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Improvement of thermal stability of nitrogen doped titania photocatalyst by addition of surfactants during solvothermal treatment

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Abstract The $TiO_{2-x}N_y$ nanocrystals with beige color were prepared by homogeneous precipitation-solvothermal process in $TiCl_3$-hexamethyleneamine-alcohol solutions with the addition of various surfactants, such as sodium dodecylbenzenesulfonate (SDBS), *n*-hexadecylamine (HAD), and *n*-hexadecyltrimethylammonium chloride (HTAC) at 190 °C for 10 h. The phase composition, crystallinity, microstructure, specific surface area, nitrogen doped amount, and photocatalytic activity of titania powders greatly changed depending on pH value and other reaction conditions. The $TiO_{2-x}N_y$ powders prepared by solvothermal treatment with surfactant additives followed by calcination in air at 400 °C showed smaller particle size, larger BET specific surface area and higher photocatalytic activity than those without surfactant. The $TiO_{2-x}N_y$ powders showed excellent visible-light absorption, thermal stability and photocatalytic activity for nitrogen monoxide destruction under irradiation of both visible-light and UV-light irradiation. About 40% and 60% nitrogen monoxide could be continuously removed with the residence time of 1.9 min by the $TiO_{2-x}N_y$ photocatalyst under irradiation of visible-light ($\lambda > 510$ nm) and UV-light ($\lambda > 290$ nm), respectively.

Introduction

Titania is the most effective photocatalyst and is widely applied in the purification of air and water, solar system, etc. Usually, anatase titania shows photocatalytic activities only under UV-light irradiation of wavelength <387 nm, corresponding to its band gap value of 3.2 eV. In order to utilize solar energy effectively, the development of visible-light induced photocatalysts has attracted many researchers' attention. It has been known that nitrogen doping is an effective method to realize the narrowing of band gap and consequently to induce the visible-light responsive photocatalytic activity [1]. In previous articles, we have successfully prepared nitrogen doped titania, $TiO_{2-x}N_y$, by some soft chemical processes such as mechanochemical treatment [2, 3] and solvothermal process [4, 5]. The phase-compositional and morphological control of the anion doped photocatalysts could be realized by the solvothermal process. Not only rutile, but also anatase and brookite single phase of $TiO_{2-x}N_y$ could be prepared [4]. In addition, the $TiO_{2-x}N_y$ with fibrous or wool-like morphologies could be prepared using different precipitants [5]. It is well known that photocatalytic activities are greatly related to the crystallinity, phase composition, BET specific surface area, microstructure and morphology of the prepared powders. Thermal stability is also an important factor in the application of $TiO_{2-x}N_y$ photocatalyst. Usually, the BET specific surface area, nitrogen doped amount and photocatalytic activity changed greatly with the prepare conditions of the samples. In the present article, the effect of surfactant additives on the thermal stability of $TiO_{2-x}N_y$ during solvothermal process was investigated.

