Characterization of Zr-Doped TiO₂ Nanocrystals Prepared by a Nonhydrolytic Sol-Gel Method at High Temperatures

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Highly crystalline and surface-modified Zr-doped TiO₂ nanorods were successfully prepared using a nonhydrolytic sol-gel method that involves the condensation of metal halides with alkoxides in anhydrous trioctylphosphine oxide (TOPO) at either 320 or 400 °C. In addition, the interaction of the cross-condensation between the Ti and Zr species was studied by characterizing the morphologies, crystalline structures, chemical compositions, surface properties, and band gaps of the nanocrystals obtained at different reaction temperatures and Zr-to-Ti stoichiometric ratios. Increases in the concentration of Zr^{4+} and in the reaction temperature led to large nanorods and regular shapes, respectively. In addition, only the anatase form was observed in the Zr-doped TiO₂ nanorods. The Zr-to-Ti ratios obtained ranged from 0.01 to 2.05, all of which were far below the stoichiometric ratios used during the preparation of the samples (0.25–4). Moreover, the Zt^{4+} units accumulated mainly at the surface of the TiO_2 nanocrystals. The band gaps of the Zr-doped TiO_2 nanorods ranged from 2.8 to 3.8 eV, which are smaller than those of pure TiO₂ (3.7 eV) or ZrO₂ (5.2 eV). The Zrdoped anatase TiO₂ nanorods prepared at 400 °C at an initial stoichiometric Zr-to-Ti ratio of 2:3 exhibited the highest photoactivities for the decomposition of rhodamine B because of the presence of trace amounts of Zr^{4+} (Zr/Ti = 0.03) in the TiO₂ and the regular shapes of these particles. DSC analysis indicated that the temperatures for forming nanocrystalline TiO₂ and ZrO₂ were 207 and 340 °C, respectively. Moreover, the reactivities of condensation between the Ti species were reduced when Zr species were involved in the NHSG reactions. The results obtained in this study clearly demonstrate that the faster kinetics for the generation of TiO_2 controls the material properties as well as the photoactivities of the nonhydrolytic sol-gel-derived nanocrystals.

Introduction

Titanium dioxide (TiO₂) is one of the most widely used photocatalysts because of its suitable band gap (ca. 3.2 eV), chemical stability, and nontoxicity.¹ In addition, zirconium dioxide (ZrO₂), which has a wide band gap (ca. 5.0 eV) and more-negative (-1.0 V vs NHE) and more-positive (4.0 V vs NHE) reducing potentials in its conduction and valence bands, respectively, relative to those of TiO2, is considered as a promising alternative photocatalyst for the degradation of a greater variety of pollutants.²⁻⁵ It has been demonstrated that incorporating Zr^{4+} into TiO_2 to form $Zr_xTi_{1-x}O_2$ can introduce lattice defects and lead to higher photoactivities than those of the pure oxides. The introduced defects not only reduce the band gaps, i.e., increase the wavelength of the activation light, but also play a role as charge-trapping centers in inhibiting charge recombination.⁶ Although the presence of a few defects improves the photoactivities of $Zr_xTi_{1-x}O_2$ systems, an excess of defects promotes charge recombination and decreases catalytic efficiency. The number of defects is dependent on the size, crystalline structure, and Zr-to-Ti ratio of the photocatalyst.^{7–9} Nanosize photocatalysts have large surface areas and sufficient numbers of surface defects to exhibit high catalytic efficiencies.

In addition, anatase TiO₂ and tetragonal ZrO₂ contain oxygen vacancies and exhibit higher catalytic performances than their other crystalline forms.^{7,10–12} Therefore, the preparation and characterization of nanosize, highly crystalline anatase and tetragonal $Zr_xTi_{1-x}O_2$ photocatalysts continues to attract a high degree of attention.

The sol-gel method is a simple and feasible process for the fabrication of nanocomposite oxides with tailored sizes. Conventionally, the sol-gel method uses a hydrolytic route that involves initial hydrolysis of the precursors and subsequent continuous condensation between the hydrolyzed precursors to form oxide gels. The hydrolytic sol-gel (HSG) route to metal oxides proceeds very efficiently at room temperature. In addition, nanoparticulates can be prepared through a combination of water-in-oil emulsion and sol-gel processing. Because the as-prepared oxides are usually amorphous, they must be calcined at high temperature for crystallization. Unfortunately, calcination results in the coalescence of particles, which increases the size and decreases the surface area of the photocatalysts.¹³

The nonhydrolytic sol-gel (NHSG) route is an alternative pathway for the preparation of metal oxides. In contrast to the HSG route, the NHSG route involves the reaction of metal halides with oxygen donors, such as metal alkoxides, alcohols, or ethers, under nonaqueous conditions.¹⁴ Several studies have investigated the nonhydrolytic sol-gel route to pure oxides and binary oxides including TiO₂, ZrTiO₄, SiTiO₄, and SiZrO₄.¹⁵⁻¹⁷

