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Synthesis and Characterization of Nano titania Particles Embedded in Mesoporous Silica with Both High Photocatalytic Activity and Adsorption Capability

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TiO₂-xSiO₂ composites with a high specific surface area (up to 645 m²/g), large pore volume, and narrow distribution with average pore sizes ranging from 15 to 20 Å have been synthesized by the sol-gel method. The results of characterization by XRD, BET, TEM, FTIR, and DRUV reveal that these TiO₂-xSiO₂ composites exhibit a core/shell structure of a nano titania/Ti-O-Si species modified titania embedded in mesoporous silica. As compared to pure anatase, the embedding of nano titania particles into the mesoporous silica matrix results in a substantial blue shift of absorption edge from 3.2 to 3.54 eV and higher UV absorption intensity, which are attributed to the formation of the Ti-O-Si species modified titania in the interface between titania and silica. The as-synthesized TiO₂-xSiO₂ composites exhibit both much higher absorption capability of organic pollutants and better photocatalytic activity for the photooxidation of benzene than pure titania. The better photocatalytic activity of as-synthesized TiO₂-xSiO₂ composites than pure titania is attributed to their high surface area, higher UV absorption intensity, and easy diffusion of absorbed pollutants on the absorption sites to photogenerated oxidizing radicals on the photoactive sites.

Introduction

Nanostructured titania as a cheap, nontoxic, efficient photocatalyst for the detoxication of air and water pollutants has received much research attention during the past two decades.¹ For its practical application, it is very important to improve the efficiency of titania-based photocatalysts because titania with high photocatalytic activity usually has a relatively lower surface area and low pore volume, which leads to its low adsorption capability of organic pollutants. This limits their practical application because in the dark or under the irradiation of weak light, these titania photocatalysts could not efficiently decrease the concentration of pollutants in air or water for later irradiation. Therefore, a photocatalyst with both high photocatalytic activity and adsorption capability is desirable. To overcome this problem, two strategies have been developed: one is the synthesis of mesoporous titania with high specific surface area² and another is the combination of titania materials with absorbent.^{3,4} For the former strategy, although many cases of the synthesis of mesoporous titania have been reported, in most of them titania exists in an amorphous or semicrystalline phase that has low photocatalytic activity. There are few reports on the synthesis of stable mesoporous titania with a crystalline wall that has a high photocatalytic activity.^{2h-j} It has been proven that the later strategy is relatively easy to accomplish. As an absorbent, silica is the best candidate as it is easy to synthesize silica with a large specific surface area and pore volume, and also, silica has no absorption in the range of UV. There have been many reports on titania-silica mixed oxides as photo-

catalysts. The methods of synthesizing titania-silica mixed oxides include grafting titania on silica support⁵ and fabricating titania-silica composites.⁶⁻¹³ By choosing silica with a high surface area and large volume, it is easy to obtain a photocatalyst with high adsorption capability by grafting titania on silica support. But its photocatalytic activity is no good because of the longer transport distance from adsorption sites to photoactive sites. It is hoped that a photocatalyst with both high photocatalytic activity and adsorption capability by fabricating titania-silica composites would be obtained. But the reported titania-silica composites with high photocatalytic activity have a relatively low specific surface area.¹⁰⁻¹³ The ideal titania-silica composite photocatalyst design would maximize the absorption behavior and the proximity of the SiO₂ adsorption zones to TiO₂ photocatalytic active ones.⁴ Here, we provide an approach to synthesize TiO₂-SiO₂ composites with nano titania/Ti-O-Si species modified titania core/shell structure embedded in mesoporous silica by the sol-gel method. These TiO₂-xSiO₂ composites have high specific surface areas (up to 645 m²/g), large pore volumes, a narrow distribution of pore sizes ranging from 15 to 20 Å, and exhibit both much higher absorption capability of organic pollutants and better photocatalytic activity for photocatalytic oxidation of benzene than pure titania. In addition, it is well-known that it is easy to synthesize microporous material with a pore size <10 Å and mesoporous materials with a pore size between 20 and 100 Å. The expansion of the micropore size from less than 10 to 10-20 Å is an important goal of the current research on microporous materials and remains a significant synthetic challenge today.^{14,15} Our method provides an facile approach to synthesize titania-silica composites with a narrow distribution of pore sizes ranging from 15 to 20 Å.

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Experimental Procedures

Preparation. A 0.165 mol/L TiOCl_2 aqueous solution was obtained by dropping known amounts of TiCl_4 into 100 mL portions of distilled water in an ice–water bath. With strong magnetic stirring, 1.37 g of H_2SO_4 was added to 110 mL of the 0.165 mol/L TiOCl_2 aqueous solution, and then a known amount of a 2.0 mol/L Na_2SiO_3 solution was added dropwise to the mixture. The pH of this mixture was controlled to 2.0 by adding a 0.3 mol/L ammonium bicarbonate solution, and then, 33 g of cetyltrimethylammonium bromide (CTAB) was added to the mixture. The mixture was aged at 90 °C in a temperature-controlled oil bath for 48 h. After crystallization, the precipitates formed in the solution were filtered, washed thoroughly with distilled water, and dried at 100 °C in air for 24 h. Finally, the template in the obtained samples was completely removed by temperature-programmed calcination in air in a quartz tube reactor. The sample was heated to 480 °C at a rate of 1 °C/min and remained at this temperature for 2 h.

