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Low-Temperature Synthesis of Mesoporous Titania−Silica Films with Pre-Formed Anatase Nanocrystals

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Titania−silica composite films with a high content of crystalline titania phase and periodic mesoporous structure were fabricated by a low temperature “brick and mortar” approach. Pre-formed titania nanocrystals were fused with surfactant-templated sol−gel silica, which acts as a structure-directing matrix and as a chemical glue. The nature of the surfactant plays the decisive role in the mesostructure formation. Using Pluronic P123 as the structure-directing agent, the structure formation of the mesoporous silica is greatly disturbed as a result of the presence of titania nanoparticles. On the contrary, the use of Pluronic F127, whose molecules are larger and whose poly(ethylene oxide) blocks are more hydrophilic, enables the preparation of composite titania−silica mesoporous architectures that can accommodate up to 50 wt % of nanocrystals and yet retain the periodicity of the porous structure. In this way, films with a high degree of crystallinity were obtained at temperatures as low as 100−150 °C and employed as active layers for the photooxidation of NO. The surface of the titania particles is not deactivated with respect to their photocatalytic activity by the surrounding silica matrix or by covalently attached ligands. The “brick and mortar” approach results in periodic mesoporous nanocomposites with photocatalytically active sites leading to functional coatings that are processed at low temperatures and thus opens new perspectives for their applicability on a wide range of substrates.

Introduction

Crystalline nanoparticles are attractive building blocks for the solution-based preparation of nanostructured materials.[1−4] In principle, the assembly of nanoparticles controlled by structure-directing agents can enable the preparation of highly crystalline porous structures with defined morphology already at low temperatures.[2,5−7] The scope of possible systems can be extended even further when the nanocrystals are dispersed in different noncrystalline matrices, thus opening the way toward novel nanocomposite systems.[8−15] However, the use of nanocrystals as building blocks imposes certain requirements on their properties. Besides a well-defined size distribution, the nanocrystals should be easily dispersible and form nonagglomerated colloidal solutions.[16] Moreover, these solutions should be compatible with the structure-directing agent and the precursor for the noncrystalline component of the matrix.

Here we report the preparation of mesoporous titania−silica composites from crystalline titania nanoparticles and mesoporous amorphous silica. Such systems have been the subject of intensive research activity, as they may combine the properties of both components, thus extending their functionality beyond that of the pure materials.[13,17−25] Such a

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(1) Sanchez, C.; Boissiere, C.; Grosso, D.; Laberty, C.; Nicole, L. *Chem. Mater.* **2008**, *20*, 682–737.
(2) Antonietti, M.; Niederberger, M.; Smarsly, B. *Dalton Trans.* **2008**, 18–24.
(3) Djerdj, I.; Arcon, D.; Jaglicic, Z.; Niederberger, M. *J. Solid State Chem.* **2008**, *181*, 1571–1581.
(4) Pinna, N.; Niederberger, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 5292–5304.
(5) Lee, D.; Rubner, M. F.; Cohen, R. E. *Nano Lett.* **2006**, *6*, 2305–2312.
(6) Page, M. G.; Nassif, N.; Borner, H. G.; Antonietti, M.; Cölfen, H. *Cryst. Growth Des.* **2008**, *8*, 1792–1794.
(7) Niederberger, M.; Cölfen, H. *Phys. Chem. Chem. Phys.* **2006**, *8*, 3271–3287.
(8) Agrios, A. G.; Cesar, I.; Comte, P.; Nazeeruddin, M. K.; Grätzel, M. *Chem. Mater.* **2006**, *18*, 5395–5397.
(9) Arumugam, P.; Xu, H.; Srivastava, S.; Rotello, V. M. *Polym. Int.* **2007**, *56*, 461–466.
(10) Boal, A. K.; Ilhan, F.; DeRouchey, J. E.; Thurn-Albrecht, T.; Russell, T. P.; Rotello, V. M. *Nature (London)* **2000**, *404*, 746–748.
(11) Liu, R.; Ren, Y.; Shi, Y.; Zhang, F.; Zhang, L.; Tu, B.; Zhao, D. *Chem. Mater.* **2008**, *20*, 1140–1146.
(12) Rajeshwar, K.; de Tacconi, N. R.; Chenthamarakshan, C. R. *Chem. Mater.* **2001**, *13*, 2765–2782.
(13) Penard, A. L.; Gacoin, T.; Boilot, J. P. *Acc. Chem. Res.* **2007**, *40*, 895–902.
(14) Boettcher, S. W.; Fan, J.; Tsung, C.-K.; Shi, Q.; Stucky, G. D. *Acc. Chem. Res.* **2007**, *40*, 784–792.
(15) Mackenzie, J. D.; Bescher, E. P. *Acc. Chem. Res.* **2007**, *40*, 810–818.
(16) Kotsokechagia, T.; Cellesi, F.; Thomas, A.; Niederberger, M.; Tirelli, N. *Langmuir* **2008**, *24*, 6988–6997.
(17) Husing, N.; Launay, B.; Doshi, D.; Kickelbick, G. *Chem. Mater.* **2002**, *14*, 2429–2432.
(18) Calleja, G.; Serrano, D. P.; Sanz, R.; Pizarro, P. *Microporous Mesoporous Mater.* **2008**, *111*, 429–440.
(19) Dong, W. Y.; Sun, Y. J.; Lee, C. W.; Hua, W. M.; Lu, X. C.; Shi, Y. F.; Zhang, S. C.; Chen, J. M.; Zhao, D. Y. *J. Am. Chem. Soc.* **2007**, *129*, 13894–13904.
(20) Zhang, X.; Zhang, F.; Chan, K. Y. *Appl. Catal. A* **2005**, *284*, 193–198.
(21) Inumaru, K.; Kasahara, T.; Yasui, M.; Yamanaka, S. *Chem. Commun.* **2005**, 2131–2133.