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Because the NHSG process is relatively slower than the HSG approach, it usually requires temperatures exceeding 80 °C. Moreover, the lower reactivity makes the morphologies and microstructures of NHSG-derived metal oxides more controllable. Trentler et al.18 prepared anatase TiO2 nanocrystals through the injection of titanium alkoxides into titanium isopropoxide/heptadecane solutions in the presence of trioctylphosphine oxide (TOPO) at 300 °C. These TiO₂ crystals had average sizes of 3.8-9.2 nm, depending on the type of the metal halide and the concentration of TOPO. Moreover, these TiO₂ nanoparticles exhibited no surface hydroxyl groups because of the coordination of the surface titanium atom to TOPO. Subsequently, Joo et al.¹⁹ reported that condensation between zirconium halides and zirconium isopropoxide at 340 °C in pure TOPO results in monodisperse, uniformly sized tetragonal ZrO₂ nanoparticles (ca. 4 nm). In addition to pure metal oxides, binary metal oxides can also be prepared through cross-condensation between different metal halide and alkoxides. Tang et al.²⁰ adapted a process similar to that of Joo et al. to prepare monodisperse $Hf_xZr_{1-x}O_2$ nanocrystals. Solid solutions with various concentrations were obtained after nonhydrolytic crosscondensations using different stoichiometric amounts of hafnium halides and zirconium alkoxides had been performed. In addition, the morphologies and crystalline phases within these solid solutions were controllable by modifying the reaction temperature and the combination of metal halide and alkoxide. Unfortunately, ZrTiO₄ solid solutions could not be formed using this method. This phenomenon is different from that of $ZrTiO_4$, for which the desired Zr-to-Ti ratios can be controlled by the initial metallic ratios in the solutions when the similar elimination of alkyl halides is conducted at low temperatures (110 °C).¹⁷ In any event, the interaction between the Zr/Ti halides and alkoxides in the presence of TOPO at high temperatures has yet to be addressed adequately. In addition, the detailed quantification of the Zr-to-Ti ratios, microstructures, electronic structures, surface properties, and photoactivities of the $Zr_xTi_{1-x}O_2$ nanocrystals resulting from various combinations of Zr and Ti species remain unclear.

In this study, we synthesized and characterized Zr-doped TiO_2 nanocrystals using an NHSG method conducted at 320 or 400 °C in liquid TOPO. Titanium chloride (TiCl₄) and zirconium chloride (ZrCl₄) were used as the precursors for TiO₂ and ZrO₂, respectively, and titanium isopropoxide and zirconium isopropoxide were used as the oxygen donors. To understand explicitly the chemistry of the cross-condensation leading to the Zr-doped TiO₂ nanocrystals, we examined the material properties—including particle sizes, shapes, crystalline phases, surface compositions, surface properties, and optical properties— of the products prepared at various stoichiometric Zr-to-Ti ratios and reaction temperatures. Moreover, we investigated the photocatalytic activities of the Zr-doped TiO₂ samples toward the degradation of rhodamine B (RhB) and elucidated how they relate to the material properties.

Experimental Section

NHSG-Derived Nanocrystals. Titanium dioxide (TiO₂) nanocrystals were prepared by condensation between titanium chloride (TiCl₄, Fluka, 99%) and Ti(OC₃H₇)₄ (Aldrich, 99.9%), whereas zirconium dioxide (ZrO₂) nanocrystals were fabricated by zirconium chloride (ZrCl₄, Strem Chemicals, 99.5%) and zirconium isopropoxide propanol complex [Zr(OC₃H₇)₄-(CH₃)₂-CHOH, Aldrich, 99.9%]. Titanium chloride (0.5 g, 2.5 mmol) and Ti(OC₃H₇)₄ (0.6 g, 2.0 mmol) were first dissolved in TOPO (5.2 g, 13.5 mmol) at 150 °C under N₂ atmosphere. This well-

TABLE 1: Metal Halides, Oxygen Donors, and Reaction Temperatures Used for the Synthesis of $Zr_xTi_{1-x}O_2$ Nanoparticles

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sample	metal halide (2.5 mmol)	oxygen donor(s)	TOPO (mmol)	temp (°C)
TiO ₂ -320	TiCl ₄	Ti(OC ₃ H ₇) ₄ (2.0 mmol)	13.5	320
$Zr_{0.2}Ti_{0.8}O_2$ -320	TiCl ₄	Ti(OC ₃ H ₇) ₄ (1.0 mmol),	13.5	320
		$Zr(OC_3H_7)_4$ •		
		(CH ₃) ₂ CHOH		
		(1.0 mmol)		
$Zr_{0.4}Ti_{0.6}O_2320$	TiCl ₄	$Zr(OC_3H_7)_4$ •	13.5	320
		(CH ₃) ₂ CHOH		
		(2.0 mmol)		
$Zr_{0.2}Ti_{0.8}O_2-400$	$TiCl_4$	Ti(OC ₃ H ₇) ₄ (1.0 mmol),	13.5	400
		$Zr(OC_{3}H_{7})_{4}$ •		
		(CH ₃) ₂ CHOH		
		(1.0 mmol)		
Zr _{0.4} Ti _{0.6} O ₂ -400	TiCl ₄	$Zr(OC_3H_7)_4$ •	13.5	400
		(CH ₃) ₂ CHOH		
		(2.0 mmol)		
$Zr_{0.6}Ti_{0.4}O_2-400$	$ZrCl_4$	$Ti(OC_{3}H_{7})_{4}$ (2.0 mmol)	21	400
Zr _{0.8} Ti _{0.2} O ₂ -400	$ZrCl_4$	$Ti(OC_{3}H_{7})_{4}$ (1.0 mmol),	21	400
		$Zr(OC_{3}H_{7})_{4}$		
		$(CH_3)_2CHOH$		
		(1.0 mmol)		
ZrO_2-400	$ZrCl_4$	$Zr(OC_3H_7)_4$ •	21	400
		$(CH_3)_2CHOH$		
		(2.0 mmol)		

