Articles

Al-Containing Porous Titanium Dioxide Networks: Sol−Gel Synthesis within Agarose Gel Template and Photocatalytic Activity

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Al-containing titania porous networks have been produced by conducting sol−gel chemistry within the porous structures of agarose gels. The use of the agarose template gives inorganic materials with a homogeneous macroporous structure. The amount of aluminum added to the titania system was studied from 0 to 10 wt % (where wt % corresponds to the ($Al_2O_3 \times 100$)/($Al_2O_3 + TiO_2$) expected from the initial precursor concentrations), and the morphology and crystallization behavior (as a function of both wt % of Al_2O_3 and heating temperature) were characterized along with a study of the photocatalytic efficiency of the materials. The 4 wt % sample was found to have the highest photocatalytic activity observed for the photodecomposition of aqueous methylene blue. For low doping amounts, 0.5 and 1 wt % Al_2O_3, the rutile phase of titania was not observed in the samples heated to 780 °C. Above 4 wt % Al_2O_3, the temperature required for the anatase to rutile phase transformation increased with increasing amounts of aluminum.

Introduction

Titanium dioxide, a wide band gap and nontoxic semiconductor, has been studied extensively in the past in a range of scientific and industrial fields, such as photoinduced water splitting,[1] organic compound degradation,[2,3] dye-sensitized solar cell (DSSC),[4] and for its self-cleaning properties.[5] A recent review on the photoinduced reactivity of titanium dioxide gives an overview of this exciting field.[6] For most applications, it is preferable to have a designed crystal structure and morphology, and nanosized grains. Template synthesis is a useful method for controlling the microstructure of a material. Many templates have been employed to prepare porous metal oxide structures, and examples of these processes have recently been reviewed.[7−11] In general, the templating technique using preformed templates and sol−gel synthesis involves the preparation of the desired template, infiltration of the required metal oxide precursor, hydrolysis and condensation chemistry, followed by removal of the template. This results in a structured metal oxide with morphological characteristics inherited from the initial template, allowing designed pore structure and pore size.

The photocatalytic activity of titanium dioxide depends on various parameters, such as the surface area, the addition of dopants and their concentration, the surface acidity, and the surface sorption properties. Many methods have been applied to modify the properties and hence to improve the photocatalytic activity of TiO_2, including doping with nitrogen,[12,13] carbon,[14] fluoride,[15] or transition metal ions.[16,17] Studies of metal ions doped into TiO_2 or metal oxides mixed with TiO_2 have resulted in changes to the surface area, surface properties, and the band gap of TiO_2,[2,17−19] hence greatly affecting its photoactive behavior.

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Recently, alumina/titania mixtures or Al-doped titania systems have been prepared for a range of applications including paint pigments,[20,21] lithium ion batteries,[22] and dye-sensitized solar cells.[23,24] However, relatively few studies[17,25−29] have detailed the influence of the addition of alumina on the photocatalytic behavior of the Al/Ti samples. The results obtained by different groups indicated in some cases that the presence of alumina was detrimental for photocatalysis (the photodegradation of 4-chlorophenol[25] and methylene blue,[26] $CHCl_3$ oxidation, and CCl_4 reduction[17]), but beneficial for the removal of nitrogen oxides,[27] bromate ion reduction,[28] and 2-chlorophenol degradation,[29] when compared to pure titanium dioxide. These seemingly contradictory results indicate the complexity of the mixed oxide or doped oxide systems that stem from the wide range of synthesis routes, different alumina to titania ratios, and hence final properties of the sample.

This study aimed to determine the most effective Al/Ti ratio for the photocatalytic degradation of methylene blue when using a mixed precursor sol−gel synthesis route. In addition to the variation in composition, control over the porous structure was also achieved by the use of agarose gels as the reaction medium in which the mixed precursor sol−gel chemistry was conducted. By infiltrating mixed alumina and titania precursor solutions into the agarose gel and then conducting hydrolysis and condensation reactions, porous networks of Al-containing titania were achieved. The morphology of the samples, the crystallization characteristics, and the surface properties were studied along with the photocatalytic activity of the samples, measured by the degradation of methylene blue.