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Experimental

The $TiO_{2-x}N_y$ nanocrystals with beige color were prepared by homogeneous precipitation-solvothermal process in $TiCl_3$-hexamethyleneamine (HMT, $C_6H_{12}N_4$)-ethanol solutions with the addition of various surfactants, such as sodium dodecylbenzenesulfonate (SDBS, $C_{12}H_{25}C_6H_4SO_3Na$, anionic surfactant), *n*-hexadecylamine (HAD, $CH_3(CH_2)_{14}CH_2NH_2$, nonionic surfactant), and *n*-hexadecyltrimethylammonium chloride (HTAC, $[CH_3(CH_2)_{15}N(CH_3)_3]Cl$, cationic surfactant). Hexamethylenetetramine (HMT) was dissolved in 20 wt.% $TiCl_3$ solution (Kanto Chem. Co. Inc. Japan) with molar ratio of HMT:$TiCl_3$ = 0.60:1, 1.20:1, and 2.11:1 to control the final pH value of the reaction solution to 1, 7 and 9, respectively. Desired amount of surfactant with mole ratio of surfactant:Ti = 0.1:1 was added into the HMT-$TiCl_3$ solution, then mixed with the same volume of ethanol before introduced into the autoclave attached with a Teflon tube followed by solvothermal treatment at 190 °C for 10 h. The powder product was separated by centrifugation, washed with distilled water and acetone three times, respectively, then vacuum dried at 80 °C overnight. The phase composition of the products was determined by X-ray diffraction analysis (XRD, Shimadzu XD-D1) using graphite-monochromized CuKα radiation. The specific surface areas were determined by the amount of nitrogen adsorption at 77 K (BET, Quantachrome NOVA 1000-TS). Microstructures were observed by a transmission electron micrograph (TEM, JEOL, and JEM-2010). The amount of nitrogen doped in titania was determined by an oxygen–nitrogen analyzer (HORIBA, EMGA-2800). In order to remove the absorbed nitrogen reagents completely, all the samples were calcined at 400 °C for 1 h before the nitrogen doped amount analysis. The photocatalytic activity for nitrogen monoxide destruction was determined by measuring the concentration of NO gas at the outlet of the reactor (373 cm^3 of internal volume) during the photo-irradiation of a constant flow (200 cm^3/min) of a mixture containing 1 ppm NO-50 vol.% air (balance N_2). The photocatalytic sample was placed in a hollow of 20 mm length × 15 mm width × 0.5 mm depth on a glass holder plate and set in the bottom center of the reactor. A 450 W high-pressure mercury arc was used as the light source. The wavelength was controlled by selecting filters, i.e., Pyrex glass for $\lambda > 290$ nm, Kenko L41 Super Pro (W) filter >400 nm and Fuji triacetyl cellulose filter >510 nm. The concentration of NO was determined using a NO_x analyzer (Yanaco, ECL-88A). For comparison, a photocatalytic reaction was also carried out using commercial titania (Degussa P25).

Results and discussion

It is known that the hydrolysis of HMT produces HCHO and NH_3 at above 70 °C. The ammonia reacts with $TiCl_3$ to form nitrogen contained $TiO_{2-x}N_y \cdot nH_2O$ precursor. Well-crystallized $TiO_{2-x}N_y$ could be formed by the followed solvothermal treatment at 190 °C:

$$TiCl_3 \xrightarrow{NH_3, H_2O,\ \text{etc.}} TiO_{2-x}N_y \cdot nH_2O \xrightarrow[\text{in autoclave}]{190\,^\circ C} TiO_{2-x}N_y \quad (1)$$

Figure 1 shows the XRD patterns of the titania powders prepared in $TiCl_3$-HMT ethanol solution with or without surfactant additive at pH 7 and 190 °C for 10 h followed by calcinations at various temperatures for 1 h. The powders prepared at pH 7 consisted of brookite/anatase mixture. The phase composition of $TiO_{2-x}N_y$ was stable until 400 °C in air. After calcination at temperature higher than 500 °C, phase transformation occurred. At temperature higher than 600 °C, single phase of rutile was obtained. The powders prepared with the addition of sodium dodecylbenzenesulfonate (SDBS) during the solvothermal treatment also possessed the same phase composition of brookite/anatase mixture. However, the powders showed quite different thermal stability. As shown in Fig. 1b, the anatase and brookite phases of the powder showed much higher thermal stability than that without SDBS surfactant. Only a little part of brookite/anatase mixture transformed to rutile phase at such high temperature as 600 °C. Even in the powders calcined at above 800 °C, a small amount of anatase/brookite still existed. Usually, titania powders showed white color, however, the powders prepared by the present research showed beige color. It is found that even if the $TiO_{2-x}N_y$ sample was calcined at such high temperature as 800 °C, it did not changed to white color, indicating the thermal stability of the Ti–N bonding in $TiO_{2-x}N_y$ powders prepared by the present research. The two-step absorption of the $TiO_{2-x}N_y$ powders was clearly existed until 600 °C (Fig. 2). The first adsorption was related the original structure of the titania, and the second adsorption was related to the existence of the nitrogen doping.