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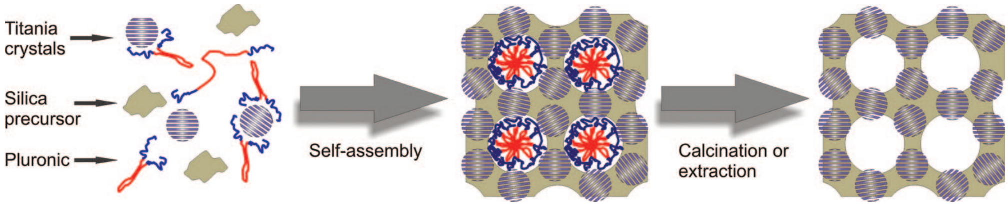
Scheme 1. Formation of Nanocomposite Titania−Silica Mesoporous Films Using Pre-Formed Titania Nanocrystals Stabilized by the Pluronic Polymer and Amorphous Sol−Gel Silica Precursor



composite can benefit, for example, from the antibacterial and self-cleaning properties of crystalline titania[26] and the mechanical and thermal stability and excellent optical properties of periodic mesoporous silica in combination with a well-defined pore architecture.[27] Combining both components, novel materials can be obtained exhibiting, for example, exceptional self-cleaning ability and high photocatalytic efficiency in gas phase reactions.

The preparation of mesoporous titania−silica coatings is a challenging task as the efficient performance of such films requires homogeneous distribution of both components, high loading and high crystallinity of the titania phase, and a controlled porosity exhibiting large accessible surface area, suitable pore size, and connectivity. Moreover, the development of effective procedures for the preparation of highly crystalline titania−silica films at low temperatures is of great interest because of the possible use of thermally less stable substrates, higher energy efficiency, and simplified processing.

In view of these requirements, several routes toward the preparation of mesoporous titania−silica composites have been explored. The most commonly used techniques are based either on a self-assembly of sol−gel processed molecular precursors of TiO_2 and SiO_2 with a structure-directing agent[14,17–20,28,29] or on grafting of titania precursors on the pre-formed mesoporous silica layers.[23−25] However, the titania phase in these composites is initially amorphous and has to be calcined at least at 400 °C to induce its crystallization. To overcome this problem, pre-formed titania nanocrystals have been combined with periodically organized mesoporous silica.[13,21,22] However, the reported methods deal with relatively large titania particles, whose size significantly exceeds that of the pore system. As a consequence, the crystals do not participate in the mesostructure formation and the potential advantage of the high surface-to-bulk ratio at the nanoscale cannot be fully exploited. To be compatible with the silica mesopore structure, the size of the titania crystals should be in the range of a few nanometers. Even if the preparation of colloidal solutions of such small nanoparticles has proven to be difficult as a result of their tendency toward irreversible agglomeration, recently a suitable synthetic technique has been developed.[3,4,16,30–32]

In this work we have used the so-called "brick and mortar" strategy[9,10,33] to prepare titania−silica composite films suitable for gas phase photocatalysis. Pre-formed titania nanocrystals were fused with surfactant-templated sol−gel silica, which acts as a structure-directing matrix and as a chemical glue (Scheme 1). Stable colloidal solutions of titania crystals 4−5 nm in size were obtained by a nonaqueous low-temperature route.[30–32] We found that the particles disperse easily in high concentration of up to 10 wt % in the presence of block-copolymers of the Pluronic family (PEO_x-PPO_y-PEO_x) to form transparent colloidal solutions. The block copolymers of the polyether type are especially useful as they stabilize the particles by weakly bonding to the particle surface without covalent functionalization; the latter could deteriorate their photocatalytic activity. At the same time, Pluronic acts as a structure-directing agent in the film assembly. The sol−gel derived silica is especially suitable as a "mortar" as it condenses already at low temperatures, thus leading to the formation of mechanically stable continuous films of high optical quality.

The different chemical composition of "bricks" and "mortar" components in these nanocomposites makes them easily distinguishable, enabling deeper insights into the role of the individual synthesis parameters on the homogeneity of particle distribution and the morphology of the mesostructure. One of the important parameters is the nature of the structure-directing agent, because it influences both the solubilization of particles and their self-assembly properties. We examined two Pluronic polymers with different lengths of hydrophilic polyethyleneoxide chains, namely, Pluronic P123 ($x, y = 20, 70$) and Pluronic F127 ($x, y = 106, 70$). To make full use of the developed procedure, we have focused on the low-temperature processing of the films. For this purpose, two different strategies to remove the template were applied, namely, calcination at the lowest possible temperature and template extraction. The calcination was deliberately performed at the lowest temperature of template combustion at 300 °C. Finally, the accessibility of the titania surface and its photocatalytic activity in the resulting composites was investigated in the photocatalytic oxidation of NO.