Characterization. X-ray diffraction (XRD) patterns were obtained on a Rigaku Dmax X-ray diffractometer using $\text{CuK}\alpha$ radiation. The BET surface area was measured on a KICT-SPA3000 using N_2 adsorption at –196 °C for the sample pre-degassing at 150 °C in a vacuum for 10 h. Transmission electron microscopy (TEM) images were obtained using a JEM-100CX electron microscope. Fourier transform infrared (FTIR) spectra were taken on Perkin-Elmer 1750 spectrometer. Diffusive reflective UV absorption spectra (DRUV) were recorded on a UV-240 UV–visible recording spectrophotometer.

Photocatalytic Activity. The photocatalytic activity of as-synthesized TiO_2 – $x\text{SiO}_2$ samples for the gas-phase photo-oxidation of benzene was tested on a homemade recirculating gas-phase photoreactor with a quartz window, which was connected to the ppBRAE meter (RAE system Inc.) to recirculate a mixture of benzene and ambient air without additional drying and to measure the concentration of the volatile organic compounds (VOCs). UVA (F8T5BLB lamp, PHILIPS) black light was used as an irradiation source. First, the sample powder was put into the reactor. After injecting a known amount of benzene in the system, UV light was immediately turned on. To compare the photocatalytic activity of TiO_2 – $x\text{SiO}_2$ samples with different compositions, the amount of TiO_2 in the samples was kept equal to 0.3300 g.

Results and Discussion

Synthesis and Characterization. In our recent work,¹⁶ we realized the amorphous–anatase transformation of titania in liquid–solid reactions at low temperatures and successfully obtained nano pure anatase titania with a higher surface area, good crystallinity, and high photocatalytic activity at low temperatures by controlling the pH value and adding a certain amount of SO_4^{2-} . Here, we extend this approach to synthesize TiO_2 – $x\text{SiO}_2$ composites to obtain anatase-contained TiO_2 – $x\text{SiO}_2$ composites and use CTAB as a template to control the porous structure in the composite. Figure 1 shows the XRD patterns of as-synthesized pure titania and TiO_2 – $x\text{SiO}_2$ composites with different compositions. It can be seen that pure titania has a pure anatase structure and that titanium in the TiO_2 – $x\text{SiO}_2$ composites exists in segregated titania with pure anatase structure. Apart from the diffraction peaks corresponding to anatase, there are no other diffraction peaks from $2\theta = 5$ –70 degree for all of the TiO_2 – $x\text{SiO}_2$ composites, indicating that silica exists in an amorphous phase. The average crystal size of anatase can be estimated by the Scherrer formula: $L = 0.89\lambda/\beta \cos \theta$. It can be seen from Table 1 that anatase in pure

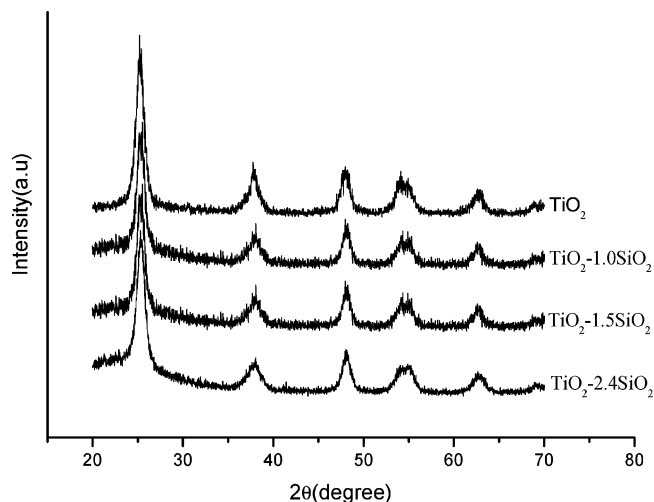


Figure 1. XRD patterns of as-synthesized pure titania and TiO_2 – $x\text{SiO}_2$ composites with different compositions.

TABLE 1: Properties of As-Synthesized TiO_2 – $x\text{SiO}_2$ Composites and Pure Titania

sample	$\text{SiO}_2/\text{TiO}_2$ molar ratio	BET surface area (m^2/g)	BJH mean pore size (Å)	BJH total volume (cm^3/g)	TiO_2 av. crystal size (nm)	photo- catalytic rate constant (min^{-1})
TiO_2 –1.0 SiO_2	1	488	17	0.44	10	0.322
TiO_2 –1.5 SiO_2	1.5	585	19	0.64	10	0.293
TiO_2 –2.4 SiO_2	2.4	645	15	0.53	9.2	0.255
TiO_2		162			9.2	0.237
$\text{TiO}_2(\text{P25})$						0.179

titania and TiO_2 – $x\text{SiO}_2$ composites has almost the same average crystal size (9–10 nm).