Figure 3 shows the effect of calcination temperature on the nitrogen doped amount and the photocatalytic activity under irradiation of visible light of wavelength >510 nm. It is accepted that electron/hole pairs are formed by the photo-excitation of titania. In the presence of oxygen, the electrons in the conduction band are immediately trapped by the molecular oxygen to form $\bullet O_2^-$, which can then generate active •OOH radicals [6–8]. At the same time, the holes are trapped by water in air to produce hydroxyl

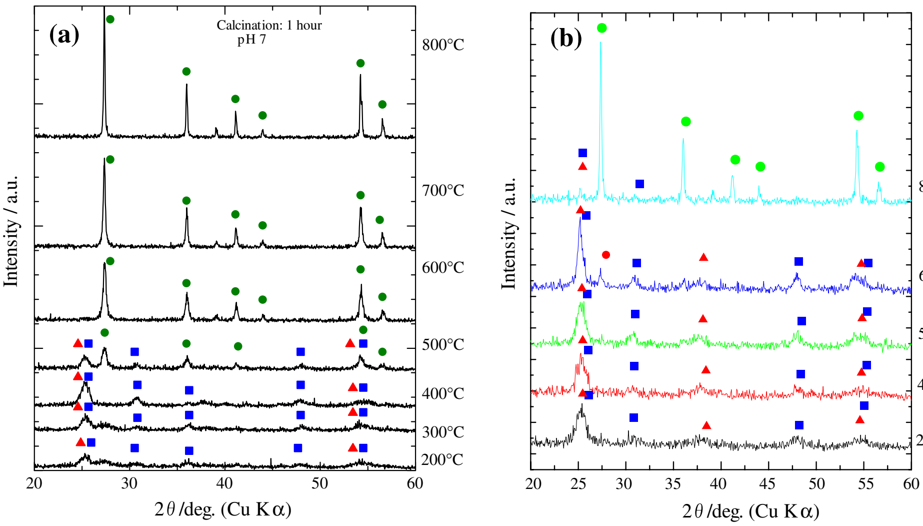

Fig. 1 XRD patterns of the nitrogen doped titania prepared by solvothermal treatment in ethanol-aqueous solution (**a**) without surfactant additive, and (**b**) with SDBS additive at 250 °C for 10 h and calcined at various temperatures for 1 h. (■) brookite, (▲) anatase, (●) rutile

radical [6–8]. The nitrogen monoxide reacts with these reactive radicals, molecular oxygen, and very small amount of water in air (humidity was about 25% in the present research) to produce HNO_2 or HNO_3. It was reported that about 20% of nitrogen monoxide was decomposed to nitrogen and oxygen directly [9]. Although the nitrogen doped amount decreased with calcination temperature, however, it was found that even if the powders was calcinated at such high temperature as 800 °C, 0.05 wt.% of residual nitrogen still existed. The samples prepared with SDBS additive during the solvothermal treatment showed almost the same behavior with those without surfactant additives. The photocatalytic activity of the samples prepared without surfactant additives decreased with calcination temperatures. On the other hand, the powders prepared with SDBS additive showed different behavior. After calcination at 400 °C for 1 h, the visible-light activity increased to about 40% NO oxidation ability. After calcinations above 500 °C, although the photocatalytic activity also decreased, the samples still showed higher NO oxidation ability than those prepared without any surfactant additives. This might be due to the removal of the absorbed surfactants in the samples and the increase in crystallinity by calcination at 400 °C. After calcination at higher temperatures, the crystalline growth proceeded and led to the increment of particle size and decrement of specific surface area, and finally led to the decrement of photocatalytic activities.