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(22) Allain, E.; Besson, S.; Durand, C.; Moreau, M.; Gacoin, T.; Boilot, J. P. *Adv. Funct. Mater.* **2007**, *17*, 549–554.
(23) Reddy, E. P.; Sun, B.; Smirniotis, P. G. *J. Phys. Chem. B* **2004**, *108*, 17198–17205.
(24) López-Muñoz, M.-J.; Grieken, R. v.; Aguado, J.; Marugán, J. *Catal. Today* **2005**, *101*, 307–314.
(25) van Grieken, R.; Aguado, J.; López-Muñoz, M. J.; Marugán, J. *J. Photochem. Photobiol. A: Chem.* **2002**, *148*, 315–322.
(26) Gaya, U. I.; Abdullah, A. H. *J. Photochem. Photobiol., C* **2008**, *9*, 1–12.
(27) Dunn, B.; Zink, J. I. *Acc. Chem. Res.* **2007**, *40*, 747–755.
(28) Ogawa, M.; Ikeue, K.; Anpo, M. *Chem. Mater.* **2001**, *13*, 2900–2904.
(29) Wu, C.-W.; Kuwabara, M. *J. Inorg. Organomet. Polym.* **2003**, *13*, 131–141.
(30) Niederberger, M.; Garnweitner, G.; Pinna, N.; Neri, G. *Prog. Solid State Chem.* **2005**, *33*, 59–70.
(31) Niederberger, M.; Bartl, M. H.; Stucky, G. D. *Chem. Mater.* **2002**, *14*, 4364–4370.
(32) Polleux, J.; Pinna, N.; Antonietti, M.; Hess, C.; Wild, U.; Schlögl, R.; Niederberger, M. *Chem.—Eur. J.* **2005**, *11*, 3541–3551.
(33) Boal, A. K.; Gray, M.; Ilhan, F.; Clavier, G. M.; Kapitzky, L.; Rotello, V. M. *Tetrahedron* **2002**, *58*, 765–770.

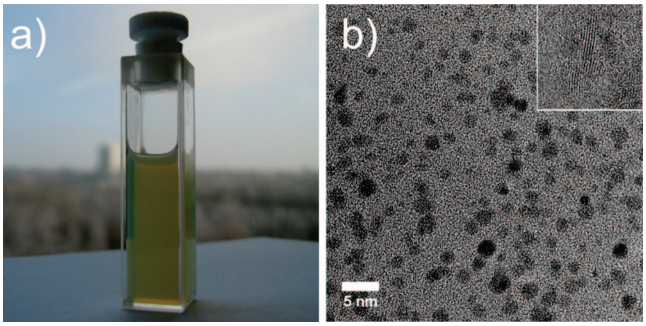

Figure 1. Colloidal solution (9 wt % in THF) of Pluronic-stabilized titania nanoparticles synthesized at 60 °C (a) and TEM image of the Pluronic-stabilized particles (b). The inset 5 nm × 5 nm in size shows the high resolution TEM (HR-TEM) of a single nanoparticle.

Results and Discussion

Completely crystalline titania nanoparticles serving as "bricks" were prepared by reacting titanium tetrachloride with benzyl alcohol at 40−150 °C.[31] Reaction time and temperature are the decisive parameters in the synthesis, resulting in anatase particles of 4−5 nm in size after treating the reaction mixture at 60 °C for 24 h (Figure 1b, Figure S4 in Supporting Information). A further increase in reaction time and temperature leads to particle agglomeration and/or particle growth.

While the obtained particles are insoluble both in water and in organic solvents, they redisperse easily at concentrations of up to 10 wt % in tetrahydrofuran in the presence of a suitable Pluronic block-copolymer (Figure 1a). The time needed to completely redisperse the particles depends on the type of Pluronic copolymer, being 2 and 12 h for Pluronic P123 and F127, respectively. The nature of the interactions of the Pluronic polymers with the surface of titania particles is still unclear, although experiments with other surfactants suggest that the poly(ethylene oxide) groups interact with the surface titanium atoms via multiple coordination bonds.[34] Apparently, the difference in hydrophilicity and the number of ethylene oxide groups in the polymer blocks have a decisive influence on their coordination and solvation behavior.

The established procedure for the preparation of the silica sol[1,35] had to be modified to make it compatible with the stability requirements of the titania colloids, especially the use of THF as a solvent and the low pH range at which titania colloids are stable. The optimized composition of silica sols contains TEOS as silica precursor, water as hydrolysis agent, HCl as a hydrolysis catalyst, and THF as a solvent in the molar ratio of 1.0:9.1:0.016:2.7. For the coating solutions, the amount of Pluronic was calculated as a weight ratio with respect to the total weight of metal oxides. The optimum amount regarding the complete redispersion of titania nanoparticles and the periodicity of the formed mesostructure was found to be 150 wt % and 100 wt % for Pluronic P123 and Pluronic F127, respectively.

For the preparation of the "brick and mortar" titania−silica nanocomposites, a certain amount of silica "mortar" was added to the copolymer-stabilized colloidal solution of nanocrystalline titania "bricks". To investigate the influence of the particles on the development of the mesostructure, the ratio of "bricks" and "mortar" components was varied. The solutions were prepared in such a way that the relative amount of the copolymer with respect to the total amount of metal oxides was kept constant.

Films Templated with Pluronic P123. X-ray diffractograms show that the addition of nanoparticles to the silica sol has a strong influence on the mesostructure of the formed films. The reference films prepared without titania particles exhibit small angle XRD patterns corresponding to mesostructured domains with a periodicity *d* of 7 nm (Figure S2, Supporting Information). When increasing the particle concentration, the mesostructure becomes less organized. Addition of more than 10% of particles leads to the almost complete disappearance of the mesostructure ordering (see Figure S2, Supporting Information).

The morphology of the composite films and the distribution of both oxides were investigated with electron microscopy. The TEM images of the films containing 10 wt % nanoparticles reveal a porous mesostructure with inclusions of titania nanocrystals, which are identified as darker spots and whose lattice fringes are observed in HR-TEM (Figure 2a). According to scanning transmission electron microscopy in high angle annular dark field mode (STEM-HAADF) coupled with EDX analysis (Figure 2b,c), the film's morphology is inhomogeneous. Addition of even small amounts of nanoparticles leads to a microphase separation and coexistence of mesoporous domains and the nonporous agglomerates (Figure 2c). EDX analysis of the corresponding areas (Figure 2b) demonstrates that the domains with periodic mesoporosity (inset 1) are composed almost solely of silica, while the nonorganized agglomerates of particles (inset 2) contain a high concentration of titania.