The N_2 adsorption–desorption isotherms of as-synthesized TiO_2 – $x\text{SiO}_2$ composites are given in Figure 2. The TiO_2 – $x\text{SiO}_2$ composites with different compositions show a type IV isotherm with a desorption hysteresis (IUPAC classification),¹⁷ which is related to the capillary condensation associated with pore channels. The BJH desorption pore size distributions of as-synthesized TiO_2 – $x\text{SiO}_2$ composites were given in Figure 3. All of the TiO_2 – $x\text{SiO}_2$ composite samples have a narrow distribution of pore size. The average pore size by BJH is 17, 19, and 15 Å for TiO_2 –1.0 SiO_2 , TiO_2 –1.5 SiO_2 , and TiO_2 –2.4 SiO_2 , respectively. Although the average pore size of the as-synthesized TiO_2 – $x\text{SiO}_2$ composites is in the range of the microporous materials, their adsorption/desorption isotherms are similar to one of the mesoporous materials, not like the typical isotherm of a microporous material. It is well-known that the vast majority of known crystalline microporous materials have a pore size <10 Å. The expansion of the pore size to 10–20 Å is an important goal of the current research on microporous materials. By our method, we successfully synthesized mesoporous material with a pore size between 15 and 20 Å. As our XRD experiments show that the as-synthesized TiO_2 – $x\text{SiO}_2$ composites have no diffraction peak in the range of the low angle ($2\theta = 1$ –10), the pores in the as-synthesized TiO_2 – $x\text{SiO}_2$ composites are not periodically arranged. With the increase of the $\text{SiO}_2/\text{TiO}_2$ molar ratio from 1 to 1.5–2.4, the specific surface area increases from 488 to 585–645 m^2/g , and the pore volume changes from 0.44 to 0.64–0.53 cm^3/g . The pure titania prepared by same procedure but without adding Na_2SiO_3 has only 162 m^2/g specific surface area.

The TEM image of the as-synthesized TiO_2 –2.4 SiO_2 composite is given in Figure 4. It can be seen that nanosized titania particles (see blank arrow) with diameters from 5 nm or so to

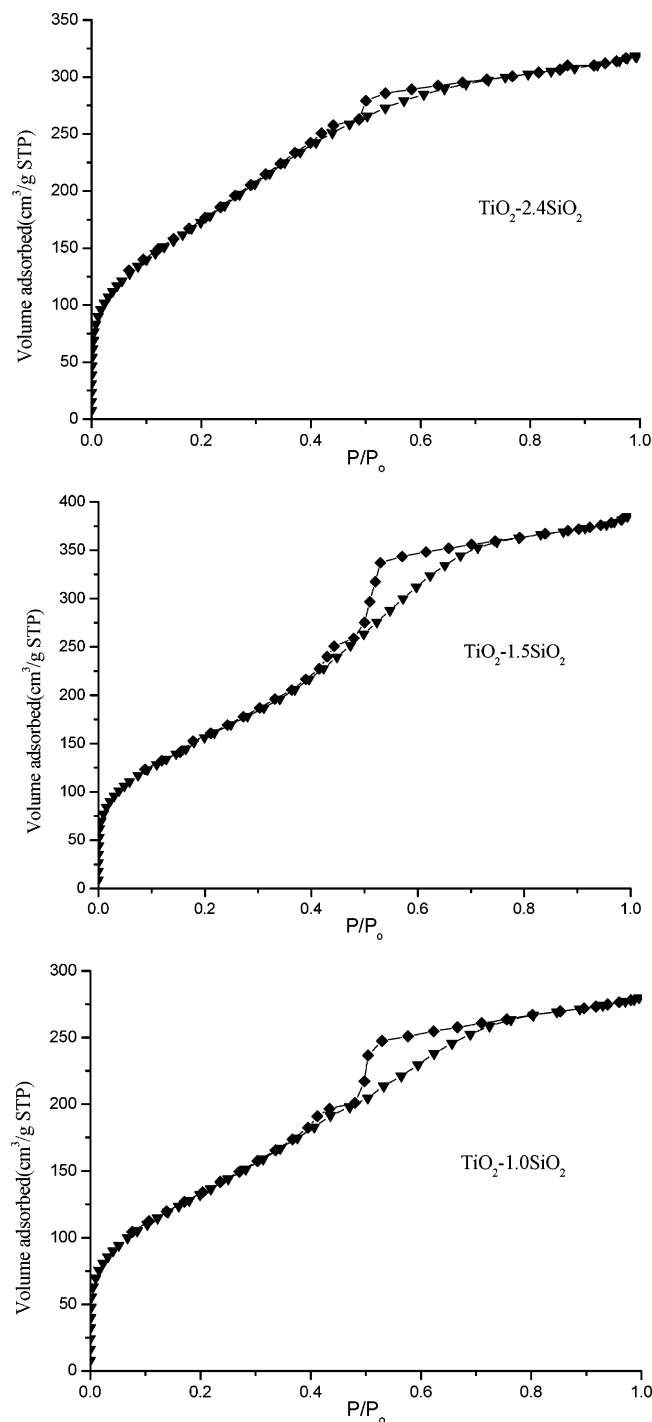


Figure 2. N₂ adsorption-desorption isotherms of as-synthesized TiO₂-xSiO₂ composites with different compositions.

less than 20 nm are embedded in the porous silica matrix (see black arrow). The silica matrix has a good porous structure with a narrow distribution of pore sizes, which is in agreement with the result obtained by the BJH analysis of the pore size distribution. The diameters of these titania particles by TEM observations are in agreement with the average crystal sizes estimated by XRD.