Figure 4 shows the XRD patterns of the powders prepared at various pH values with or without surfactant additives. It is obvious that the phase composition strongly related to the pH value of the reaction system. The powders prepared at pH 1, 7, and 9 in $TiCl_3$-HMT ethanol solutions consisted of single phase of brookite, mixture of anatase/brookite, and single phase of rutile. On the other hand, no

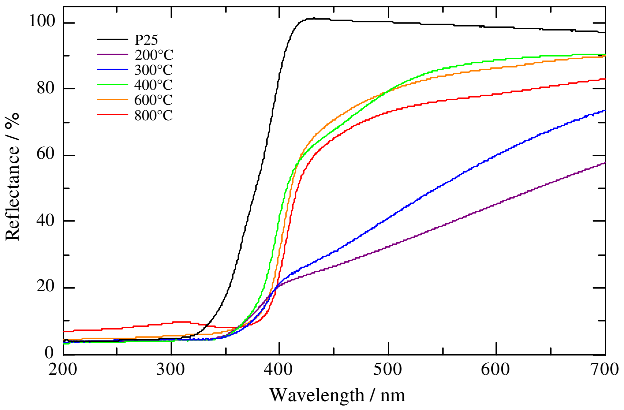

Fig. 2 DRS spectra of the nitrogen doped titania prepared by solvothermal treatment in ethanol-aqueous solution at 250 °C for 10 h and calcined at various temperatures for 1 h

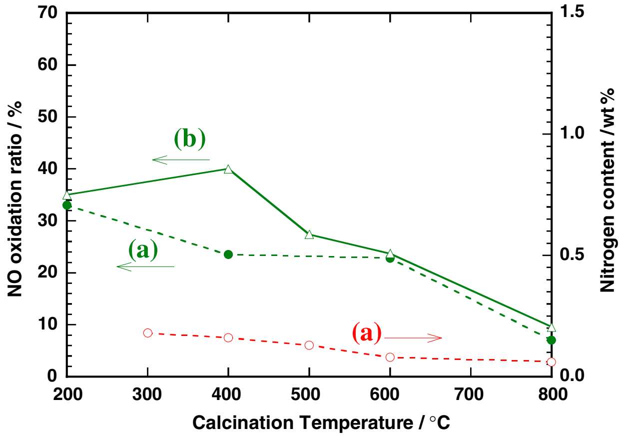

Fig. 3 Nitrogen doped amounts (*left axis*) and photocatalytic activities (*right axis*) under visible light of $\lambda > 510$ nm irradiation of the nitrogen doped titania prepared by solvothermal treatment in ethanol-aqueous solution at 250 °C for 10 h followed by calcination at various temperatures for 1 h. (**a**) without surfactant additive; (**b**) with SDBS additive

