

## Cellulose/TiO<sub>2</sub> Hybrid Spherical Microbeads Prepared by a Viscose Phase Separation Method: Control of the Distribution of TiO<sub>2</sub> Particles in a Sphering System

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**ABSTRACT:** Cellulose/TiO<sub>2</sub> hybrid spherical microbeads were prepared by a one-step phase separation method using a cellulose xanthate aqueous solution and a sodium polyacrylate aqueous solution. Various types of cellulose/TiO<sub>2</sub> hybrid spherical microbeads were obtained by using the several kinds of TiO<sub>2</sub> particles. The resulting hybrid spherical microbeads showed respective differences in the distribution of TiO<sub>2</sub> particles. EPMA observation of the surface of hybrid spherical microbead clearly showed where the TiO<sub>2</sub> particles were distributed. In addition, the extent of coverage by TiO<sub>2</sub> particles of the surface was also confirmed by external appearance, because the surface of cellulose/TiO<sub>2</sub> hybrid spherical microbeads on which there were relatively few TiO<sub>2</sub> particles appeared dark yellow. In contrast, the cellulose/TiO<sub>2</sub> hybrid spherical microbeads on which TiO<sub>2</sub> particles aggregated densely appeared white. It was suggested that the distribution of TiO<sub>2</sub> particles on the hybrid spherical microbeads was related to electric repulsion between the CSS<sup>-</sup> group and TiO<sub>2</sub>. The narrower the zeta potential distribution of TiO<sub>2</sub> particles in the sphering pH condition (*i.e.*, in pH 13 aqueous solution) is, the more TiO<sub>2</sub> particles were driven out from the cellulose xanthate domain. [DOI 10.1295/polymj.37.186]

**KEY WORDS** Cellulose / TiO<sub>2</sub> / Zeta Potential / Spherical Microbeads / Viscose / Phase Separation /

Cellulose, which has been used in various matrix-forming materials, has long been explored for its potential as a building material. In particular, spherical microbeads of cellulose have been used as chromatographic packing materials,<sup>1–3</sup> immobilization supports of microbes<sup>4</sup> and cosmetic materials.<sup>5,6</sup> Hoogendam *et al.* prepared the organic/inorganic hybrid materials using hydroxyethyl cellulose and inorganic oxides, such as SiO<sub>2</sub>, TiO<sub>2</sub>, and Fe<sub>2</sub>O<sub>3</sub>, as materials for the cosmetics, pharmaceuticals and coating.<sup>7</sup> Gilchrist *et al.* prepared the organic/inorganic hybrid materials using cellulose and TiO<sub>2</sub> as the matrix of an anion exchanger for adsorbent of protein.<sup>8</sup> Lei *et al.* were successful in preparation of TiO<sub>2</sub>-densified perfectly spherical microbeads cellulose as an anion exchanger by means of W/O phase separation using cellulose xanthate and dichlorobenzene.<sup>9</sup> The control of TiO<sub>2</sub> particles on the cellulose surface is considered to be important for the adsorption behavior of various solutes. On the other hand, cellulose microbeads prepared by the phase separation phenomenon between cellulose xanthate and polyacrylic acid aqueous solution, namely the “viscose phase separation method”,

were monodisperse and spherical.<sup>10</sup> We succeeded in preparation of cellulose/TiO<sub>2</sub> hybrid spherical microbeads the surface of which was covered densely with TiO<sub>2</sub> particles by a “viscose phase separation method”, and could develop carbon/TiO<sub>2</sub> hybrid spherical microbeads by means of their carbonization. In addition, it was confirmed that the efficiency of the carbon/TiO<sub>2</sub> hybrid spherical microbeads for removal of acetaldehyde as a photoassisted-catalysis was more effective than that of naked TiO<sub>2</sub>.<sup>11</sup> In contrast, Taoda *et al.* developed hybrid silica microbeads coated sparsely with TiO<sub>2</sub>.<sup>12</sup> Nonami *et al.* developed an adsorbent that modified the surface of TiO<sub>2</sub> particle with apatite partially.<sup>13</sup> The contact area of TiO<sub>2</sub> particles with organic material in TiO<sub>2</sub>-composite was reduced in order to avoid the composite's photo-degradation by active TiO<sub>2</sub> particles. Yamashita *et al.* could develop the deodorant fiber that hybridized sparsely photocatalytic TiO<sub>2</sub> particles to cellulose fiber.<sup>14</sup> They tried to avoid photo-degradation of cellulose fiber by active TiO<sub>2</sub> particles using modified TiO<sub>2</sub>. Therefore, it is important for the photoassisted-catalytic adsorbent using cellulose as a matrix that TiO<sub>2</sub> particles were

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controlled on the surface of cellulose microbeads.