Figure 5 shows the FT-IR spectra for the as-synthesized pure titania and TiO₂-xSiO₂ composites with different compositions. The peaks at 965 and 1077 cm⁻¹ indicate the band for the ν (Ti-O-Si) vibration¹⁸ and asymmetric ν (Si-O-Si) vibration,¹¹ respectively. The formation of the Ti-O-Si bond arises from two possibilities: first, a small amount of Ti (IV) substituting

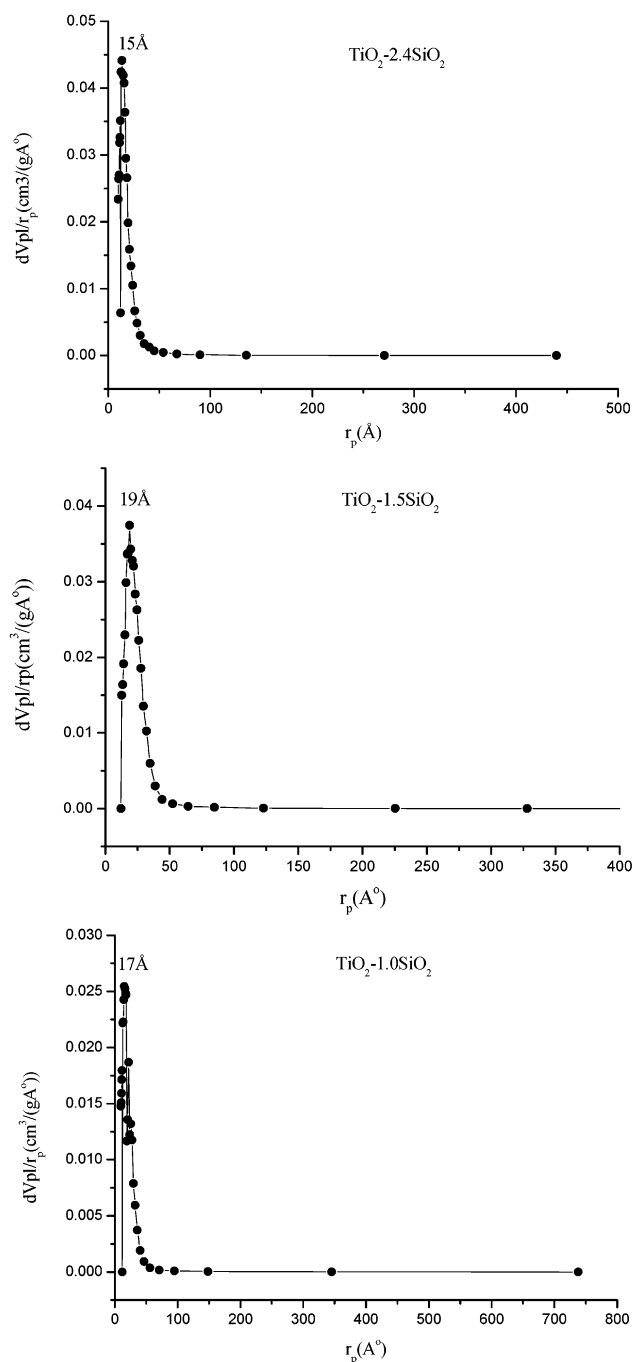


Figure 3. BJH desorption pore size distribution of as-synthesized TiO₂-xSiO₂ composites with different compositions.

for Si (IV) in the framework of mesoporous silica and, second, the connection of embedded anatase titania particles to the mesoporous silica matrix through the Si-O-Ti bonds in the interface between silica and titania. The broad absorption peak appearing near 3400 cm⁻¹ relates to a stretching vibration of -OH. The peak at 1620 cm⁻¹ is assigned to water.¹⁸

Figure 6 gives the diffuse reflectance UV-vis spectra of as-synthesized pure titania and TiO₂-xSiO₂ composites with different compositions. As compared to pure anatase titania, the embedding of titania into the mesoporous SiO₂ matrix results in a substantial blue shift of the absorption edge (Figure 6A). The plot of transformed Kubelka-Munch function versus the energy of light affords a band gap of 3.20 eV (386 nm) and 3.54 eV (349 nm) for the as-synthesized pure titania and TiO₂-xSiO₂ composites, respectively (Figure 6B). The TiO₂-xSiO₂