To sum up, the addition of the colloidal titania nanoparticles to the silica sol−gel precursor templated with Pluronic P123 as a structure-directing agent has a strong influence on the self-assembly and the meso-organization of the films. Only at very low concentration can the particles be incorporated into the mesoporous silica matrix with a homogeneous distribution in the bulk of the film (Figure 2a). Higher particle concentrations beyond 20% lead to strong distortion or complete disorder of the mesoporous structure (Figure S3, Supporting Information). Therefore, Pluronic P123 is not a suitable stabilizing agent for achieving a homogeneous distribution of nanoparticles within the silica phase. As high particle concentrations can be important for certain applications, the influence of a different template on the dispersibility of the particles and their final distribution in the films was investigated.

Films Templated with Pluronic F127. *Mesostructure Characterization.* In contrast to Pluronic P123, the use of the larger and more hydrophilic Pluronic F127 block copolymer permits the preparation of composite titania−silica mesoporous architectures that can accommodate a larger amount of nanocrystals without any significant perturbation of the mesostructure periodicity. Even for films with a

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(34) Yang, P. D.; Zhao, D. Y.; Margolese, D. I.; Chmelka, B. F.; Stucky, G. D. *Nature (London)* **1998**, *396*, 152–155.

(35) Zhao, D.; Yang, P.; Melosh, N.; Feng, J.; Chmelka, B. F.; Stucky, G. D. *Adv. Mater.* **1998**, *10*, 1380−1385.

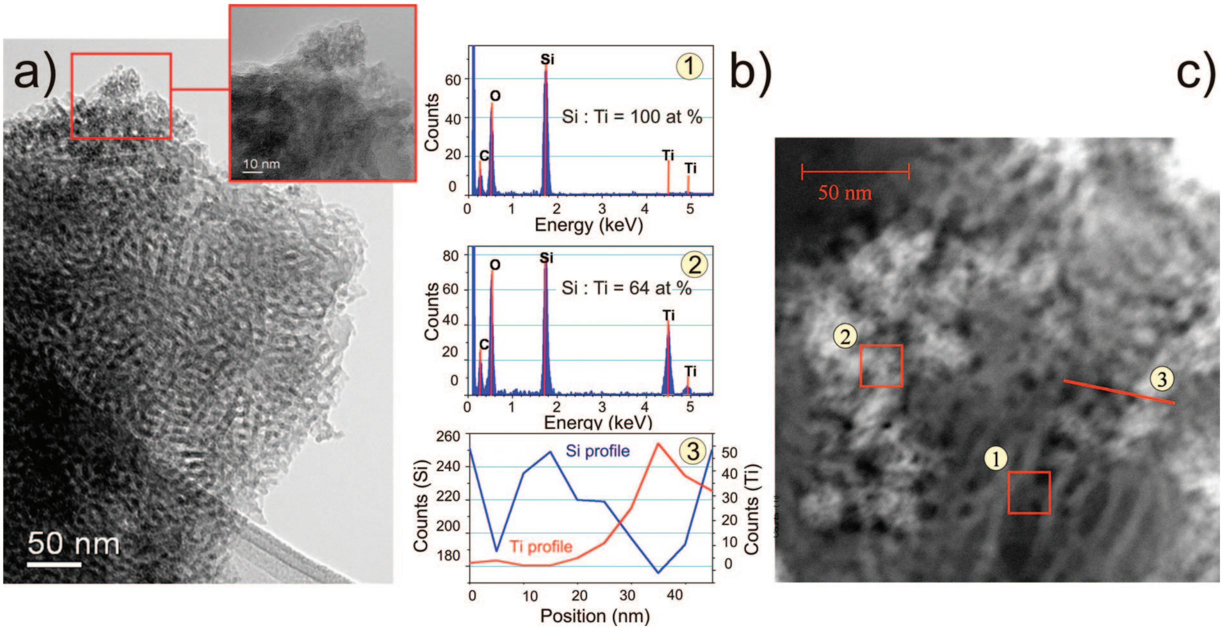

Figure 2. Electron microscopy of the titania−silica film templated with Pluronic P123 and containing 10% particles after calcination at 300 °C: (a) TEM image demonstrating the mesoporous film structure with embedded titania nanocrystals, which are shown in the inset, (c) STEM-HAADF image, and (b) EDX analysis of the selected areas marked in (c).

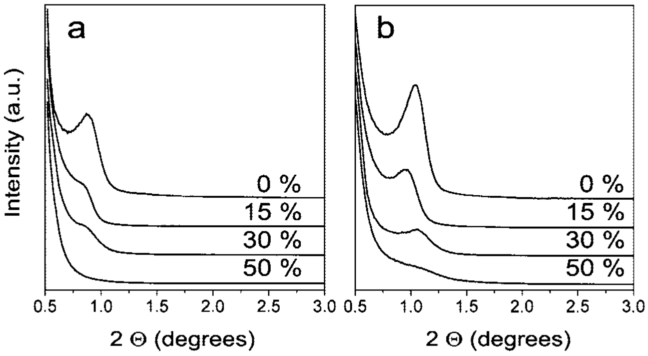

Figure 3. Small-angle XRD patterns of titania−silica “brick and mortar” films with various particle contents templated with Pluronic F127 after treatment at 100 °C (a) and 300 °C (b). The presence of the diffraction peak at low angles for the composite films with different particle contents demonstrates the preservation of the pore ordering after particle addition, although the decrease of the diffraction peak intensity demonstrates the decrease in the pore structure periodicity with increasing particle content.

particle content of up to 30 wt %, the diffraction signals at small angles are still observed, indicating the presence of a periodic mesostructure (Figure 3).