Experimental Section

Materials. The agarose powder used for the template preparation was of Molecular Biology Grade from Scientifix. The metal alkoxide precursors, titanium isopropoxide (TIP, 97%) and aluminum isopropoxide (AIP, 98%), were purchased from Aldrich. Ethanol (99.5%) and isopropanol (99.5%) were from Univar. The methylene blue used to determine photodegradation efficiencies was from BDH.

All chemicals were used as received. The water used in all experiments was produced in a Millipore Milli-Q purification system and had a resistivity higher than 18.2 MΩ cm.

Synthesis. *Agarose Gel.* Agarose powder was added slowly to water to make a 3 wt % aqueous agarose solution under vigorous stirring at room temperature, and then heated to boiling for 5 min, acquiring a clear solution. The solution was poured gently into test tubes and cooled to room temperature, forming a transparent agarose gel. The tubes were then covered with Parafilm and left overnight. The prepared gel was cut with a scalpel into small pieces in water. Because isopropanol was used as the solvent for the titanium precursor, the agarose gel underwent solvent exchange. The gel pieces were transferred from a water solution to a water:ethanol (2:1 by volume) solution for at least 6 h, followed by transfer to a water:ethanol (1:2 by volume) solution and finally placed into ethanol. Using similar solvent ratios and soaking times, the gel pieces were then transferred from the ethanol into isopropanol. The agarose gel pieces were stored in the isopropanol ready for use.

Al/TiO$_2$. The required amount of AIP powder was dissolved in a 70 wt % TIP isopropanol solution by reflux (80 °C) for 1 h. The agarose gel pieces were soaked in this solution for 16 h, followed by 8 h in an isopropanol/water (1:1 by volume) solution for hydrolysis. The white hybrid amorphous titania/agarose pieces were dried in air at room temperature for 36 h, and then placed in an oven at 60 °C for 5 h. Finally, the samples were calcined in a laboratory furnace (31165A, B&L Tetlow) under flowing air at 450 °C for 10 h (heating ramp 3.5 °C min^{-1}) to remove the agarose template and induce crystallization of the inorganic.

Characterization. Thermogravimetric and differential thermal analyses were conducted on a Mettler Toledo TGA/SDTA851e thermogravimetric analyzer. The specific surface area of the samples was determined by nitrogen sorption on a Micromeritics Tristar 3000 surface area and porosity analyzer. A Philips XL 30 FEG scanning electron microscope (SEM) was used to examine both the original agarose gel template structure (after drying using a critical point drying technique) and the prepared inorganic materials. For X-ray powder diffraction (XRD), the materials were crushed and ground to a fine powder by an agate mortar, and then 10 wt % high purity Si powder (SRM 640b, NIST) was mixed as a reference. The XRD data were collected on a Philips PW 1800 powder X-ray diffractometer with Cu Kα radiation. The UV−vis reflecting spectra of the ground fine powder were recorded on a Cary 5G UV−vis−NIR spectrophotometer. A Varian ICP-MS was used to determine the Al/Ti ratio of the samples after dissolution in an $HF + HNO_3$ mixture at 110 °C for 2 h.

Photocatalytic Activity Measurement. The ground sample (0.32 g) was placed into an aqueous methylene blue (MB) solution (12.5 mg L^{-1}, 160 mL, pH $\approx$ 6), which was then stirred vigorously in the dark for 30 min. The suspension was poured into a cylindrical reactor surrounded with 10 mm thick recirculated cooling water at 20 °C. A 150 W ARC lamp (Cathodeon Ltd.) with a UV bandpass filter (Kopp Glass, 9863 filter with > 80% transmission from 290−360 nm) was used as the UV source through a quartz window of the reactor. The suspension in the photoreactor was magnetically stirred. The amount of MB after 40 min illumination was determined by running the UV−vis spectrum, detected on a Cary UV−vis spectrophotometer, of the solution after removal of the particulate inorganic by centrifugation. The initial and final concentrations of MB were calculated from the absorbance at 664 nm.