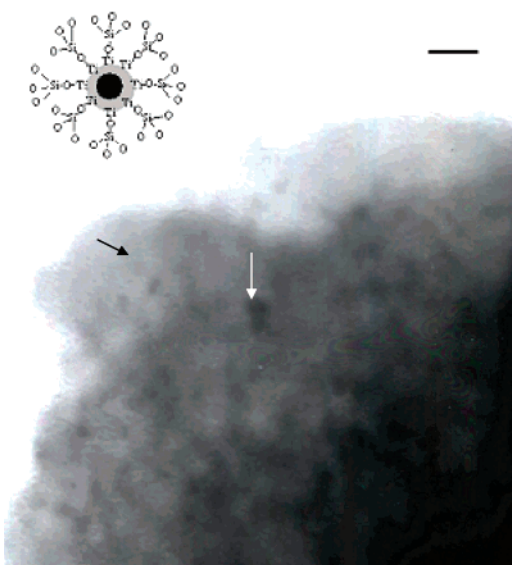


Figure 4. TEM image of as-synthesized $\text{TiO}_2\text{-}2.4\text{SiO}_2$ (scale bar is 20 nm). Inset gives the schematic illustration of the titania/Ti-O-Si species modified titania core/shell structure.

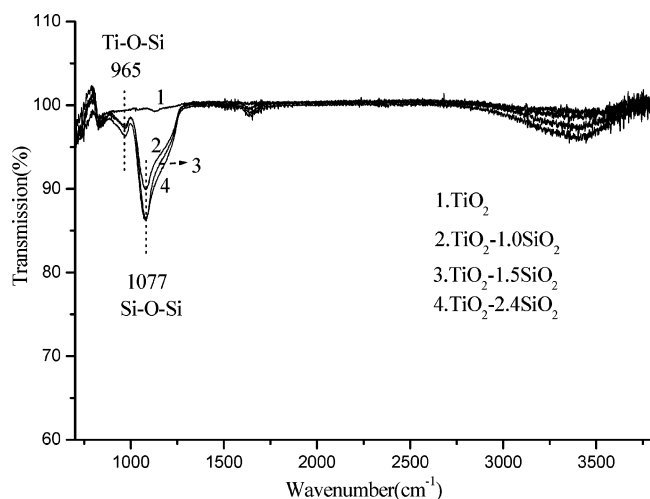


Figure 5. FT-IR spectra for the as-synthesized pure titania and $\text{TiO}_2\text{-}x\text{SiO}_2$ with different compositions.

composites with different compositions have the same band gap. Anderson et al.^{4b} synthesized a mixed $\text{TiO}_2/\text{SiO}_2$ material by the sol-gel method and observed a similar blue shift of the mixed $\text{TiO}_2/\text{SiO}_2$ material in comparison to pure titania. Zhang et al.¹⁹ also prepared a $\text{SiO}_2\text{-TiO}_2$ composite by the sol-gel method, but they reported that there was no obvious difference in the band gap between $\text{SiO}_2\text{-TiO}_2$ composite and pure titania. These reported results show that the synthesizing condition plays a very important role in the position of the band gap of the $\text{SiO}_2\text{-TiO}_2$ composite. In our experiment, the results of XRD show that the segregated anatase titania in as-synthesized $\text{TiO}_2\text{-}x\text{SiO}_2$ composites has almost the same average crystal size as the pure anatase titania (Table 1). Obviously, this larger band gap of as-synthesized $\text{TiO}_2\text{-}x\text{SiO}_2$ composites than pure titania could not be contributed to the quantum size effect caused by the size difference of the titania domain between as-synthesized $\text{TiO}_2\text{-}x\text{SiO}_2$ composites and pure titania. If there is not any interaction between the embedded nano titania particles and the mesoporous silica matrix, then the as-synthesized $\text{TiO}_2\text{-}x\text{SiO}_2$ composites should have same band gap to pure titania as they have the same anatase phase with almost the same average