TEM images of the films with different particle concentrations calcined at 300 °C are shown in Figure 4. The pure silica films feature a periodic mesoporous structure with ellipsoidal pores 8.5 × 5.5 nm in size and periodic distances of 13 by 10 nm as derived from the Fourier transform of the images (inset). The addition of particles leads only to some slight deterioration of the mesostructure periodicity and an increase in the pore size ranging from 9 to 11 nm. The titania crystals form small agglomerates of 5 to 14 nm in diameter, which are homogeneously embedded within the pore walls throughout the complete volume of the films. The pores have a spherical rather than ellipsoidal shape, probably due to the presence of nanocrystals in the walls that might reduce the pore shrinkage during calcination.

Obviously, Pluronic F127 is much more suitable for the self-assembly of titania nanoparticles with silica precursor compared to the smaller and more hydrophobic Pluronic P123. The mesostructure is able to include up to 30 wt % of particles without significant changes.

Crystallinity and Porosity of Low-Temperature Processed Films. The crystalline anatase phase in the films can be easily detected by its Raman modes at 144 cm^{-1} (E_g), 398 cm^{-1} (B_{1g}), 518 cm^{-1} (A_{1g}), and 639 cm^{-1} (E_g).[36,37] As seen in the Raman spectra, the intensity of titania vibrational modes increases consistently with the particle content in the precursor solution (Figure 5A).

The Pluronic F127 template was removed either by calcination at 300 °C or by extraction with EtOH at 80 °C. The efficiency of the template removal in both cases was also followed by Raman spectroscopy. The Raman spectra of differently treated films with identical composition were normalized using the anatase band at 144 cm^{-1}, assuming that the amount and size of titania crystals are maintained after calcination. Figure 5B shows that the C−H stretching vibrations of Pluronic polyalkyleneoxide moieties in the range of 2700−3100 cm^{-1} observed in the freshly deposited film vanish after its calcination at 300 °C because of the combustion of the template. The intensity of these peaks also drastically decreases after extraction of films with EtOH under reflux for 4 h and further decreases after prolonged extraction for 16 h, demonstrating the efficiency of this procedure for the removal of the template.

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(36) Baddour-Hadjean, R.; Bach, S.; Smirnov, M.; Pereira-Ramos, J. P. *J. Raman Spectrosc.* **2004**, *35*, 577–585.

(37) Smirnov, M.; Baddour-Hadjean, R. *J. Chem. Phys.* **2004**, *121*, 2348–2355.

(38) Guo, C.; Liu, H.; Wang, J.; Chen, J. *J. Colloid Interface Sci.* **1999**, *209*, 368–373.

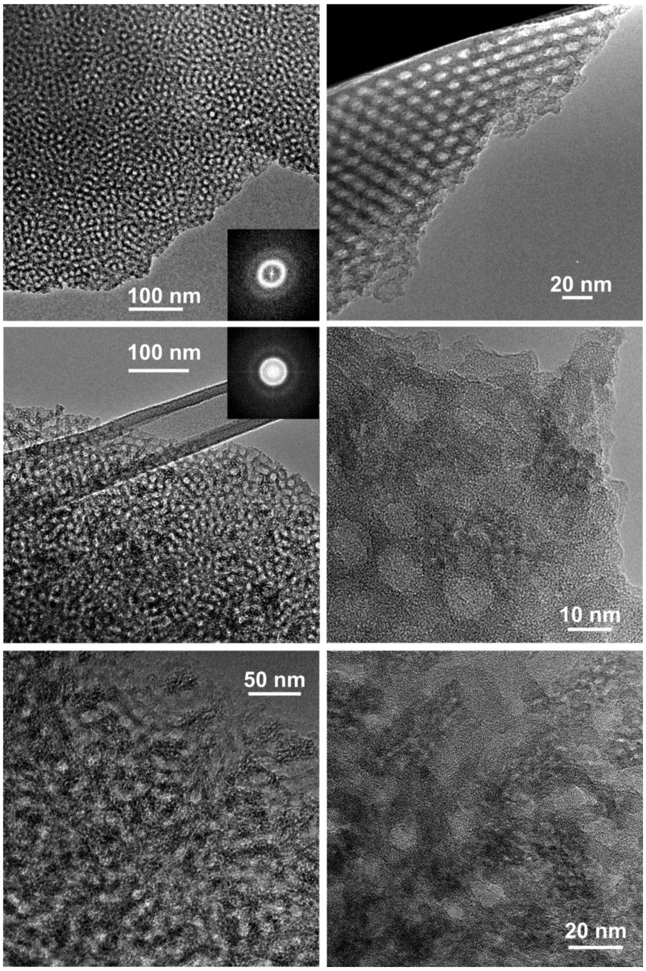

Figure 4. TEM images of titania−silica "brick and mortar" films templated with Pluronic F127 containing 0 wt % particles (first row), 15 wt % particles (second row), and 30 wt % particles (last row) after calcination at 300 °C. The insets show the Fourier transform of the same picture revealing the periodic mesopore structure.