Results and Discussion

The facile preparation of the agarose gel[30] made it the template of choice for this study. After the agarose was dissolved in hot water, it gelled on cooling to form a porous network structure (Figure 1a). The agarose gel is homogeneous in its structure with pore sizes of approximately 100 nm.

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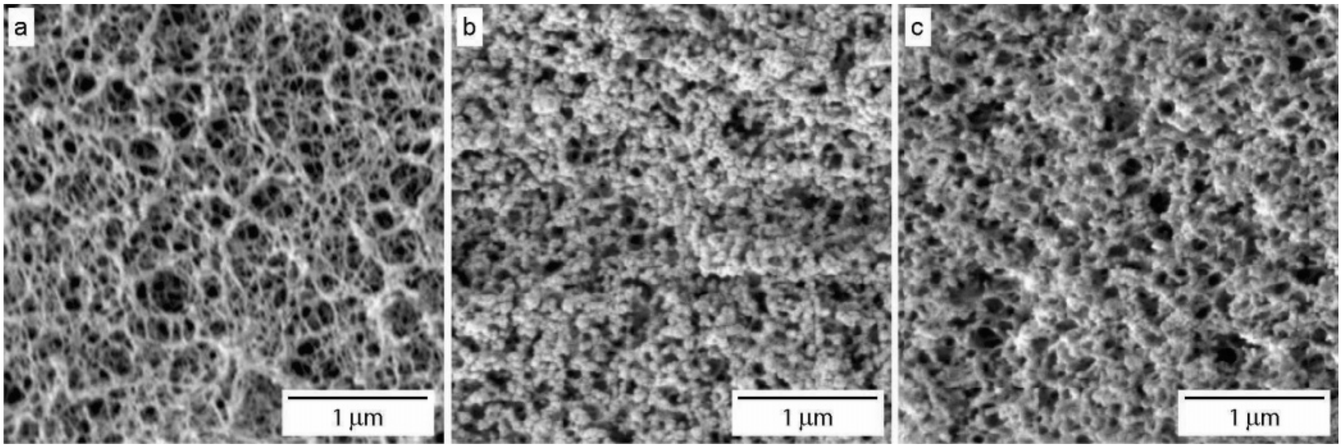

Figure 1. SEM images of (a) the agarose gel used as the template; (b) the titania porous network (calcined at 450 °C); and (c) the 4 wt % Al-doped titania network (calcined at 450 °C).

Table 1. Properties of the Prepared Inorganic Porous Samples

expected[a] Al_2O_3 wt %	expected[a] Al/Ti (atomic)	crystallite size[b] nm	SA[c] $m^2\ g^{-1}$	final Al/Ti (atomic)[d]	anatase fraction[e]
0.0	0.000	14.5 ± 0.4	48 ± 2	0.000	0.28
0.5	0.008	12.6 ± 0.3	73 ± 3	0.008	0.94
1.0	0.016	12.0 ± 0.3	79 ± 3	0.018	1.00
2.0	0.032	11.1 ± 0.2	85 ± 3	0.033	0.45
4.0	0.065	10.1 ± 0.2	98 ± 4	0.063	0.14
6.0	0.100	10.0 ± 0.2	115 ± 5	0.089	0.18
8.0	0.136	9.9 ± 0.2	146 ± 6	0.152	0.58
10.0	0.174	9.9 ± 0.2	198 ± 8	0.123	0.47

[a] As calculated from initial precursor concentrations. [b] Calculated from XRD (samples calcined at 450 °C for 10 h). [c] Surface area (SA) obtained by applying BET theory to the gas sorption data (samples calcined at 450 °C for 10 h). [d] Al/Ti atomic ratio determined from ICP. [e] Anatase fraction of titania sample calculated as detailed in text for samples heated to 780 °C.