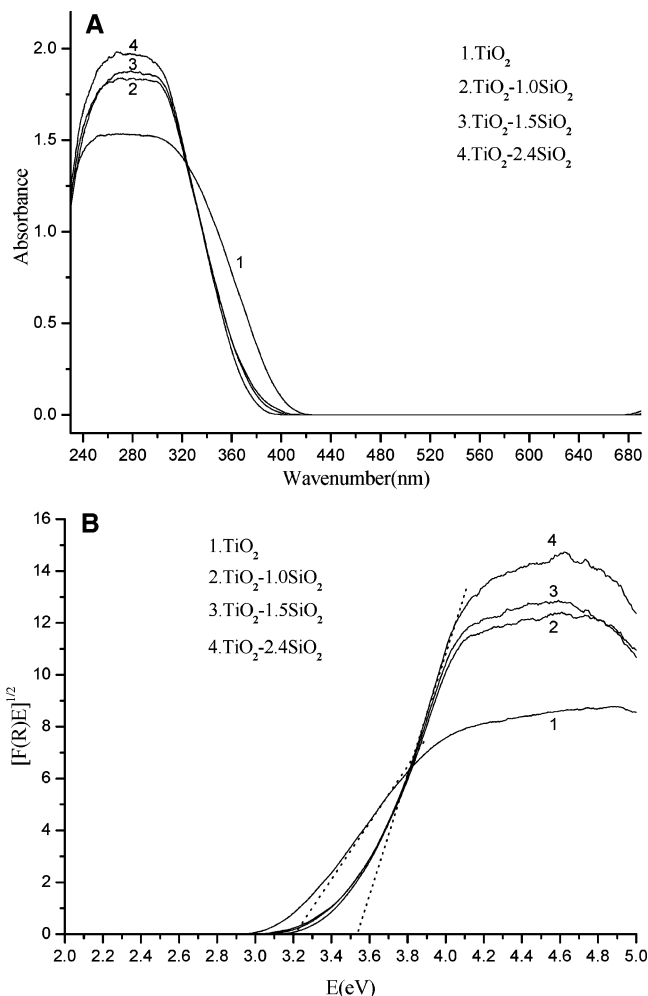
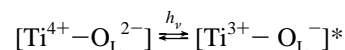


Figure 6. Diffuse reflectance UV-vis spectra of as-synthesized pure titania and $\text{TiO}_2\text{-}x\text{SiO}_2$ composites with different compositions: (A) absorbance vs the wavelength of the light absorbed. (B) Kubelka-Munk function vs the energy of the light absorbed.

crystal size. Obviously, the embedded anatase titania particles connect to the mesoporous silica matrix through Si-O-Ti bonds in the interface between silica and titania, which leads to the difference of the band gap between the as-synthesized $\text{TiO}_2\text{-}x\text{SiO}_2$ composites and pure titania.

The absorption band in the range of UV is assigned to the ligand-metal charge transfer (LMCT) from O to Ti (IV)²⁰



The position of this band is affected by the coordination geometry around the titanium atom (e.g., ordination number) and the size of the titanium oxide species. The absorption edge is shifted to a longer wavelength as the coordination number of Ti increases and as the size of the aggregated species becomes larger.^{18a,21} More precisely, the bands in the region of 210–240 nm are attributed to the oxygen to tetrahedral Ti (IV) ligand to metal charge transfer, whereas the bands at higher wavelengths ($\lambda > 240$ nm) are due to tetrahedral Ti (IV) sites that undergo a change to an octahedral coordination.^{20a} The presence of a strong absorption in the range of 280–300 nm is due to octahedral titanium species in highly dispersed TiO_2 particles with a particle size smaller than 5 nm.²² The absorption bands in the range of 350–400 nm arise from the separated TiO_2 phase with a particle size larger than 5 nm.²³

Recently, in situ high-temperature XANES has been performed on titanium-containing silica sol–gels, and the results revealed the existence of TiO_6 sites that could be reversibly converted to TiO_4 sites by heating to 150–250 °C.²⁴ Pickup et al.²⁵ have characterized $(\text{TiO}_2)_x(\text{SiO}_2)_{1-x}$ sol–gel glass by using neutron diffraction with isotropic substitution of titanium and ^{17}O and ^{49}Ti solid-state NMR with isotopic enrichment and obtained similar results. FTIR results show that a Si–O–Ti bond exists in the as-synthesized TiO_2 – $x\text{SiO}_2$ composites. In silica, Si is tetrahedrally coordinated with each oxygen bonding to two silicon atoms. In titania, Ti is octahedrally coordinated with each oxygen bonding to titanium atoms. Therefore, we think that when the Ti–O–Ti bond in titania and the Si–O–Si bond in silica are broken, the formation of a new bond of Si–O–Ti leads to the decrease of the coordination number of Ti (IV) on the interface of titania and silica in the as-synthesized TiO_2 – $x\text{SiO}_2$ composites during the synthesis and following the calcination step. The decrease of the coordination number of Ti (IV) results in the blue shifting of the absorption edge.^{18a,21} Therefore, the blue shifting of the absorption edge (from 3.20 to 3.54 eV) of as-synthesized TiO_2 – $x\text{SiO}_2$ as compared to nano pure titania is reasonably assigned to the formation of the Si–O–Ti species modified titania. In the as-synthesized TiO_2 – $x\text{SiO}_2$ composites, it is proven by XRD and TEM that there are segregated anatase titania particles with average crystal sizes of 9–10 nm, which are embedded in the mesoporous silica matrix. It seems that there should be two absorption edges: pure titania (3.2 eV) and Si–O–Ti species modified titania (3.54 eV). But DRUV results show that there is only the absorption edge of Si–O–Ti species modified titania, so it can be reasonably concluded that the embedded anatase titania nanoparticles are surrounded by a shell composed of Si–O–Ti species modified titania (the inset in Figure 4 gives the schematic illustration of this core/shell structure). The formation of the Si–O–Ti species modified titania shell restrains the absorption of the titania core. It also can be seen in Figure 6A that the as-synthesized TiO_2 – $x\text{SiO}_2$ composites exhibit higher absorption intensity than pure titania.