mixed solution was then heated to 320 °C and underwent the condensation reaction at this temperature for 3 h with vigorous stirring at 500 rpm. Afterward, the solution was cooled to 60 °C, and acetone was added to precipitate TiO₂ nanocrystals. The precipitate was harvested by centrifugation at 11000 rpm and washed with acetone several times to remove excess TOPO. For ZrO₂ preparation, 0.6 g of ZrCl₄ (2.5 mmol) and 0.8 g of Zr(OC₃H₇)₄-(CH₃)₂CHOH (2.0 mmol) were dissolved in 8.0 g of TOPO (21 mmol). The ratio of metal chloride to alkoxide is similar to that used by Joo et al.,¹⁹ which means that the metal chloride was in excess. In contrast to TiO₂, ZrO₂ particles were produced only when the temperature rose to 400 °C. For the synthesis of Zr-doped TiO₂ nanocrystals, various molar ratios of M(O'Pr)₄ and M'Cl₄ (M and M' represent Ti and/or Zr) were used. The samples are denoted as $Zr_xTi_{1-x}O_2-t$, where x represents the reactants in the ratio of Zr/(Zr + Ti) and t denotes the reaction temperature. The nonhydrolytic reaction was carried out at 320 or 400 °C when x was smaller than 0.5 and 400 °C for x larger than 0.5. All recipes and reaction conditions are summarized in Table 1. Unless otherwise mentioned, all of the NHSG reactions were conducted in hot trioctylphosphine oxide (TOPO, Strem Chemicals, 99%) liquid and under N2 atmosphere.

Characterization. The thermal behaviors of the NHSG reactions were investigated by differential scanning calorimetry (DSC, Setaram Labsys DSC 131) under a N₂ flow of 20 mL/ min and at a heating rate of 10 °C/min from 25 to 550 °C. The samples for DSC were prepared by dissolving the reactants in TOPO at 150 °C and then cooling the mixture to room temperature under N2 atmosphere. The TiCl4/Ti(OPr)4/TOPO mixture was a viscous yellow liquid, and the ZrCl₄/Zr(OⁱPr)₄/TOPO mixture was an opaque white solid. The particle sizes and shapes of the NHSG-derived nanocrystals were characterized by highresolution transmission electron microscopy (HRTEM, JEOL JEM-4000EX) at an accelerating voltage of 400 kV. The crystalline properties of the nanocrystals were identified by X-ray diffractometry (XRD, Rigaku) using Cu K α radiation (λ = 1.5405 Å) and operating at an accelerating voltage of 30 kV and an emission current of 20 mA. The X-ray diffraction patterns

were acquired over the 2θ range from 20° to 90° at a sampling width of 0.02° and a scanning speed of 4°/min. The elemental compositions (Zr/Ti) of the binary metal oxides were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS, Perkin-Elmer, SCIEX ELAN 5000). The surface chemical compositions of the nanocrystals were examined by X-ray photoelectron spectroscopy (XPS, Physical Electronics, ESCA PHI 1600) using an Al Ka X-ray source (1486.6 eV). The photoelectrons were collected into the analyzer with a 23.5 eV passing energy. The collection step was 1.0 eV for the widerange scan and 0.1 eV for high-resolution analysis in selected energy intervals. All analytical processes were carried out under ultrahigh vacuum conditions with the pressure maintained below 1.4×10^{-9} Torr. The shifts of the photoelectron peaks in the XPS spectra resulting from charging effects were referenced to the O(1s) line taken as 530.2 eV. The surface elemental ratios were estimated from the integrated peak areas of the elements and normalized to their sensitivity factors. The functional groups of the nanoparticles were identified by Fourier transform infrared spectrometry (FTIR, Horiba) scanning from 400 to 4000 cm^{-1} with a resolution of 4 cm⁻¹ for 100 scans. Samples for FTIR measurements were well-mixed with KBr and then pressed as pellets. The optical properties and band gaps of the nanoparticles were determined by UV-vis spectrophotometry (Hitachi 3010) scanning from 800 to 190 nm using the absorption of hexane as the reference. Samples for the UV-vis measurements were well-dispersed in hexane in a quartz cuvette with an optical length of 10 mm.

Photocatalytic Activities. Rhodamine B (RhB) was selected as the target compound to examine the photoactivity of the NHSG-derived $Zr_xTi_{1-x}O_2$ materials. The nanocrystalline catalysts were suspended in RhB solutions (0.05 mM) to give a final concentration of 1 g/L in the dark. Prior to illumination, the solutions were purged with O_2 in the dark for 30 min to ensure equilibrium among the catalysts, RhB, and oxygen. Thereafter, the solutions were kept under constant O_2 equilibrium condition during photocatalysis. Photocatalysis was carried out in a fused-silica tube irradiated by UV light at a wavelength of 305 nm. The decolored solutions were analyzed by UV–vis spectrophotometer scanning from 700 to 400 nm.

Results and Discussion

Chemical Compositions. To examine the chemical states of the Ti and Zr species after the nonhydrolytic sol-gel reaction, the NHSG-derived samples were analyzed using XPS (see Supporting Information, Figure S1). The binding energy of Zr(3d_{5/2}) centered at 182.3 eV in the ZrO₂ spectrum, and that of Ti(2p_{3/2}) was at 459.0 eV in the TiO₂ spectrum. Similarly to pure TiO₂ and ZrO₂, Zr($3d_{5/2}$) and Ti($2p_{3/2}$) in Zr_xTi_{1-x}O₂ nanocrystals exhibited binding energies in the ranges 182.3-182.5 and 458.7-459.0 eV, respectively. These values are in good agreement with the reported values for TiO₂, ZrO₂, and ZrTiO₄,²¹ which indicates the formation of Ti-O and Zr-O bonds in the samples via the nonhydrolytic reactions. Table 2 lists the actual Zr-to-Ti ratios of the $Zr_xTi_{1-x}O_2$ nanocrystals as analyzed using both ICP-MS and XPS. The Zr-to-Ti ratios of the binary oxides determined by ICP-MS ranged from 0.01 to 2.05, whereas a range of 0.02-2.29 was obtained through XPS analysis. It is noted that ICP-MS is an instrumental method that can determine the total concentrations of elements in $Zr_xTi_{1-x}O_2$ nanocrystals suspended in solution, whereas XPS is usually employed for the analysis of chemical species on the surfaces of nanocrystals. The similar Zr-to-Ti ratios obtained in these two methods reveal that most of the Zr⁴⁺ ions accumulated in



Figure 1. DSC curves of the NHSG reactions leading to TiO_2 (solid line), ZrO_2 (dashed line), and $Zr_{0.25}Ti_{0.75}O_2$ (dashed-dotted line) in the presence of TOPO.