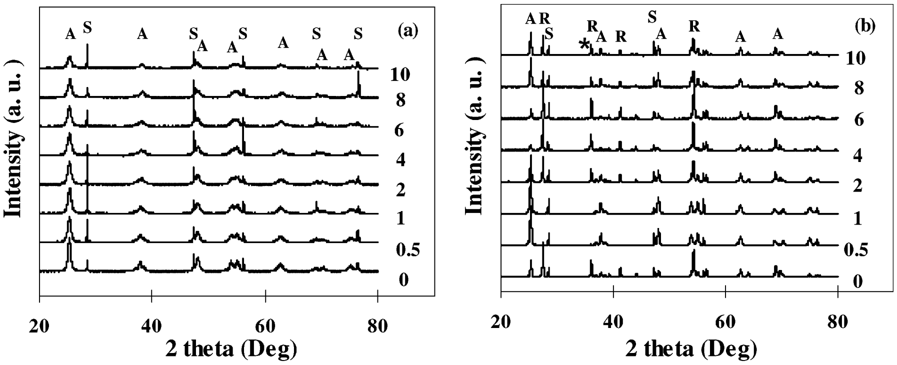

Figure 2. XRD patterns of the samples (0−10 wt %) calcined for 10 h at (a) 450 °C and (b) 780 °C (S, silicon, A, anatase, R, rutile, *, α-Al_2O_3).

The precursors, TIP and AIP, were first mixed and refluxed to form homogeneous solutions of the required weight percent. The agarose gel pieces were soaked in the metal precursor solutions, which, after hydrolysis and condensation, deposited metal oxide on the walls of the structured template. The metal oxide content of the organic/inorganic hybrid materials (i.e., before calcination) was rather consistent across the samples, calculated to be 65.8 ± 0.8% from TGA. From the ICP results, the expected Al/Ti atomic ratio and the observed Al/Ti atomic ratio (Table 1) were consistent up to 4 wt %, and thereafter the observed ratio varied from that expected with an overall increase in Al in the final product with increasing Al in the precursor solution. SEM images of the porous metal oxide networks (achieved by removal of the template at 450 °C in an air atmosphere) showed a morphology similar to those in Figure 1b and c for the 0 and 4 wt % samples. The high porosity and homogeneity of the inorganic structures resemble that of the initial agarose template.

Wide-angle X-ray diffraction was used to determine the crystal phase structure of the synthesized titania-based materials. The XRD patterns of the samples after calcination at 450 °C for 10 h showed only the anatase (A) phase (Figure 2a). By comparison with Si peaks, the cell parameters of the anatase phase were calculated (Figure 3). The *a*-dimension shows no significant change, while the *c*-dimension decreases with the increasing amount of Al added until 4 wt %, after which there was little change. Because Al^{3+} has an ionic radius of 0.54 Å,[31] it could substitute Ti^{4+} (0.61

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(31) *CRC Handbook of Chemistry and Physics*, 85th ed.; Lide, D. R., Ed.; CRC Press LLC: Boca Raton, FL, 2004−2005; pp 12−14.

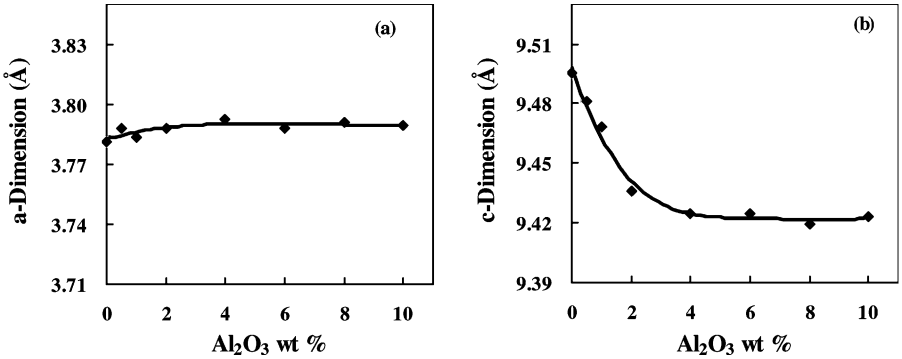

Figure 3. Changes in anatase crystal cell parameters with increasing Al content: (a) *a*-dimension and (b) *c*-dimension.