The textural properties of the films containing different amounts of titania particles, de-templated either by calcination or extraction, were quantitatively studied by Kr adsorption at 77 K (Figure 6, Table 1). The concentration of nanoparticles in the films calcined at 300 °C has a decisive effect on the porosity. The films prepared without any TiO_2 nanoparticles exhibit very small surface area and pore volume (Figure 6, inset), which we attribute to pore blocking preventing the access of adsorbate molecules at the very low temperature of the adsorption experiment. Apparently, the voids in the film (see the TEM image in Figure 4a) are linked only via narrow pores (microporous defects or cracks), thus replicating the space occupied by the spherical micelles embedded within the unperturbed siliceous framework. The samples containing 10−15% of TiO_2 nanoparticles have a much larger specific surface area and pore volume, with a smaller degree of pore blocking as follows from the shape of the hysteresis loop. The presence of the TiO_2 nanoparticles appears to open the continuous siliceous framework and facilitate the access of krypton. Furthermore, TiO_2 nanoparticles may act as an oxidation catalyst, accelerating the complete removal of the template. The porosity of the films containing 30% of nanoparticles is well-developed, featuring very narrow pore size distribution, very large pore volume, and the absence of pore blocking. The narrowness of the pore size distribution follows from the steepness of the adsorption and desorption branches; however, at this point it is difficult to determine the actual pore size distribution because of the properties of Kr far below its triple point.

The increase in particle content to 50% leads to a deterioration of the mesoporous system, which is characterized by a wider pore-size distribution and smaller pore volume, the large specific surface area being, however, preserved. Extracted films prepared without particles do not show mesoporous sorption characteristics, probably due to the fact that the pores are still partially filled with the template, which cannot be completely removed by extraction. This was confirmed by the observation that calcination at 400 °C leads to a substantial gain in surface area and pore volume (Table 1, Figure S4, Supporting Information). Films containing 10−15 wt % of nanoparticles are characterized by two steps on their desorption branch, which corresponds to a bimodal pore system. Characteristically, the calcined and extracted samples containing 30 wt % of nanoparticles are practically identical with respect to their porosity. This supports the hypothesis that the structure of the solid phase is strongly affected by the presence of nanocrystals such that extraction is sufficient for the removal of the polymer. The extracted films containing 50 wt % of nanoparticles exhibit a pore volume 70% larger than the calcined ones, which could be attributed to a substantial shrinkage of the silica matrix upon treatment at higher temperatures.

Titania Accessibility and Photocatalytic Activity. To assess the functionality of titania crystals in the composite films, the activity of composite films was tested in the photocatalytic oxidation of NO (Table 2). This reaction was selected for two reasons. First, it is of environmental importance as one of the technologies for the removal of NO, which is present in the range of several hundred ppb in the atmosphere of large cities. Second, it has been suggested as an ISO standard for testing the photocatalytic activity of materials in the gaseous phase. The adsorbed NO molecules react first with $OH^•$ or $HO_2^•$ radicals to form adsorbed HNO_2, which is further photooxidized to NO_2. NO_2 is either desorbed or converted to HNO_3. The degree of conversion to HNO_3 depends on the residence time of NO_2 in the adsorbed state and is substantially enhanced by the porosity of the employed photocatalyst. Large-surface mesoporous films containing crystalline TiO_2 are especially effective when the photodecomposition mechanism requires adsorption of species prior to reaction on the surface. The amount of adsorbed substances is increased due to the large surface area, which enhances their decomposition.

For the photooxidation of NO, both extracted and calcined films were tested. Here we selected the films with the organized periodic mesostructure, that is, those with a titania particle content up to 30%. While films of pure silica are inactive, the activity of those containing TiO_2 nanocrystals increases almost linearly with the TiO_2 content (Figure 7), approaching the conversion efficiency of 3.9−4% for the films composed solely of titania particles taken as a reference. This linearity confirms the homogeneous distribution of the

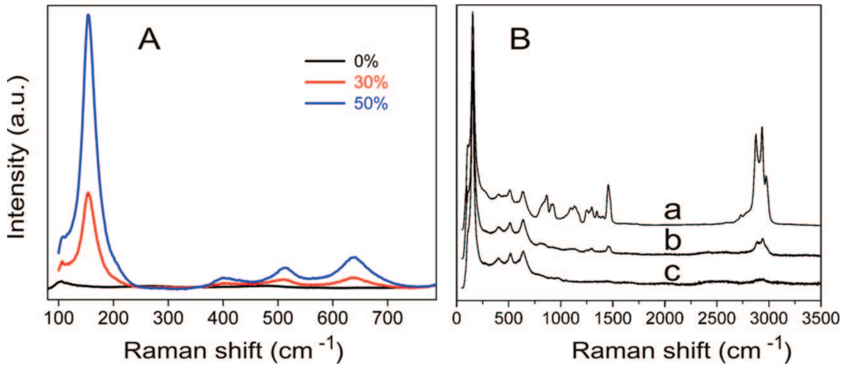

Figure 5. (A) Raman spectra of titania−silica “bricks and mortar” films templated with Pluronic F127 and containing various amount of particles. The spectra were normalized to the intensity of the C−H stretching vibrations of Pluronic.[38] (B) Raman spectra of composite titania−silica films with 30 wt % of nanoparticles templated with Pluronic F127 and subjected to different postsynthesis treatments: nontreated (a), treated at 100 °C and extracted with EtOH under reflux (b), and calcined at 300 °C (c).

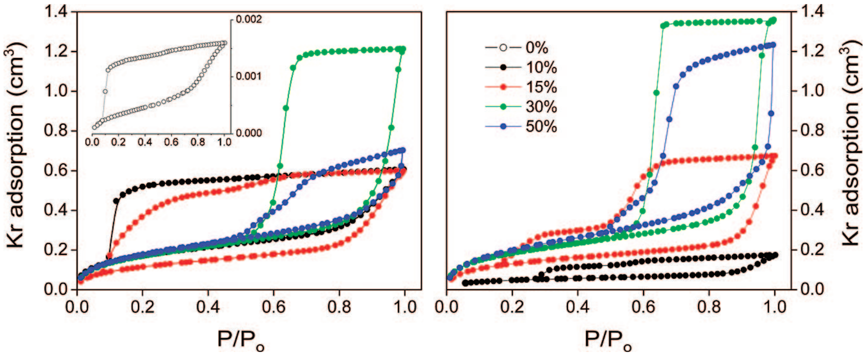

Figure 6. Adsorption isotherms of Kr at 77 K on titania−silica “bricks and mortar” films templated with Pluronic F127 and containing various amounts of particles: calcined at 300 °C (left) and treated at 150 °C followed by extraction with EtOH under reflux (right). The inset shows an adsorption isotherm for a film containing 0% of titania nanocrystals.