 TABLE 2:
 Zr-to-Ti Molar Ratios and Actual Compositions

 of the Binary Oxide Nanoparticles
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	Zr-to-Ti molar ratio ^a		
$Zr_{x}Ti_{1-x}O_{2}$ nanocrystals	ICP-MS	XPS	actual composition
Zr _{0.2} Ti _{0.8} O ₂ -320	0.03	b	Zr _{0.03} Ti _{0.97} O ₂ -320
Zr _{0.4} Ti _{0.6} O ₂ -320	0.05	0.02	Zr _{0.05} Ti _{0.95} O ₂ -320
Zr _{0.2} Ti _{0.8} O ₂ -400	0.01	b	Zr _{0.01} Ti _{0.99} O ₂ -400
Zr _{0.4} Ti _{0.6} O ₂ -400	0.03	0.05	Zr _{0.03} Ti _{0.97} O ₂ -400
Zr _{0.6} Ti _{0.4} O ₂ -400	0.34	0.33	Zr _{0.25} Ti _{0.75} O ₂ -400
Zr _{0.8} Ti _{0.2} O ₂ -400	2.05	2.29	Zr _{0.67} Ti _{0.33} O ₂ -400

^{*a*} Molar ratios were determined by ICP-MS and XPS. ^{*b*} Detection of Zr was not possible.

the surface layer of the nanocrystals. When the value of *x* was greater than 0.5, the actual Zr-to-Ti ratios in the nanocrystals increased with increasing content of Zr in the reaction mixture. No such trend occurred, however, when the value of *x* was below 0.5. The similar Zr-to-Ti ratios (0.01-0.05) in the Zr_{0.2}-Ti_{0.8}O₂ and Zr_{0.4}Ti_{0.6}O₂ samples prepared at 320 and 400 °C indicate that increasing temperature had little effect on the degree of incorporation of Zr into the TiO₂ lattice.

Regardless of the initial Zr-to-Ti ratio used for the synthesis of the binary oxides, the final Zr-to-Ti ratios in the products were always much smaller than the theoretical stoichiometry. This phenomenon is attributed to the different kinetics of condensation between Ti and Zr species. Actually, the formation of TiO₂ through the condensation of TiCl₄ with Ti(OC₃H₇)₄ occurs at 320 °C, but a higher temperature (400 °C) is required for the preparation of ZrO₂. Because the actual compositions of Zr_xTi_{1-x}O₂ are different from the stoichiometric values, we use the actual ratios based on ICP-MS results for further discussion.

Heat Flows during NHSG Reactions. To understand the different dynamic properties of the NHSG reactions that form TiO₂, ZrO₂, and Zr_xTi_{1-x}O₂, we used DSC to examine the heat flows of these reactions. Figure 1 displays the heat flows of the NHSG reactions forming TiO₂, ZrO₂, and Zr_{0.25}Ti_{0.75}O₂-400 in the presence of TOPO. The NHSG reaction leading to TiO₂ exhibited two endothermic peaks in the temperature range from 180 to 270 °C. The endothermic peak centered at 207 °C is ascribed to the condensation between \equiv Ti–Cl and \equiv Ti–(OC₃H₇), and the peak ranging between 218 and 270 °C is attributed to the halide/titanyl exchange. This exchange results in the breaking and reforming of Ti–O bonds, which is considered to be necessary for the crystallization of TiO₂.¹⁸ The DSC trace for the NHSG reaction leading to ZrO₂ exhibited two

significant endothermic peaks centered at 51 and 340 °C, which are attributed to the liquefaction of the $ZrCl_4/Zr(O^{i}Pr)_4/TOPO$ complex and the condensation of \equiv Zr—Cl with \equiv Zr—(OC₃H₇), respectively. The DSC results clearly indicate that the temperatures for the formation of TiO₂ nanocrystals (207 °C) are lower than those required for the generation of NHSG-derived ZrO₂ (340 °C), which means the the condensation reactivity of Ti species is higher than that of Zr species.

To understand the interaction between the Ti and Zr species, the DSC curve of Zr_{0.25}Ti_{0.75}O₂ was further examined. Similarly to ZrO₂, Zr_{0.25}Ti_{0.75}O₂ exhibited endothermic melting of the TOPO complex at 65 °C. However, the endothermic melting process was not obvious in the DSC curve of TiO2. This is mainly attributed to the fact that TiCl₄/Ti(OⁱPr)₄/TOPO mixture is a viscous liquid, whereas the ZrCl₄/Zr(OⁱPr)₄/TOPO and ZrCl₄/Ti(OⁱPr)₄/TOPO mixtures are solids at room temperature. The Zr_{0.25}Ti_{0.75}O₂ sample exhibited an endothermic peak of condensation centered at 300 °C. Because the elemental analysis showed that TiO_2 is the dominant component in $Zr_{0.25}Ti_{0.75}O_2$, this condensation mainly occurs between \equiv Ti-Cl and \equiv Ti- $(O^{i}Pr)$, which result from ligand exchange between $\equiv Ti - (O^{i} - O^{i})$ Pr) and \equiv Zr–Cl at low temperatures. Ligand exchange between metal chlorides and metal alkoxides has been demonstrated to produce metal chloroalkoxides, and thus homogeneous as well as heterogeneous condensations can occur.¹⁷ It is noted that the temperature for condensation between the Ti species for Zr_{0.25}- $Ti_{0.75}O_2$ (300 °C) was higher than that for TiO₂ (207 °C), which suggests that the Ti species in the Zr_{0.25}Ti_{0.75}O₂ precursor solution is different from that in the TiO₂ precursor solution. Arnal et al.¹⁶ reported that metal chloroalkoxides are present in oligomeric structures because of the formation of alkoxo bridges. In this study, titanium zirconium chloroalkoxide oligomers could be produced in the Zr_{0.25}Ti_{0.75}O₂ precursor solution after ligand exchange. Compared to the pure titanium chloroalkoxide isomers, the Ti species have a lower reactivity to condense with each other to form Ti-O-Ti bonds when Zr species coexist with Ti species.