Å)[31] within the anatase lattice,[32] which would result in a reduction in lattice parameters. From the XRD data, it appears that 4 wt % is the maximum amount of Al substitution. This corresponds to approximately one Al^{3+} substitution in every 4 unit cells of anatase.

The crystal size (Table 1) determined by applying the Scherrer equation to the (101) anatase peak decreased with the increasing presence of Al to 4 wt %. Further increasing the Al quantity above 4 wt % gave no significant change in crystal size. However, the surface area showed a continued increase with Al addition, reaching ~200 m^2 g^{-1} at 10 wt % (Table 1). In general, it is the size of crystals present that determines the specific surface area, but in this case the increase of surface area is clearly not a result of the decreasing crystal size. The increased surface area is believed to be due to the addition of amorphous metal oxide material, which was not observed with XRD.

Further evidence was obtained to support this claim from the XRD patterns of the materials calcined at 780 °C (Figure 2b). For the samples containing 4 wt % or greater, a peak due to the α-Al_2O_3 crystal was observed with the anatase and rutile peaks, indicating crystallization of amorphous alumina that existed in the materials calcined at 450 °C. The XRD results suggest a maximum Al substitution at 4 wt %, above which the excess Al is not incorporated in the anatase solid solution, but remains as a separate phase. The amorphous material that remained in the samples above 4 wt % when heated at 450 °C contributed to the significant increase in the surface area.

The DTA (differential thermal analysis) data (Supporting Information) show a phase-transformation exothermal peak only when the alumina concentration is larger than 3 wt %. At these quantities, the addition of Al reduces transformation of the amorphous to anatase phase change (Figure 4) with a linear relation between the temperature of the exothermic transformation peak and the quantity of Al added to the sample. No clear amorphous titania to anatase phase transformation thermal peaks could be detected in the DTA data when the Al content is less than 4 wt %.

From the XRD data (Figure 2b) of the materials calcined at 780 °C, the TiO_2 phase composition can be calculated (Table 1) by the following equation:[33]

$$F_x = 1/(1 + 1.26*I_R/I_A)$$

where F_x is the fraction of anatase in the materials, I_A is the intensity of the (101) reflection of anatase, and I_R is the intensity of the (110) reflection of rutile. As shown in Figure 2b, a small amount of Al-doping (less than 1 wt %) makes the anatase phase more stable in the samples. However, when the doping amount was increased from 1 to 4 wt %, the anatase fraction decreased and more anatase transformed to rutile. When the amount of Al increased above 4 wt %, the anatase fraction increased again.

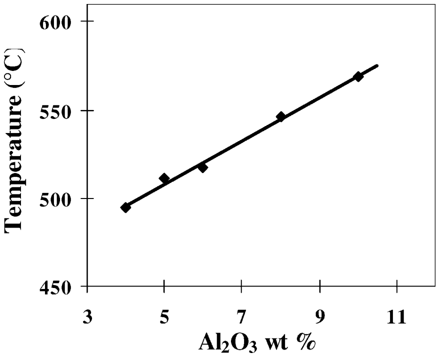

Figure 4. Temperature at which amorphous titania to anatase phase transformation occurs, determined from exothermic peak in the DTA data.