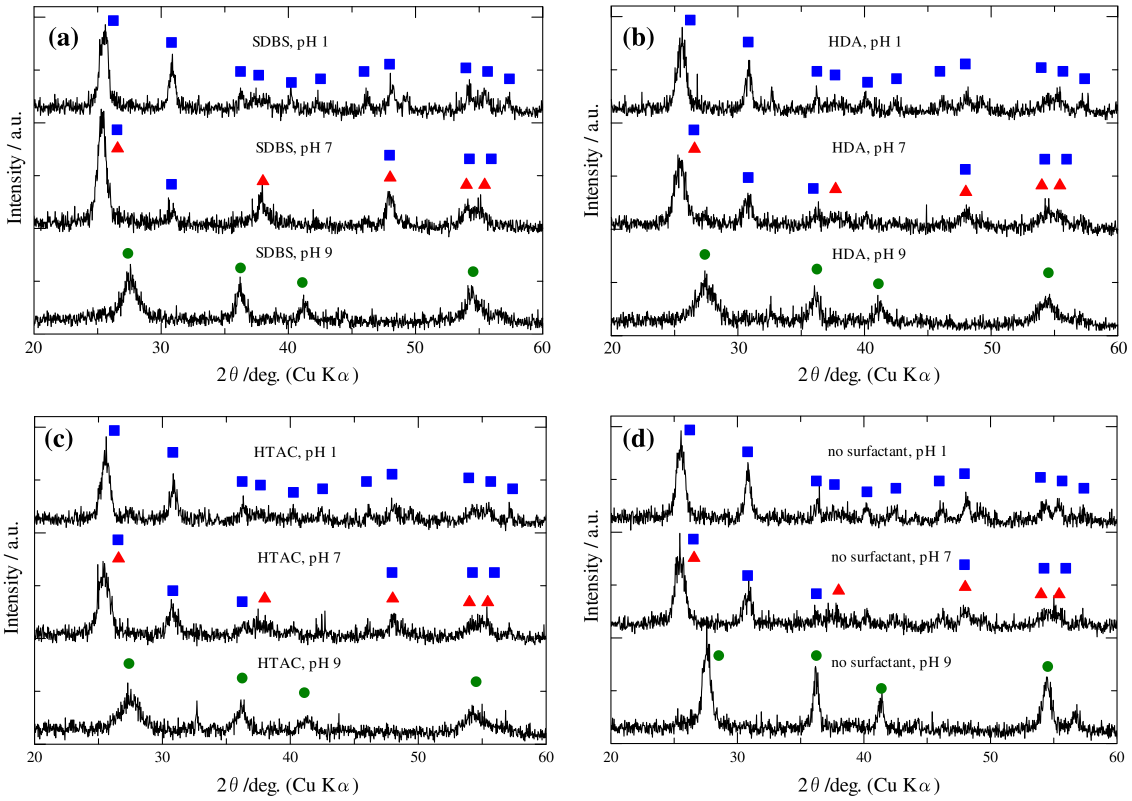

Fig. 4 XRD patterns of the nitrogen doped titania prepared by solvothermal treatment in ethanol-aqueous solution with different surfactants and pH value at 250 °C for 1 h followed by calcination in air at 400 °C for 1 h. (**a**) SDBS, (**b**) HDA, (**c**) HTAC, (**d**) no surfactant. (■) brookite, (▲) anatase, (●) rutile

obvious difference on the phase compositions could be observed by addition of various surfactants such as sodium dodecylbenzenesulfonate (SDBS, anionic surfactant), *n*-hexadecylamine (HAD, nonionic surfactant), and *n*-hexadecyltrimethylammonium chloride (HTAC, cationic surfactant). The reason might be related to the comparatively low concentration of the surfactant (surfactant:Ti = 0.1:1). In addition, the surfactants had almost no effect on the pH value of the reaction system, which greatly affect the phase composition, morphology and photocatalytic activity of the nitrogen doped titania [4, 10].

Figure 5 shows the TEM images of the powders prepared by solvothermal treatment with anionic, nonionic and cationic surfactants together with those after calcination at 400 °C for 1 h. Although the samples showed similar morphologies, it was obvious that the powders prepared with surfactant additives (Fig. 5f–h) possessed smaller particle size than that without surfactant addition (Fig. 5e). The powders prepared without surfactant additive possessed particles with about 10 nm in diameter and 30 nm in length. On the other hand, the powders prepared with addition of various surfactants possessed particles with about 7–8 nm in diameter and 15–18 nm in length. In the case of no-surfactant additives, because of the fine particle size and high surface energy of the as-prepared powders, it grew to large crystallines after calcination at 400 °C. It might be suggested that the existence of surfactant molecules adsorbed on the surface of the nitrogen doped titania crystallines of the samples (b), (c) and (d). The surfactant molecules depressed the crystalline growth of the primary particles. After calcinations at 400 °C, smaller particle size was kept.