Table 1. Textural Parameters and Porosity of Films Calcined at 300 °C or Treated at 150°C with Subsequent Extraction with EtOH, Respectively[a]

TiO_2, wt %	treatment	S_{spec}, cm^2/cm^2	V_{spec}, mm^3/cm^2	character of porosity, *D*, nm
0%	calc	17.4	0.0020	pore blocking
	extr	∼0		
	extr + calc 400 °C	264.9	0.0197	voids + micropores
20%	calc	213.5	0.0202	pore blocking
	extr	59.3	0.0059	bimodal
30%	calc	167.0	0.0229	less pore blocking
	extr	166.8	0.0232	bimodal
50%	calc	230.0	0.0425	7.4
	extr	236.3	0.0465	7.9
70%	calc	240.4	0.0246	wide pore size distribution
	extr	258.0	0.0413	6.4

[a] S_{spec} and V_{spec}, BET surface area and pore volume, are related to the geometric size of the support, respectively; $D = 4V/S$, effective pore size calculated from the pore volume and surface area.

Table 2. Efficiency of NO Conversion in Photocatalytic Measurements for Calcined and Extracted Films with Various Particle Contents Measured Directly after Switching on the Light (time = 5 min) and after 2 h of Illumination

conversion (%)	calcined				extracted			
particle content	0%	10%	15%	30%	0%	10%	15%	30%
light on	0.00	0.69	1.48	1.92	0.00	0.69	1.13	2.19
after 2 h	0.00	0.89	0.99	0.99	0.00	0.69	0.79	1.29

particles and their good accessibility for molecules from the gas phase. We also note that the activities of low-temperature extracted films are as high as those of calcined films. This opens up new perspectives for the preparation of crystalline photocatalytic coatings at low temperatures, which would make even plastic substrates acceptable for this application. Further increases of the photocatalytic activity of those films are expected for thicker films and for films with particle contents over 50 wt %.

Possible Self-Assembly Mechanism of the Composite Titania−Silica Mesostructures. The obtained experimental data demonstrate that the composite titania−silica films with organized mesoporous architecture can be assembled from the Pluronic-stabilized nanoparticles and hydrolyzed silica precursor. We now address the question of how this meso-organization takes place. In a classical evaporation-induced self-assembly (EISA) process, the mesostructure formation is directed by the micelles of a surfactant, which self-assemble in the presence of inorganic precursors into supramolecular periodic structures. In contrast, in the “brick and mortar” procedure used here, the surfactant molecules are

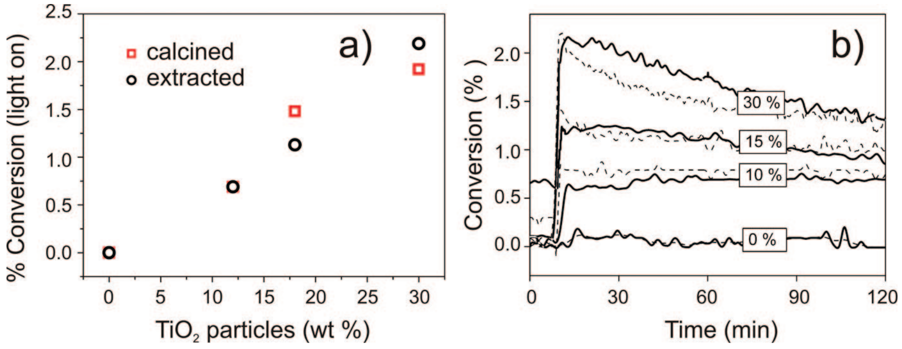

Figure 7. Photocatalytic activity of extracted (black) and calcined (red) titania−silica films with different particle contents in the photocatalytic oxidation of NO measured after switching on the light (time = 5 min) (a) and the corresponding photocatalysis measurement curves of extracted (solid lines) and calcined (dashed lines) samples (b).

at least partially bound to the nanocrystals' surface, thus lowering the concentration of free surfactant in solution and altering the conditions for the micelle formation. Therefore, several different ways of interaction between particles, silica precursor, and template have to be considered for the final EISA step.

We can hypothesize two extreme cases for the self-assembly process. In the first case, the surfactant-stabilized particles act themselves as the structure building blocks and arrange in a liquid-crystalline periodic structure, which is impregnated by the silica oligomers. In the second case, addition of silica precursor leads to partial or complete desorption of the surface-bound template due to replacement by hydrolyzed silica, and a self-assembly of liberated surfactant molecules with inorganic components takes place in a classical EISA process. Although experimental proof on the different routes of self-assembly could not yet be obtained, the structural resemblance of the pure silica sample with the composite films gives evidence that their formation mechanism does not differ significantly. Another point is that no formation of periodic structure is observed for the polymer-stabilized particles without a silica component. We therefore propose that the mesostructure formation follows rather the second case and that it involves several dynamic equilibrium steps such as adsorption/desorption of surfactant on/from the titania or silica surface, reversible interactions between titania and silica components, or participation of partly particle-bound template in micelle formation. These equilibrium steps should be influenced by the surface chemistry of titania particles and the nature of the surfactant, as was demonstrated for two different types of Pluronic molecules.