Photocatalytic Activity. Carcinogenic benzene existing in gasoline, paints, etc. is one of the main air pollutants. In this work, we chose the gas-phase photo detoxication of benzene to evaluate the as-synthesized photocatalysts. When a certain amount of benzene is injected into the photocatalytic reactor, there are two factors as follows to lead to the changing of the concentration of benzene in the reactor: the adsorption of benzene on the surface of photocatalyst and the photooxidation of benzene. The as-synthesized TiO_2 – $x\text{SiO}_2$ composite photocatalysts have a much higher surface area than the pure TiO_2 sample, which results in their much higher adsorption capability to benzene. To compare the photocatalytic activity of TiO_2 – $x\text{SiO}_2$ samples with different compositions, the amounts of TiO_2 in the samples and injected benzene remained equal. Figure 7A shows the amounts of total volatile organic compounds (VOCs) with the UVA light irradiation time. In the absence of irradiation, there is only absorption of benzene on the sample. For Degussa P25 titania, during the initial 3 min after the injection of benzene, the concentration decreases from 54 797 to 51 017 ppb, and later the concentration remains almost unchanged, indicating that the absorption of benzene reaches equilibrium after an initial 3 min. A similar situation takes place for the TiO_2 – $x\text{SiO}_2$ composite samples, but there is a much larger decrease of the concentration of benzene (from 59 990 to 20 852 ppb) for the TiO_2 –1.5 SiO_2 sample during the initial 3 min after the injection of benzene than Degussa P25 titania. Despite the weight

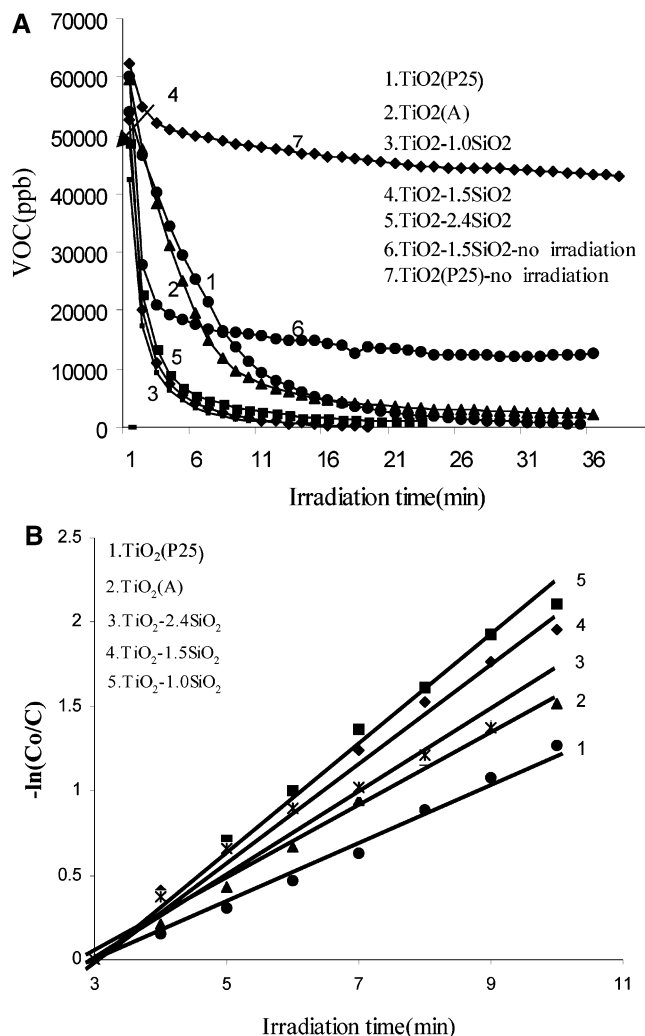


Figure 7. Amounts of total volatile organic compounds (VOCs) (A) and $\ln(C_0/C)$ with the UVA light irradiation time.

difference between Degussa P25 titania (0.3300 g) and TiO_2 –1.5 SiO_2 sample (0.7013 g equivalent to 0.3300 g of pure titania), the TiO_2 –1.5 SiO_2 composite sample still exhibits a much higher adsorption capability of benzene than Degussa P25 titania, which is attributed to its much higher specific surface area and pore volume than pure titania. These adsorption experiments in the absence of irradiation show that the further decreasing of the concentration of benzene in the reactor after the initial 3 min or so is caused by photocatalytic oxidation of benzene. So, we choose the data after irradiation for 3 min to determine the rate constant. It is well-known that photocatalytic oxidation of organic pollutants follows Langmuir–Hinshelwood kinetics.¹² Therefore, this kind of reaction can be represented as follows: $-dC/dt = kt$. It can be integrated as follows:

$$C = C_0 \exp(-kt) \text{ or } \ln(C_0/C) = kt.$$

where C_0 is the initial concentration of reactant and k is a rate constant.