The endothermic peak for Zr_{0.25}Ti_{0.75}O₂ appearing at 334 °C in the DCS curve can be assigned to the formation of Zr-O-Ti bonds through cross-condensation. This cross-condensation is responsible for the incorporation of Zr into the TiO₂ lattice. However, the low Zr-to-Ti ratios reveal that the formation of $Zr_{x}Ti_{1-x}O_{2}$ nanocrystals is kinetically controlled because the temperature required for the formation of TiO₂ is lower than that for the formation of binary oxides. The relatively rapid formation of TiO₂ nanocrystals results in the inefficient condensation of Zr species during a dynamic equilibrium. The Zr components were lost either because the reaction temperature (320 °C) was too low to form ZrO₂ or because the ZrO₂ particles that formed were too small to be recovered through centrifugation at 11000 rpm at 400 °C. In contrast to the ineffective incorporation of Zr into TiO₂ in this study, Vioux et al.¹⁷ reported that amorphous zirconium titanate gels with Zr-to-Ti ratios equal to those of the initial solutions were obtained using a similar cross-condensation process at 110 °C. In addition, the temperature of condensation between Ti-Cl and Ti-O'Pr was reported to be 100 °C,¹⁶ which is lower than the temperature for the condensation of pure TiO2 (207 °C) obtained in this study. This discrepancy is due to the fact that TOPO modifies the thermodynamic properties and kinetics of the nonhydrolytic sol-gel reactions by forming Lewis adducts with the precursors.

Microstructures. To identify the effect of the preparation conditions on the microstructures of Zr-doped TiO₂, the NHSG-derived $Zr_xTi_{1-x}O_2$ samples were further analyzed using HR-



Figure 2. HRTEM images of NHSG-derived nanocrystals: (a) $Zr_{0.03}$ - $Ti_{0.97}O_2$ -320, (b) $Zr_{0.01}Ti_{0.99}O_2$ -400, (c) $Zr_{0.03}Ti_{0.97}O_2$ -400, (d) $Zr_{0.25}$ - $Ti_{0.75}O_2$ -400.

TEM and XRD. Figure 2 shows HRTEM images of $Zr_{0.03}$ -Ti_{0.97}O₂-320, $Zr_{0.01}Ti_{0.99}O_2$ -400, $Zr_{0.03}Ti_{0.97}O_2$ -400, and $Zr_{0.25}$ -Ti_{0.75}O₂-400 nanocrystals. The HRTEM images indicate that the NHSG-derived TiO₂ and ZrO₂ nanocrystals were almost spherical, except for a few that have irregular shapes as a result of aggregation (see Supporting Information, Figure S2). The sizes of the TiO₂ and ZrO₂ particles, as observed from low-magnification TEM images, were ca. 4.5 and 3.0 nm, respectively. Highly crystalline structures and single crystallinity were observed for both the TiO₂ and ZrO₂ particles in high-magnification TEM images. Because TOPO plays the role of a capping agent that isolates the NHSG-derived nanocrystals, these relatively small ZrO₂ nanocrystals arose from the lower metal-to-TOPO ratio that we used in these NHSG reactions.

The Zr_{0.03}Ti_{0.97}O₂ nanocrystals prepared at 320 °C exhibited irregular shapes and a wide size distribution. A similar phenomenon was also observed for Zr_{0.05}Ti_{0.95}O₂-320 (see Supporting Information, Figure S2). The sizes and shapes became more uniform when the reaction temperature rose to 400 °C. The Zr_{0.03}Ti_{0.97}O₂-400 and Zr_{0.25}Ti_{0.75}O₂-400 nanoparticles became faceted nanorods at 400 °C (Figure 2c,d). The lengths and widths of the Zr_{0.03}Ti_{0.97}O₂-400 nanorods were of ca. 15.0 and 8.0 nm, respectively, whereas the corresponding dimensions of the Zr_{0.25}-Ti_{0.75}O₂-400 nanorods were ca. 30.0 and 14.0 nm, respectively. The high-magnification HRTEM images showed that the nanorods existed in a single crystalline domain but contained a considerable number of defects on their edges. In addition, the Zr_{0.25}Ti_{0.75}O₂-400 nanorods were covered with a thin layer of amorphous material. A similar amorphous structure was dominant in the $Zr_{0.67}Ti_{0.33}O_2$ -400 sample.