Conclusion

The "brick and mortar" approach utilizing Pluronic-stabilized crystalline titania nanoparticles and amorphous sol−gel derived silica precursors enables the fabrication of composite titania−silica films with periodic mesoporous architecture. The nature of the Pluronic surfactant plays a decisive role in the mesostructure formation. The structure formation is greatly disturbed due to the presence of particles when Pluronic P123 is utilized as the structure-directing agent. In contrast, the use of larger and more hydrophilic Pluronic F127 enables the preparation of composite titania−silica mesoporous architectures that can accommodate up to 50 wt % of nanocrystals without significant deformation of the mesostructure periodicity. Films with a high degree of crystallinity can be obtained at temperatures as low as 100−150 °C, and the surface of the titania particles is not deactivated with respect to their photocatalytic activity by the surrounding silica matrix or by covalently attached ligands. This makes the "brick and mortar" approach very promising for the preparation of crystalline functional coatings under very mild conditions that are even acceptable for plastic substrates and opens new perspectives for the fabrication of novel mesoporous crystalline composite materials.

Experimental Part

Preparation of Titania Nanoparticles and Titania−Silica Films. Titanium dioxide nanoparticles were synthesized following a modified procedure by Niederberger et al.[31] Titanium tetrachloride (1.5 mL, 13.7 mmol) was dissolved in toluene (10 mL) and added to benzyl alcohol (30 mL, 290.8 mmol) under continuous stirring. The solution was kept at 60 °C for 20 h and then cooled down to room temperature. The particles were separated by centrifugation at 50 000 rcf for 30 min and used without further treatment. As such, the particles contain about 55 wt % of benzyl alcohol according to thermogravimetric analysis; this was taken into account for the adjustment of the TiO_2 content. In a typical synthesis, a solution of Pluronic P123 ($PEO_{20}PPO_{70}PEO_{20}$, 0.6 g) or Pluronic F127 ($PEO_{106}PPO_{70}PEO_{106}$, 0.55 g) in THF (5 mL) was added to nonwashed particles previously separated by centrifugation and stirred overnight until the particles were homogeneously redispersed. Subsequently, the desired amount of silica sol−gel (SG, see below) solution was added followed by stirring for several minutes. The final solutions were transparent or translucent, being of yellow to orange color. If the final solution was not transparent, then some amount of concentrated hydrochloric acid was added dropwise until the solution turned transparent. The SG solution was prepared by adding hydrochloric acid (0.1 M, 11 mL, 1.1 mmol) to tetraethyl orthosilicate (15 mL, 67.3 mmol) in 15 mL of THF under continuous stirring and was stirred for 15 h at room temperature. The compositions of the solutions with different TiO_2/SiO_2 ratios are listed in Table 3 (the values in brackets correspond to the amount of pure oxide).

The films were deposited by dip-coating at 23 ± 2 °C and a relative humidity of 45 ± 10% at a withdrawal rate of 1.8 mm/s and either calcined at 300 °C (with a ramp of 0.6 °C min^{-1}) for 30 min or treated at 100−150 °C for 15 h for their subsequent

Table 3. Composition of the Solutions Used for the Dip-Coating of Thin Films

TiO_2/MO_2, wt %	amount of nanoparticles/ TiO_2	amount of SG (mL)/ SiO_2 (g)
0	0	5.6 mL (0.55 g)
10	0.11 g (0.05 g)	4.5 mL (0.44 g)
15	0.16 g (0.07 g)	3.9 mL (0.38 g)
30	0.27 g (0.12 g)	2.8 mL (0.28 g)
50	0.38 g (0.17 g)	1.7 mL (0.17 g)

extraction with ethanol. The extraction was performed at 80 °C under reflux for 4 to 18 h. The thickness of the obtained films was approximately 300 nm as measured by profilometry (Dektak 150, Veeco Instr.)

Characterization of the Films. High resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscopy in high angle annular dark field mode (STEM-HAADF) were performed using a FEI Titan 80-300 equipped with a field emission gun operated at 300 kV. The particulate samples were prepared by evaporating a drop of a diluted solution of particles with small amounts of Pluronic P123 in THF on a Plano holey carbon coated copper grid. HRTEM of films was carried out by scraping the thin-film samples off the substrate onto a holey carbon coated copper grid. The porosity of the films was determined by the analysis of adsorption isotherms of Kr at the boiling point of liquid nitrogen (approximately 77 K) using an ASAP 2010 apparatus (Micromeritics). Raman spectra were recorded with a LabRAM HR UV−vis (Horiba Jobin Yvon) Raman microscope (Olympus BX41) with a Symphony CCD detection system using a HeNe laser at 632.8 nm. The spectra were taken from material removed from the substrate. X-ray diffraction was carried out in reflection mode using a Scintag XDS 2000 (Scintag Inc.) with Ni-filtered Cu Kα radiation.

The experimental setup for the photocatalytic tests consisted of a gas supply part, the photoreactor, and a chemiluminiscent NO-NOx gas analyzer (Horiba ambient monitor APNA-360). The gaseous reaction mixture was prepared by mixing streams of dry air (1500 mL/min), wet air (1500 mL/min, relative humidity of 100%), and 50 ppm NO/N_2 (approximately 60 mL/min), to obtain a final concentration of NO of 1 ppm at a relative humidity of 50%. The photoreactor was illuminated by four 8 W black lights, thus achieving a UV light intensity of 1 mW/cm^2. Prior to the photocatalytic tests, the photoreactor was purged with the NO/water vapor/air mixture without illumination until a steady NO concentration was achieved at the outlet. 100% NO conversion is equivalent to a photonic efficiency of $\xi = 0.14\%$ assuming a mean irradiation wavelength of 350 nm.

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Supporting Information Available: XRD patterns, TEM images, and adsorption isotherms (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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