic acids with different concentration after calcination at 450^{O}C for 4h.

	S_{BET} (m^2/g)	Total V_P (cc/g)	D_P BJH des (nm)	D_P BJH ads (nm)
TiO_2	127	0.4	9.6	12.2
TiO_2SA0.1M	128	0.4	10.1	12.6
TiO_2SA0.01M	137	0.4	9.6	12.6
TiO_2NA0.1M	133	0.3	8.0	9.0
TiO_2NA0.01M	127	0.4	9.6	12.4
TiO_2HA0.1M	137	0.4	9.8	12.4
TiO_2HA0.01M	131	0.4	9.6	12.6
TiO_2PA0.1M	130	0.3	8.7	10.1
TiO_2PA0.01M	137	0.4	9.8	12.3

The trend we observe for mesoporous TiO_2 is in agreement with the anion sequence proposed by Tang *at al.* ($SO_4^{2-} > NO_3^- > Br^- > Cl^-$) for their influence on the phase transformation of silica mesostructures templated by non-ionic copolymers[11].

In this sequence the dual effect of the anion radius and hydration is considered to explain the effect on the silica phase transformation. In particular, it is proposed that highly hydrated ions lead to dehydration of the EO group of P123, decreasing the packing parameter of the copolymer. Perchlorate anions show one of the lowest known hydration energy, thus they show only a weak dehydration effect upon interaction with the copolymers keeping a relatively small impact on the packing parameter. Therefore, only at high concentration of perchloric acid (TiO_2PA1M) the dehydration effect is appreciable and a contraction of the P123 polymers occurs and thus a smaller pore size is achieved. On the other hand, the presence of nitrate (only at defined concentrations, see below) and sulfate anions leads to a dilation of the copolymer resulting in larger pores when the concentration increases. Chlorine anions are known to represent a border line in the proposed anions sequence, thus their effect on the copolymer may be the weakest resulting in little changes in the pore size.

However, interactions between the inorganic anions and the titanium dioxide clusters cannot be excluded and they have to be considered to fully explain the experimental results. In fact, although there are no examples where only the kind of acid has been varied among all the synthesis parameters, it is reasonable to expect a substantial influence of the type of acid on the TiO_2 cluster formation[25]

Sulfate anions are involved in the formation process of TiO_2 as they strongly interact with the $Ti_2O_6^{2-}$ octahedra influencing their orientation and, thus, accelerating the anatase nucleus growth[26,27]. This may result in a faster but more disorderly condensation, leading to loss of mesostructure ordering and broader PSD of both (see Figure 1B, Figure 2B, C and Table S.I. 1) indicating less homogeneous bulk pore and pore opening sizes. The DRIFT spectrum of TiO_2SA1M (Figure S.I. 7) shows the three peaks characteristic of the HSO_4^- (1210 cm^{-1}) and SO_4^{2-} (1130 and 1040 cm^{-1}) vibrations[28,29], confirming the strong interactions between these anions and the TiO_2. The sulfate anions probably interact with the TiO_2 surface via the Ti^{+4} sites displacing the physisorbed water molecules. This results in the disappearance of the IR band at 1560 cm^{-1} due to the vibration of H_2O coordinated to the Ti^{4+} sites[30], which is observed in the DRIFT spectra of all the other samples (Figure S.I. 7).

On the contrary, perchlorate anions show the lowest affinity for titanium dioxide[31] and the complex they form in solution with Ti (IV) is not stable[32], thus when $HClO_4$ is added, the clusters have the minimum repulsion. As a consequence, the clusters condensation might be faster leading to the very narrow PSD (see Table S.I. 1) responsible for the broader hysteresis (see Figure 2A).

A peculiar response to the use of HNO_3 is observed as the effect of this acid strongly depends on the concentration. In fact, TiO_2NA0.1M shows bulk pores and pore openings smaller than TiO_2 while an increase in concentration leads to the above discussed reverse effect of a small dilation of the pore size in comparison to TiO_2. Different studies have reported that the use of nitric acid in the synthesis of titanium dioxide has a strong impact on the a stabilization of the inorganic frameworks[33,34]. The dual effect of the HNO_3 on the hydration of the P123 polymer and on the stabilization of the TiO_2 frameworks might be related to the concentration of NO_3^- in solution. In particular, the dilatation of the P123 micelles leading to larger pores may predominate at higher concentration (TiO_2NA1M), while the stabilization of the TiO_2 frameworks leading to smaller pores may prevail at low acid concentration (TiO_2NA0.1M).

The weak effect of Cl^- anions is further explained by the low affinity between this anions and the titanium dioxide[35].

It has to be remarked that the effect of all the investigated inorganic anions on the size of both the bulk pores and the pore openings of mesoporous TiO_2 is negligible at 0.01M concentration (Figure S.I. 6 A, B).

In conclusion, we show a new and easy approach to achieve tunable bulk pore and pore opening sizes in mesoporous TiO_2 templated by non-ionic copolymers by addition of inorganic acids at a well-chosen concentration during the synthesis. Furthermore, the mesoporous TiO_2 synthetized at high acid concentration shows more uniform pores than the TiO_2 where no acid was used, with the exception of the H_2SO_4 material. Although the effect of the acid treatment might vary with the synthesis route, the observed effect represent a fundamental improvement in controlling the pore size of mesoporous TiO_2.

Author Contributions. V. Meynen and S. Loreto designed the research and analyzed and interpreted all data. S. Loreto performed most of the experiments and wrote the paper. H.

Vanrompay performed the HAADF-STEM measurements, M. Mertens performed the XRD analysis. S. Bals contributed to the interpretation of the HAADF-STEM results and revised the paper.

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Keywords: copolymers • mesoporous TiO_2 • pore size • inorganic acids • template

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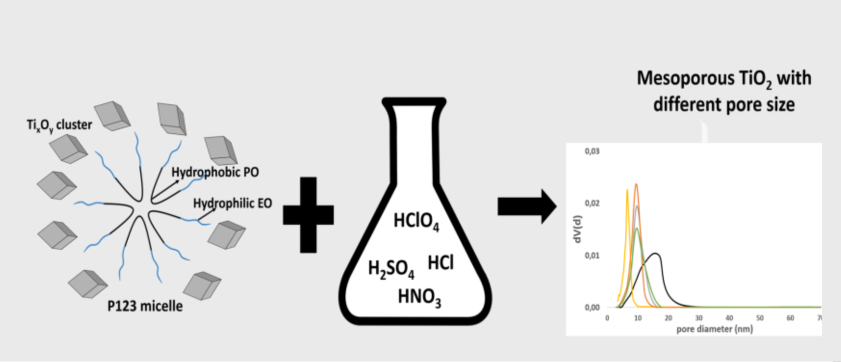

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In this work, the use of inorganic acids during soft templating synthesis with non-ionic copolymers is revealed as an easy possibility to tune the pore size of mesoporous TiO_2. Various inorganic acids in different concentrations are investigated for their effect on pore size and uniformity of distribution. An intertwined effect of pH and anion is clearly visible depending on the acid applied.