In this study, we prepared various types of cellulose/TiO<sub>2</sub> hybrid spherical microbeads by using several kinds of TiO<sub>2</sub> particles with the objective of controlling the appearance of the TiO<sub>2</sub> component. Differences relative to the composition of TiO<sub>2</sub> particles were observed in the distribution of TiO<sub>2</sub> contained in hybrid spherical microbeads. Therefore, the relationships between hybrid spherical microbeads and the composition of TiO<sub>2</sub> particles used were examined and the mechanism of the hybrid-sphering process was discussed.

## EXPERIMENTAL

### Materials

Cellulose/TiO<sub>2</sub> hybrid spherical microbeads were prepared by a one-step phase separation method using cellulose xanthate aqueous solution and sodium polyacrylate aqueous solution.<sup>11</sup> The characteristics of TiO<sub>2</sub> powder are shown in Table I. The hybrid spherical microbeads prepared by "viscose phase separation method" are summarized in Table II. The dispersion of the various kinds of TiO<sub>2</sub> powder in a cellulose xanthate aqueous solution (Cellulose Content, 9.5 wt %, RENGO Co., Ltd., Osaka, Japan) (325 g) was carried out by stirring successively at 5000 rpm using a homogenizer (PROCESS HOMOGENIZER PH91, SMT Co.). The dispersion-solution was mixed with 30 wt % aqueous solution (1320 g) of sodium polyacrylate (Aquaric DL-453, *M<sub>w</sub>*: 50000, Nippon Shokubai Co., Ltd., Osaka, Japan) containing NaOH

**Table I.** Characteristics of TiO<sub>2</sub> powders

TiO <sub>2</sub> no.	Bulk gravity	Diameter
TiO <sub>2</sub> -1 P-25 <sup>a</sup>	0.15	21 nm <sup>d</sup>
TiO <sub>2</sub> -2 TKP-101 <sup>b</sup>	0.58	6 nm <sup>d</sup>
TiO <sub>2</sub> -3 ST-01 <sup>c</sup>	0.41	7 nm <sup>d</sup>

<sup>a</sup>purchased from Degussa Co., Ltd. <sup>b</sup>purchased from Tayca Corp. <sup>c</sup>purchased from Ishihara Sangyo Kaisha, Ltd. <sup>d</sup>the value in the manufacture's literature.

**Table II.** Abbreviations and elemental analysis of hybrid spherical microbeads

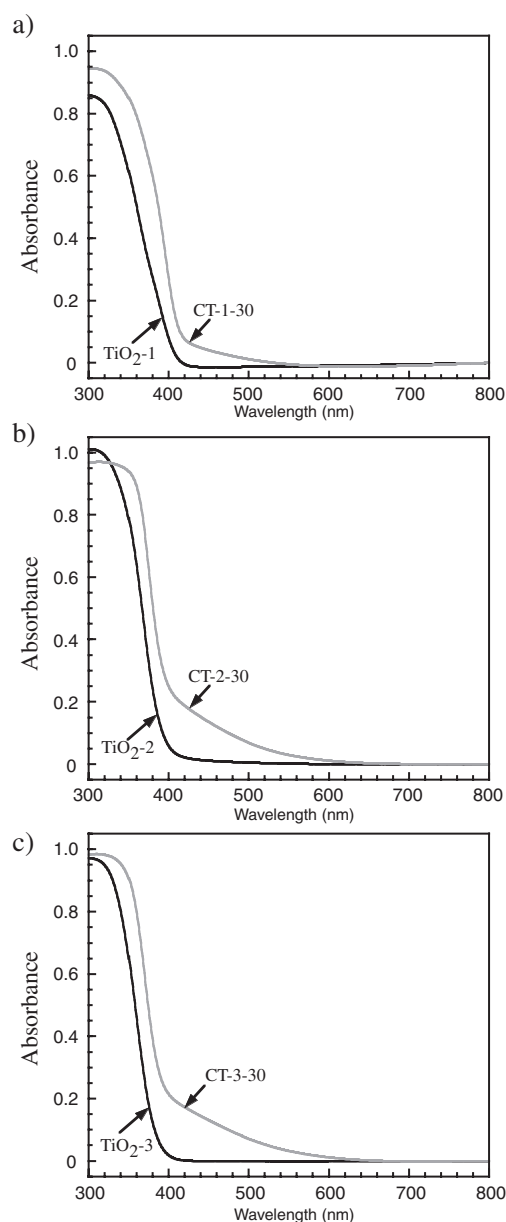
Microbeads	wt % <sup>a</sup>			TiO <sub>2</sub> (wt %) content	
	TiO <sub>2</sub> -1	TiO <sub>2</sub> -2	TiO <sub>2</sub> -3	Calcd.	Found
CT-1-30	29.6			29.6	27.7
CT-1-15	15.0			15.0	14.7
CT-2-30		29.6		29.6	21.5
CT-2-61		61.2		61.2	55.3
CT-3-30			29.6	29.6	23.9
CT-3-53			52.8	52.8	45.7