Figure 6 shows the pore size distribution of the prepared samples with different surfactant additives followed by calcination at 400 °C. It is observed that the powders prepared without surfactant additives showed a comparatively larger pore size distribution around 30 nm. On the other hand, the powders prepared with various surfactant additives possessed smaller pore size distribution around 15–20 nm. Some smaller pore size distribution around 7–8 nm could be also observed in the samples (b), (c) and (d). It is accepted that pH value also affects the particle size during the solvothermal process. In previous research, it was found that smaller particles crystallines could be formed at comparatively higher pH values [4]. However, it was found that pH value during the solvothermal process had no obvious affect on the pore size distribution, which related to the agglomeration state of the particles strongly.

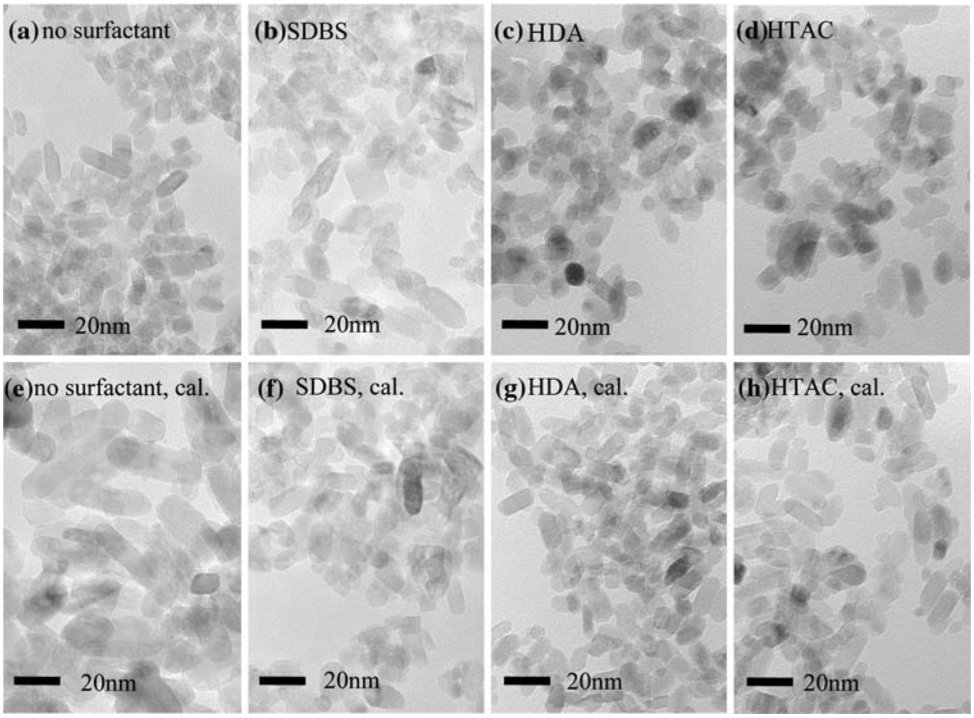

Fig. 5 TEM photographs of the nitrogen doped titania prepared by solvothermal treatment in ethanol-aqueous solution at pH 7 and 190 °C for 10 h (*upper side*), and calcined at 400 °C for 1 h (*under side*). (**a**) Without surfactant additives, (**e**) calcined and with (**b**) SDBS, (**f**) calcined; (**c**) HAD, (**g**) calcined; (**d**) HTAC, (**h**) calcined additives

Figure 7 shows the specific surface areas and visible-light induced photocatalytic deNO$_x$ activities of the powders prepared by solvothermal treatment in ethanol-aqueous solution at different pH values with and without SDBS surfactant additives. The BET specific surfaces increased with the pH values. It might be suggested that at higher pH values, more crystallines formed at the same time because of the more precipitants existed. In the case of no-surfactant additives, as shown in TEM images, the particle size increased and lead to the decrement of the specific surface areas. It is well known that the photocatalytic activity strongly related to the specific surface area of the well-crystallized particles [6]. The visible-light induced photocatalytic activity decreased to about 23% of deNO$_x$ degree after calcination at 400 °C. This is related to the decrement of specific surface area after calcination. With the additive of SDBS during the solvothermal treatment, it was observed that specific surface areas increased after calcination at 400 °C. As shown in TEM images, almost no particle size change could be observed before and after calcination. The increment of specific surface area was related to the removal of surfactants adsorbed on the surface of the $TiO_{2-x}N_y$ crystallines. However, in the case of pH 9, because of the very large specific surface area and high surface energy, the particle was very easy to be sintered to form large particles. The visible-light induced photocatalytic activity also decreased after calcination the sample prepared at pH 9. The visible-light induced photocatalytic activity agreed with the change of specific surface area well.