Figure 3 displays the XRD patterns of TiO₂, ZrO₂, and $Zr_xTi_{1-x}O_2$ samples with various values of *x*. The TiO₂ and ZrO₂ particles obtained crystallized in the anatase and tetragonal forms, respectively, without further calcination. In addition, the $Zr_{0.03}Ti_{0.97}O_2$ -320, $Zr_{0.05}Ti_{0.95}O_2$ -320, $Zr_{0.01}Ti_{0.99}O_2$ -400, $Zr_{0.03}$ -Ti_{0.97}O₂-400, and $Zr_{0.25}Ti_{0.75}O_2$ -400 samples exhibited only



Figure 3. XRD patterns of TiO₂, ZrO₂, and Zr_xTi_{1-x}O₂ nanocrystals.

anatase structures, and no ZrO2 or ZrTiO4 diffraction peaks were identified, even though substantial amounts of Zr reactants had been added to participate in the nonhydrolytic reactions. This result is mainly due to the fact that the Zr⁴⁺ ions serve only as dopants in the TiO₂ matrix. Moreover, the diffraction peak of the $(101)_a$ profile of $Zr_{0.25}Ti_{0.75}O_2$ -400 shifted slightly to a lower value of 2θ when compared to that of the pure TiO₂ nanocrystals, revealing that the Zr^{4+} ions, with a larger ionic radius (0.79 Å) than Ti^{4+} (0.68 Å), were incorporated into the TiO_2 lattice to form dilute $Zr_xTi_{1-x}O_2$ solid solutions. The XRD results show the poor crystallinity of the Zr_{0.67}Ti_{0.33}O₂-400 sample, which is in agreement with the observation of the amorphous structure in its HRTEM image. The Zr-to-Ti ratio of 2.05 in the Zr_{0.67}-Ti_{0.33}O₂-400 sample clearly indicates that substantial amounts of TiO_2 are present in the ZrO_2 matrix. These results suggest that higher temperatures are required for crystallization of the binary oxide solutions than for crystallization of pure TiO₂ and ZrO₂ in the nonhydrolytic sol-gel reactions. Vioux et al.¹⁷ found that an NHSG-derived ZrTiO₄ sample crystallized at 700 °C. The high temperatures required for crystallized $Zr_xTi_{1-x}O_2$ solid solutions at high Zr concentrations probably arise because the anatase TiO₂ and tetragonal ZrO₂ structures are not compatible with each other. The anatase Zr_{0.25}Ti_{0.75}O₂-400 nanocrystals contained amorphous structures at their edges. It has been previously demonstrated that the solubility of Zr4+ units in solgel-derived anatase TiO₂ is below the Zr-to-Ti ratio of 0.075.²² The excess Zr^{4+} ions (i.e., 0.34 > 0.075) in the $Zr_{0.25}Ti_{0.75}O_2$ -400 sample would primarily accumulate at the surface of the anatase TiO2 nanocrystals because of slow condensation involving the Zr species and segregation of the Zr⁴⁺ ions to maintain phase stability. Therefore, the amorphous material at the edges of the Zr_{0.25}Ti_{0.75}O₂-400 nanorods presumably comprises crosslinked Zr and Ti binary oxides that are unable to crystallize in this nonhydrolytic sol-gel reaction.

The average crystallite sizes of anatase TiO₂ and tetragonal ZrO₂, calculated using Scherrer's equation from the broadening of diffraction peaks of the (101)_a and (101)_t profiles, were 4.6 and 3.0 nm, respectively. These values are close to the particle sizes observed in the TEM images. Because of the single crystallinity of the NHSG-derived nanocrystals, the size distributions and variations were examined from the TEM images. The TiO₂ and ZrO₂ nanoparticle sizes have uncertainties of ± 1.0 and ± 0.9 nm, respectively. The crystallite sizes of the Zr_{0.03}-Ti_{0.97}O₂-320 and Zr_{0.05}Ti_{0.95}O₂-320 samples were 5.2 ± 1.4 and 6.7 ± 2.5 nm, respectively; i.e., an increased Zr-to-Ti ratio increased the crystallite sizes. In addition, both the crystallite sizes and the size distributions of the Zr_{0.01}Ti_{0.99}O₂-400 (5.6 ± 1.0 nm) and Zr_{0.03}Ti_{0.97}O₂-400 (7.7 ± 1.9 nm) samples were larger than those obtained at 320 °C, indicating that increasing

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reaction temperature makes the crystallite sizes larger and more uniform. The $Zr_{0.25}Ti_{0.75}O_2\text{-}400$ sample exhibited the largest crystallite size of 12.6 \pm 2.5 nm because it was prepared at a high Zr-to-Ti ratio and reaction temperature.

The TEM observations and XRD results reveal that the initial Zr-to-Ti ratio and reaction temperature affect the sizes and shapes of the NHSG-derived $Zr_xTi_{1-x}O_2$ nanocrystals. The initial Zr-to-Ti ratio affects the morphology of the $Zr_xTi_{1-x}O_2$ samples by affecting the condensation rate. It has been suggested that the rate of alkyl halide elimination governs the nucleation and growth of nanocrystals.¹⁸ In this study, because the presence of Zr species retarded the formation of TiO₂, the sizes of the nanocrystals increased as the Zr-to-Ti ratio increased. In addition to the crystallite sizes, the different reactivities between Ti and Zr species also play the crucial role in the shapes and size distributions of the NHSG-derived nanocrystals. At 320 °C, the growth of TiO₂ nanocrystals is inhibited at the end where the Ti species are hybridized with less-reactive Zr species, thus resulting in the irregular shape of Zr-doped TiO₂. However, this low reactivity can be kinetically promoted by increasing the reaction temperature. Trentler et al.¹⁸ suggested that the formation and breaking of Ti-O bonds at elevated temperatures helps to erase the defects and, hence, result in more-crystalline structures. In this study, increasing temperature encourages the rearrangement of Ti and O atoms, leading to the elimination of the defects caused by Zr⁴⁺ and the formation of regularly shaped nanocrystals. This phenomenon was not observed when a similar reaction protocol was used for the preparation of $Hf_xZr_{1-x}O_2$ nanoparticles.²⁰ This discrepancy might be due to the fact that Zr and Hf species have similar reactivities, whereas the Ti species have a higher reactivity than the Zr species in the nonhydrolytic sol-gel reactions.