<sup>a</sup>weight percent for cellulose containing in viscose

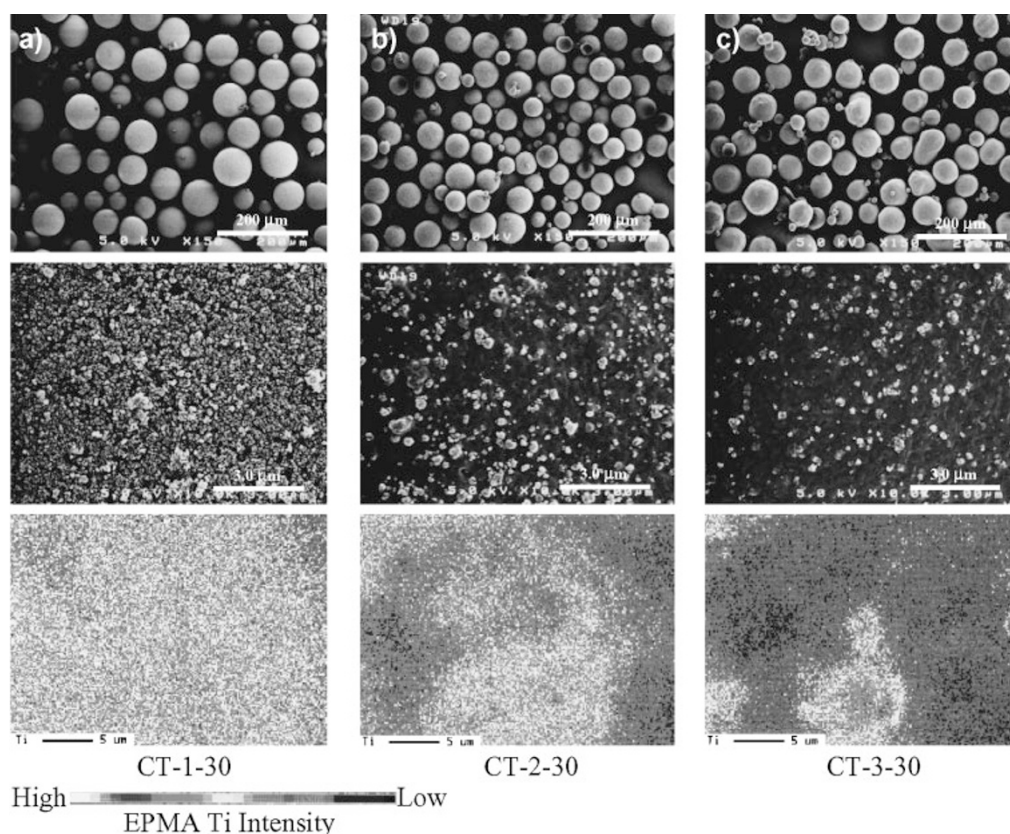
(48 g), and suspended by stirring at 120 rpm at 80 °C for 1 h. After heating and congealing, the cellulose/TiO<sub>2</sub> hybrid spherical microbeads were washed with hydrochloric acid aqueous solution and water.