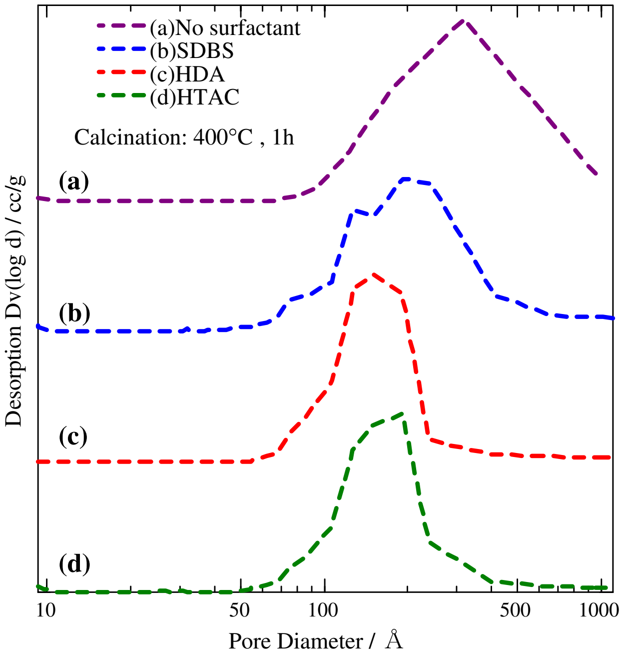

Fig. 6 Pore size distribution of the nitrogen doped titania powders prepared by solvothermal treatment in ethanol-aqueous solution at 190 °C for 10 h followed by calcination at 400 °C for 1 h. (**a**) Without surfactant additives, and with addition of (**b**) SDBS, (**c**) HAD, (**d**) HTAC

Figure 8 shows the visible-light and UV-light induced photocatalytic deNO$_x$ activities of the powders prepared by