Figure 7B confirms that the photocatalytic oxidation of benzene on as-synthesized pure titania and TiO_2 – $x\text{SiO}_2$ samples follows Langmuir–Hinshelwood kinetics. Table 1 lists their apparent rate constants. It can be seen that the as-synthesized TiO_2 – $x\text{SiO}_2$ composites have better photocatalytic activity than pure titania and Degussa P25 titania, a benchmarking photocatalyst. These results show that the embedding of nano titania particles in mesoporous silica not only greatly increases its

adsorption capability but also improves its photocatalytic activity. For the as-synthesized TiO_2 - $x\text{SiO}_2$ composites with different compositions, their photocatalytic activities decrease in the following order: TiO_2 -2.4 SiO_2 < TiO_2 -1.5 SiO_2 < TiO_2 -1.0 SiO_2 .

It has been widely accepted that there is a corresponding relation between the UV absorption intensity and the activity of photocatalysts. The strong UV absorption intensity implies that more photogenerated electrons could be promoted from the valence band into the conduction band, and more separate electrons or holes could be produced, which help to enhance the photocatalytic activity. The stronger the UV-absorption intensity is, the higher the activity is.¹⁹ Therefore, the higher photocatalytic activity of the as-synthesized TiO_2 - $x\text{SiO}_2$ composites than pure titania is partially attributed to its higher UV absorption intensity than pure titania. Both UV absorption intensity and specific surface area of as-synthesized TiO_2 - $x\text{SiO}_2$ composites with different compositions increase with the increase of the molar ratio of $\text{SiO}_2/\text{TiO}_2$ (see Table 1 and Figure 6), but the photocatalytic activity decreases with the increase of the molar ratio of $\text{SiO}_2/\text{TiO}_2$. With the increase of the molar ratio of $\text{SiO}_2/\text{TiO}_2$, the average crystal size of nano titania remains almost unchanged, so each nano titania particle is surrounded by a larger amount of mesoporous silica, which leads to the increase of the average distance from the photoactive sites to the adsorption sites. The longer transport distance from the photoactive sites to the adsorption sites decreases the efficiency of the photogenerated oxidizing radicals, such as the hydroxyl radical or the species resulting from the reduction of O_2 (e.g., $\text{HO}_2\cdot$), to the absorbed pollutants, which leads to the decrease of the photocatalytic activity of the as-synthesized TiO_2 - $x\text{SiO}_2$ composites with the increase of the molar ratio of $\text{SiO}_2/\text{TiO}_2$. These results show that maximizing the proximity of the adsorption sites to the photoactive sites is also important for designing an ideal photocatalyst except for increasing the specific surface area of the TiO_2 - $x\text{SiO}_2$ composites.

As compared to pure titania, the as-synthesized TiO_2 - $x\text{SiO}_2$ composites, which are composed of nano titania/Ti—O—Si species modified titania core/shell structure embedded in mesoporous silica, have several advantages as follows. First, the much higher specific surface area and pore volume of the as-synthesized mesoporous TiO_2 - $x\text{SiO}_2$ composites than pure titania result in their high absorption capability of organic pollutants. The as-synthesized mesoporous TiO_2 - $x\text{SiO}_2$ composites can be used as a reservoir of organic pollutants that decrease greatly the concentration of pollutants in air or solution even in the dark or under the irradiation of weak light. Second, the nice mesoporous structure with narrow pore size distribution and large pore volume facilitates the mass transfer of pollutants to absorption sites and outside-diffusion of the products from the photocatalytic active sites during photocatalytic reaction. The easy proximity of the adsorption sites to the photoactive sites in this structure improves the efficiency of the absorbed pollutants diffusing to photogenerated oxidizing radicals, which is favorable to enhance photocatalytic activity. Third, the nano titania/Ti—O—Si species modified titania core/shell structure embedded in mesoporous silica increases the UV absorption intensity, which leads to the improvement of its photocatalytic activity.

Conclusion

In summary, TiO_2 - $x\text{SiO}_2$ composites with nano titania/Ti—O—Si species modified titania core/shell structure embedded in a mesoporous silica matrix have been synthesized by the sol—

gel method. These TiO_2 - $x\text{SiO}_2$ composites have a high specific surface area (up to 645 m^2/g), large pore volume, and narrow distribution with average pore sizes ranging from 15 to 20 Å. As compared to pure anatase titania, the embedding of nano titania into the mesoporous silica matrix results in a substantial blue shift of the absorption edge from 3.2 to 3.54 eV and a higher UV absorption intensity, which arises from the formation of a Ti—O—Si species modifying titania in the interface between titania and silica. The as-synthesized TiO_2 - $x\text{SiO}_2$ composites exhibit both much higher absorption capability of organic pollutants and better photocatalytic activity for the photo-oxidation of benzene than pure titania. The better photocatalytic activity of as-synthesized TiO_2 - $x\text{SiO}_2$ composites than pure titania is attributed to their high surface area, higher UV absorption intensity, and easy diffusion of absorbed pollutants to photogenerated oxidizing radicals.

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