Surface Properties. In contrast to the hydrophilic surfaces of the metal oxides obtained using the conventional HSG method, the surfaces of the metal oxides obtained in this study were hydrophobic. The nanocrystals were readily soluble in hexane, but they were difficult to suspend in water. The XPS results indicate the existence of substantial amounts of carbon and small amounts of phosphorus on the surfaces of the nanocrystals, suggesting that some TOPO residues existed on the surface of the metal oxides (see Supporting Information, Figure S3). The C-to-P molar ratio ranged between 18 and 20, which is lower than that expected for TOPO (C/P = 24). In addition, the O*-to-P ratios (where O* denotes oxygen atoms other than M-O atoms) were in the range 2-3, which is larger than the intrinsic value (O/P = 1) expected for TOPO (see Supporting Information, Table 1S). These results imply that the TOPO molecules were decomposed during the high-temperature reactions. To investigate the interactions between TOPO and the nanocrystals, we used FTIR spectroscopy to further characterize the functional groups present on the surfaces of the nanocrystals. Figure 4 displays the FTIR spectra of TOPO, the as-prepared nanocrystals, and the nanocrystals obtained after photocatalysis. The spectrum of TOPO exhibited a significant absorption at 1146 cm^{-1} that was due to P=O stretching. The corresponding most intense absorptions for the TiO₂ and ZrO₂ nanocrystals appeared at 1065 cm⁻¹. The shift from 1146 to 1065 cm⁻¹ indicates that the P=O groups were chelated to the surface Zr⁴⁺ or Ti⁴⁺ centers. Figure 5 presents a cartoon illustration of the surface structure of an NHSG-derived nanocrystal based on the XPS and FTIR spectroscopic data. The surfaces of the nanocrystals are covered by TOPO units, which are chemically bonded to the surface through chelation of the P=O oxygen atoms or through defunctionalization of the P=O groups



Figure 4. FTIR spectra of pure TOPO and TOPO-capped ZrO_2 and TiO₂ nanocrystals, the latter recorded before and after photocatalysis.



Figure 5. Surface chemical structures of NHSG-derived nanocrystals.

to form new P—O—M bonds. After photocatalysis, the intensity of the signal for TOPO decreased, implying that a certain amount of TOPO decomposed during photocatalysis. The P-to-Ti and C-to-P elemental ratios of the NHSG-derived TiO₂ before and after photocatalysis were further analyzed by XPS. The P-to-Ti ratio remained at a similar value (2.01), whereas the C-to-P ratio decreased from 19.1 to 11.1 after photocatalysis. These XPS and IR results reveal that photocatalysis causes the decomposition of the surface TOPO through the removal of organic parts and the transformation of P=O functional groups to other phosphorus species.

Optical Properties. The band gaps and quantum effects on the optical properties of the nanocrystals were determined by UV-vis spectrophotometry. Figure 6 presents the UV-vis spectra of the TiO₂, ZO₂, and $Zr_xTi_{1-x}O_2$ nanocrystals suspended in hexane. The TiO₂ nanocrystals showed a steep increase in their absorptions at wavelengths below 333 nm, and the ZrO₂ nanocrystals exhibited significant absorptions at wavelengths below 234 nm. The band gaps of the pure TiO_2 and ZrO_2 nanocrystals, derived from the onsets of these significant absorptions, were 3.7 and 5.3 eV, respectively, which are larger than those of bulk TiO₂ (3.2 eV) and ZrO₂ (5.0 eV).^{1,23} This phenomenon indicates that quantum effects occurred and that the nanocrystals obtained were quantum-sized. The anatase Zrdoped TiO₂ crystals exhibited absorptions that extended to longer wavelengths. The band gaps of the Zr-doped TiO₂ crystals ranged between 2.8 and 3.6 eV, i.e., they were smaller than those of pure TiO₂ or ZrO₂ nanocrystals. Presumably, these red shifts and reduced band gaps resulted either from defects caused by trace amounts of Zr^{4+} in the TiO_2 lattice or from increased crystal domains. We note that the $Zr_{0.25}Ti_{0.75}O_2$ -400 sample exhibited marked absorptions up to 600 nm. This extrinsic band gap absorption of $Zr_{0.25}Ti_{0.75}O_2$ -400 is attributed to the accumulation of substantial amounts of Zr^{4+} at the surface of the TiO₂ anatase crystals. A similar effect occurred for amorphous Zr_{0.67}Ti_{0.33}O₂-400, which contained mainly ZrO₂



Figure 6. UV-vis spectra of NHSG-derived nanocrystals.



Figure 7. Photodegradation of RhB in the presence of NHSG-derived nanocrystals.

with TiO₂ in a comparative amount (Zr/Ti = 2.1) and exhibited a band gap of 3.8 eV. Large amounts of Ti⁴⁺ in the ZrO₂ matrix not only inhibited the crystallization of ZrO₂ but also greatly reduced the band gap of ZrO₂ from 5.3 to 3.8 eV.

Photoactivities of the NHSG-Derived Nanocrystals. We examined the photoactivities of the NHSG-derived nanocrystals by considering the decoloration of RhB monitored at 554 nm. Figure 7 shows the change in RhB concentration as a function of irradiation time. In the absence of a photocatalyst, RhB was stable when illuminated with UV light at 305 nm. The rapid degradation of RhB in the presence of the prepared nanocrystals indicates that each of the TOPO-capped photocatalysts exhibited photoactivity. Although the band transitions of ZrO_2 nanocrystals occur below 234 nm, electron transitions between the defect levels and bands result in the ZrO_2 nanocrystals having photocatalytic functions at 305 nm. The photodecomposition of RhB

followed pseudo-first-order kinetics. The $Zr_{0.03}Ti_{0.97}O_2-400$ sample ($k = 0.40 \text{ min}^{-1}$) exhibited the highest rate of decomposition of RhB, followed by $Zr_{0.25}Ti_{0.75}O_2-400$ ($k = 0.28 \text{ min}^{-1}$), $Zr_{0.01}Ti_{0.99}O_2-400$ ($k = 0.13 \text{ min}^{-1}$), $Zr_{0.05}Ti_{0.95}O_2-320$ ($k = 0.10 \text{ min}^{-1}$), $Zr_{0.03}Ti_{0.97}O_2-320$ ($k = 0.07 \text{ min}^{-1}$), TiO_2-320 ($k = 0.04 \text{ min}^{-1}$), $Zr_{0.67}Ti_{0.33}O_2-400$ ($k = 0.01 \text{ min}^{-1}$), and then ZrO_2 ($k = 3.2 \times 10^{-3} \text{ min}^{-1}$).