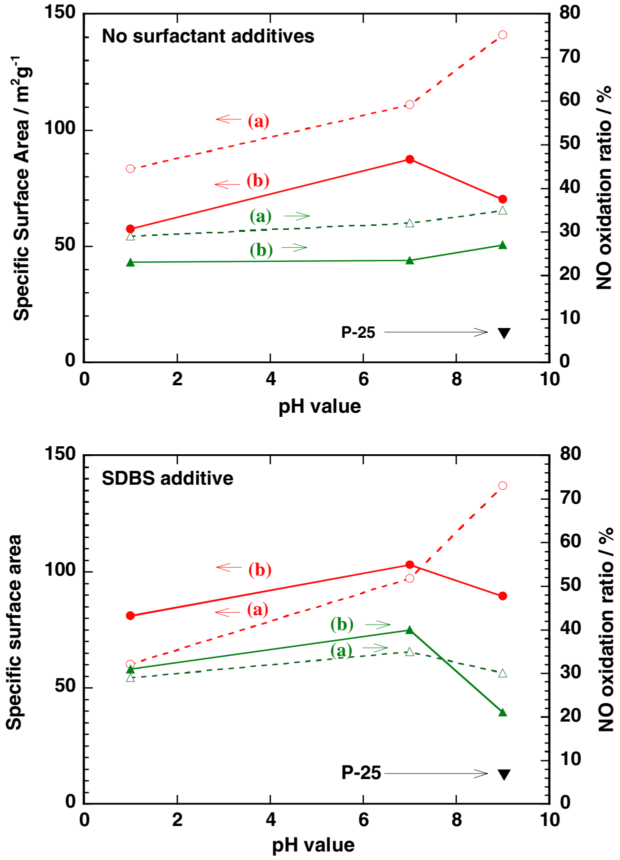

Fig. 7 Specific surface areas (*circled marks*) and visible-light ($\lambda > 510$ nm) induced photocatalytic deNO$_x$ activities (*triangle marks*) of the powders prepared by solvothermal treatment in ethanol-aqueous solution at different pH values and 190 °C for 10 h with or without SDBS surfactant additives. (**a**) as prepared by solvothermal treatment (*open marks*); (**b**) calcined (**a**) at 400 °C for 1 h (*solid marks*). For comparison, P25 standard sample was also characterized

solvothermal treatment in ethanol-aqueous solution at pH 7 with various surfactant additives followed by calcination at 400 °C. It is obvious that all the samples prepared by the present method showed much high visible-light and UV-light induced photocatalytic activity than that of standard commercial powders P25. Not only anionic surfactant, but also non-ionic and cationic surfactant showed the same positive effect on the increment of NO oxidation photocatalytic activity. Compared with that of non-surfactant additives, visible-light induced photocatalytic activity could be greatly improved by the addition of some anionic, non-ionic, or cationic surfactants during the solvothermal treatment.

Conclusions

Based on the above results, the following conclusions might be drawn:

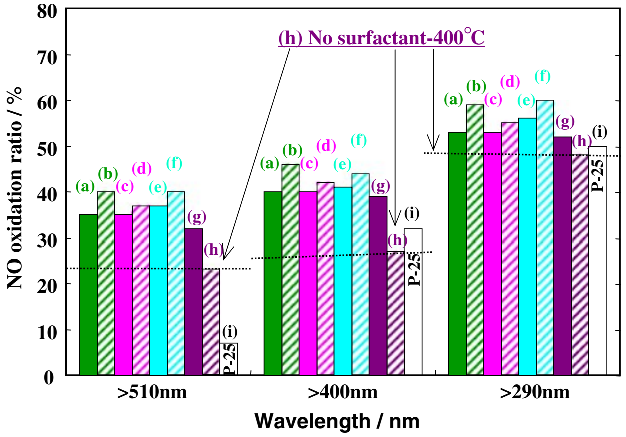

Fig. 8 Visible-light and UV-light induced photocatalytic deNO$_x$ activities of the powders prepared by solvothermal treatment in ethanol-aqueous solution at pH 7, 190 °C for 10 h (**a**) with SDBS, (**b**) calcined (**a**) at 400 °C for 1 h; (**c**) with HAD, (**d**) calcined (**c**) at 400 °C for 1 h; (**e**) with HTAC, (**f**) calcined (**e**) at 400 °C for 1 h; (**g**) without surfactant additive, (**h**) calcined (**g**) at 400 °C for 1 h. For comparison, P25 standard sample was also characterized

The phase composition, crystallinity, microstructure, specific surface area, nitrogen doped amount, and photocatalytic activity of titania powders greatly changed depending on pH value and other reaction conditions. The $TiO_{2-x}N_y$ powders prepared by solvothermal treatment with surfactant additives followed by calcination in air at 400 °C showed smaller particle size, larger BET specific surface area, higher photocatalytic activity and higher thermal stability than those without surfactant. The $TiO_{2-x}N_y$ powders showed excellent visible-light absorption, thermal stability and photocatalytic activity for nitrogen monoxide destruction under irradiation of both visible-light and UV-light irradiation. About 40% and 60% nitrogen monoxide could be continuously removed by the $TiO_{2-x}N_y$ photocatalyst under irradiation of visible-light ($\lambda > 510$ nm) and UV-light ($\lambda > 290$ nm), respectively.

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