Al-doping in titania has been shown to affect the anatase to rutile phase transformation temperature with enhanced anatase stability reported for a range of dopant amounts from 1.3 to 11.3 wt %.[32,34,35] The results obtained in this work show an initial increase and then a decrease in anatase stability with increasing alumina doping to 4 wt %. Both anatase and rutile crystal structures of TiO_2 have a tetragonal symmetry, but the ions in anatase are more loosely packed than that in rutile. As Al^{3+} is smaller than Ti^{4+}, lattice deformation from Al^{3+} substitution for Ti^{4+} is present in the anatase solid solution.[32] In the samples containing less than 1 wt % alumina, this deformation energy must be released for the anatase to rutile (A−R) phase transition to occur, thereby stabilizing the anatase phase.[32] Increasing the doping quantity between 1 and 4 wt % in the anatase phase resulted in a continuous decrease in the lattice parameter *c*-dimension, while the *a*-dimension remained relatively constant, suggesting that Al^{3+} is substituting for Ti^{4+} preferentially on the body centered and face centered lattice sites in the anatase

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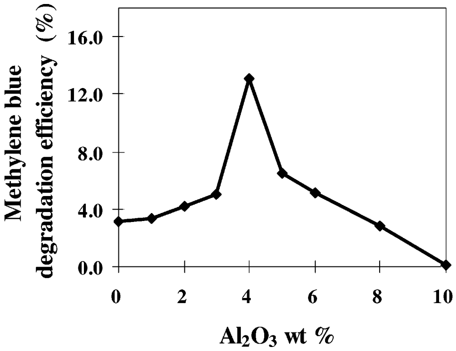

Figure 5. Photodegradation of MB as determined from UV−vis spectroscopy after 40 min of light illumination.

structure.[36] The increase in lattice substitution will introduce more oxygen deficiencies (ODs) into the anatase crystals, providing space for movement of the anions and cations in titania and thus facilitating the phase transformation from anatase to rutile,[32] resulting in a less stable anatase phase above 1 wt %. However, for Al_2O_3 contents above 4 wt %, the Al substitution within the anatase solid solution has reached its maximum (i.e., no more ODs are produced within the anatase solid solution), and any additional Al exists as amorphous alumina. This dispersion of alumina among the anatase particles is believed to stabilize the anatase crystal by grain-boundary pinning in which grain growth is hindered due to increased apparent activation energy for rutile nucleation at the titania−alumina interfaces.[34]

The UV−vis spectra (not shown) do not show a significant change in the wavelength at which reflectance is observed; only a slight blue shift is noted with the increasing quantity of Al-dopant up to 4 wt %. The band gap calculated from this absorption edge shift of the UV−vis spectra increased from 3.08 to 3.15 eV. Hence, the addition of Al induced only a small change in the titania band gap.

The degradation of methylene blue (MB) was used to evaluate the photocatalytic activity of the prepared materials. At 4 wt %, the prepared material was most efficient in degrading the MB (Figure 5), about 4 times as effective as the nondoped titania. These results agree with the improved efficiency that has been observed for porous metal oxide/titania systems as compared to titania materials for the photodecomposition of 2-chlorophenol.[29,37,38] The trend observed in Figure 5 can be explained by the Al doping. The titania absorbs the UV light, which results in redox reactions that degrade the MB. The doping of Al to 4 wt % decreased the crystal size of the anatase and thus increased the photoactive surface area of the prepared materials. Above 4 wt %, the excess amorphous alumina on the surface of titania particles decreases accessibility to photoactive surface, which causes the drop in the degradation efficiency.

Conclusion

Infiltration of mixed metal oxide precursor solutions into agarose gel followed by hydrolysis and condensation reactions resulted in porous network structures of titania/alumina. Doping with Al to 4 wt % decreased the size of the anatase crystal for samples heated to 450 °C, with a corresponding increase in the surface area of the prepared materials. However, at aluminum quantities greater than 4 wt %, the anatase crystal size remained relatively constant, and the surface area continued to increase. The maximum Al-doping using this preparation method was 4 wt %; for increased quantities of Al, amorphous Al_2O_3 was formed in the sample. The presence of the amorphous Al_2O_3 contributed to the increased surface area and hindered the anatase−rutile transformation when the sample was heated to higher temperatures. For the photodegradation of methylene blue, the 4 wt % sample (450 °C) was most efficient.

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Supporting Information Available: Differential thermal analysis data of the samples (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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