The $Zr_{x}Ti_{1-x}O_{2}$ nanocrystals exhibited higher degradation efficiencies than did the pure TiO₂ and ZrO₂ samples. Moreover, the stoichiometry of the reactants and the reaction temperature during the synthesis of the nanoparticles affected the photoactivities of these NHSG-derived nanocrystals. The degradation efficiencies increased with increasing Zr-to-Ti ratio. For the samples prepared at 400 °C, we observed the highest photoactivity when the Zr-to-Ti ratio in the $Zr_xTi_{1-x}O_2$ nanocrystals was 0.03. In contrast, the $Zr_xTi_{1-x}O_2$ sample prepared with the same Zr-to-Ti ratio (0.03) but at 320 °C exhibited a lower rate of degradation of RhB. It has been demonstrated that the photoactivities of photocatalysts are mainly related to the amounts of defects. A few defects in a TiO₂ matrix, resulting from the presence of dopants, can play the role of trapping centers to inhibit charge recombination and improve the photoactivity.²⁴ On the contrary, an excessive number of defects can induce charge recombination and decrease the degree of effective charge. We attribute the highest photoactivity of the $Zr_{0.03}Ti_{0.97}O_2$ -400 samples to their moderate content of Zr^{4+} ions in the TiO₂ lattice (Zr-to-Ti ratio of 0.03) and the poor photoactivity of the photocatalysts prepared at low temperature to the great number of surface defects that resulted from the irregular shapes of these particles.

We also compared the photoactivity of the NHSG-derived photocatalysts with that of Degussa P25 TiO₂ in terms of the decoloration of RhB (see Supporting Information, Figure S4). Similarly, the photodecomposition of RhB by Degussa P25 TiO₂ followed pseudo-first-order kinetics, and the pseudo-first-order rate constant (k) was 0.58 min^{-1} . Although Degussa P25 showed a higher apparent photoactivity than the NHSG-derived nanocrystals, the intrinsic photoactivities of the NHSG-derived TiO₂ nanocrystals ($k = 0.02 \text{ g} \cdot \text{m}^{-2} \cdot \text{min}^{-1}$) were 1.7 times higher than that of Degussa P25 ($k = 1.2 \times 10^{-2} \text{ g} \cdot \text{m}^{-2} \cdot \text{min}^{-1}$) when normalized to the surface area, because the TOPO-capped TiO₂ $(2 \text{ m}^2/\text{g})$ has a much smaller specific surface area than Degussa P25 (50 m^2/g). The high intrinsic photoactivities of the NHSGderived nanocrystals are presumably due to the fact that the surface TOPO enhances the adsorption of RhB onto the photocatalysts.

Conclusions

We have successfully prepared Zr-doped anatase TiO₂ nanorods through the cross-condensation of Zr/TiCl₄ with Zr/ Ti(OⁱPr)₄ in anhydrous TOPO at either 320 or 400 °C. The kinetics of the alkyl halide elimination involving the Ti and Zr species plays a crucial role in determining the morphologies, chemical compositions, and crystalline phases of the Zr-doped TiO₂ nanorods. Because the condensation between the Ti species is faster than that between the Zr species, the kinetically controlled reactions cause anatase TiO₂ to be the dominant structure in the nanorods, with the Zr⁴⁺ ions appearing only as dopants accumulating at the surfaces of the nanocrystals for various initial Zr-to-Ti ratios used in preparation. The existence of less-reactive Zr species in the reaction mixtures retards the nucleation of TiO₂. Therefore, increasing the concentration of Zr species in the precursor solutions increases the sizes of the nanocrystals, and increasing reaction temperatures promote

regular shapes of the nanorods. The photoreactivities of the Zrdoped TiO₂ materials are associated with the amounts of dopants and the shapes of the nanorods. The photocatalysts having the optimal Zr-to-Ti ratio of 0.03 and regular shapes exhibit the highest photoactivities. The TOPO moieties, which we used as capping agents, were chemically bound to the surface of the nanocrystals, either through direct donation of their P=O groups to the surface metal centers or through reformation. The influence of surface TOPO on the mechanisms and dynamics of photocatalysis requires further studies to better understand the photocatalytic chemistry of such surface-modified photocatalysts.

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Supporting Information Available: HRTEM images of NHSG-derived TiO₂, ZrO_2 , $Zr_{0.05}Ti_{0.95}O_2$ -320, and $Zr_{0.67}Ti_{0.33}O_2$ -400 nanocrystals; Ti(2p) and Zr(3d) XPS spectra of $Zr_xTi_{1-x}O_2$ nanocrystals; O(1s), P(2p), and C(1s) XPS spectra of NHSG-derived TiO₂ nanocrystals; C-to-O*-to-P molar ratios estimated from the integrated peak areas of the XPS spectra normalized by their atomic sensitivity factors; and photodecomposition of RhB in the presence of Degussa P-25 TiO₂. This material is available free of charge via the Internet at http://pubs.acs.org.

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