### Measurement

The zeta potentials of TiO<sub>2</sub> powder were measured by the electrophoresis using Laser Doppler method (Zetasizer nano, Sysmex Corporation, Kobe, Japan). Electron micrographs of the hybrid spherical microbeads were obtained using a field emission scanning electron microscope (FE-SEM) (Hitachi S-4000, Hitachi, Ltd., Tokyo, Japan), and electron probe microanalysis (EPMA) was carried out using a JEOL JXA-



**Figure 1.** Diffuse reflectance spectra of the obtained hybrid spherical microbeads and naked TiO<sub>2</sub> powders: (a) CT-1-30 and TiO<sub>2</sub>-1, (b) CT-2-30 and TiO<sub>2</sub>-2, (c) CT-3-30 and TiO<sub>2</sub>-3.

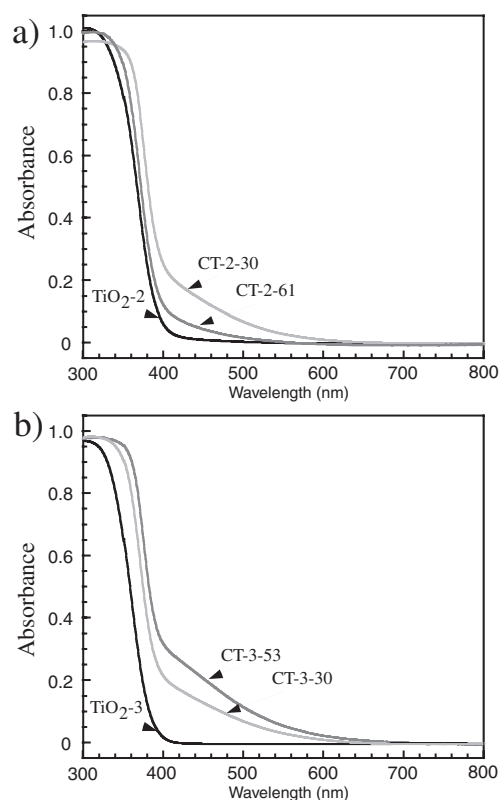


**Figure 2.** SEM (upper and middle) and EPMA element map images (lower) for Ti of hybrid spherical microbeads: (a) CT-1-30, (b) CT-2-30, (c) CT-3-30. SEM: magnification;  $\times 150$  (upper) and  $\times 10000$  (middle), respectively. EPMA: magnification:  $\times 2500$  (lower).

8900 WD/ED (JEOL, Tokyo, Japan). Since only Ti was detected as component element of particles, Ti was performed by EPMA. Diffuse reflectance spectra were measured with a UV-vis spectrophotometer with integrating sphere equipment (JASCO V-560/ISV-469, JASCO, Tokyo, Japan). The cutting of a spherical microbead was carried out with a ultra microtoam (ULTRACUT S, Leica Microsystems).

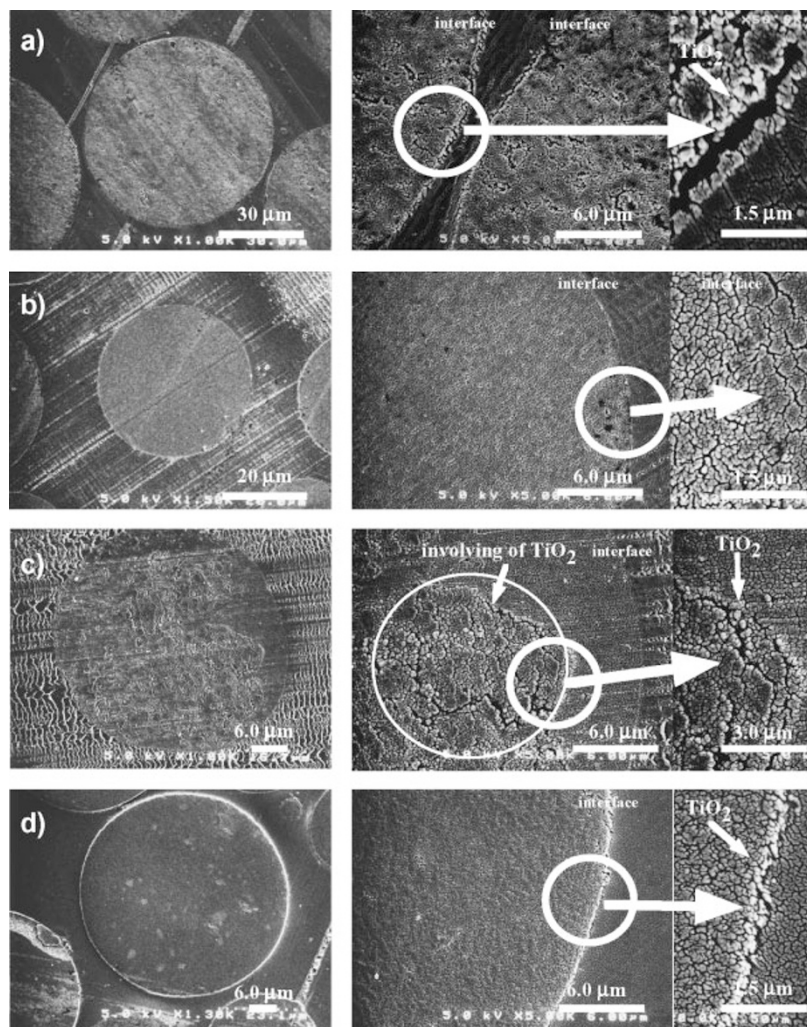
## RESULTS AND DISCUSSION

We obtained three types of hybrid spherical microbeads with hybridized cellulose and three kinds of  $\text{TiO}_2$  powders ( $\text{TiO}_2$ -1,  $\text{TiO}_2$ -2 and  $\text{TiO}_2$ -3) by the viscose phase separation method. The degree of appearance of  $\text{TiO}_2$  on the surface of the spherical microbeads was found to depend on the type of  $\text{TiO}_2$  powder used. The diffuse reflectance spectra of the obtained hybrid spherical microbeads, together with those of the naked  $\text{TiO}_2$  powders are shown in Figure 1a–c.  $\text{TiO}_2$ -1,  $\text{TiO}_2$ -2 and  $\text{TiO}_2$ -3 showed no photoabsorption in the visible region. CT-1-30 spherical microbeads showed the least photoabsorption in the visible region, and their diffuse reflectance spectrum was closest to that of naked  $\text{TiO}_2$  powder of  $\text{TiO}_2$ -1,  $\text{TiO}_2$ -2 or  $\text{TiO}_2$ -3. Figure 2a–c show the SEM and EPMA images of the hybrid spherical microbeads.



**Figure 3.** Diffuse reflectance spectra of CT-2 and CT-3 series: (a) CT-2-30, CT-2-61 and  $\text{TiO}_2$ -2, (b) CT-3-30, CT-3-53 and  $\text{TiO}_2$ -3.



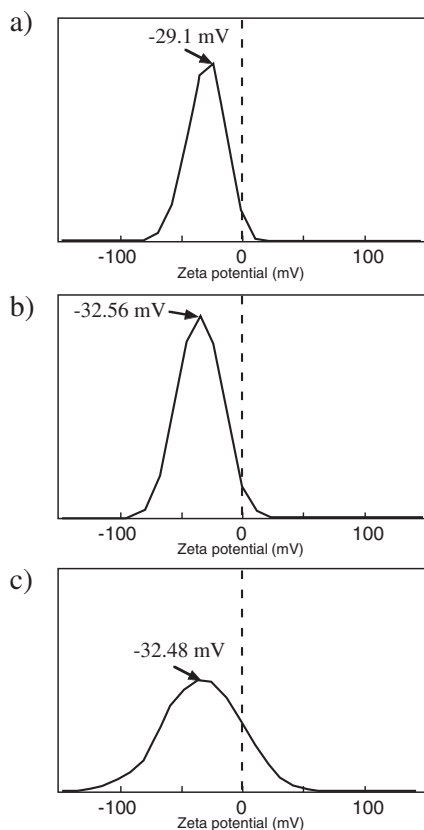


**Figure 4.** Cross sectional SEM images of Cellulose/TiO<sub>2</sub> hybrid spherical microbeads: (a) CT-1-30, (b) cellulose, (c) CT-3-30, (d) CT-1-15.

Despite the fact that an equal weight (30 wt % for cellulose) of the three kinds of TiO<sub>2</sub> powders were respectively mixed into viscose in the process of spherifying, it was confirmed that the distributions of TiO<sub>2</sub> particles containing in hybrid spherical microbeads depend on the specific type of TiO<sub>2</sub>. The degree of appearance of TiO<sub>2</sub> particles on the surface of the microbeads was in the order of CT-1-30 > CT-2-30 > CT-3-30. The amounts of TiO<sub>2</sub> contained in the spherical microbeads were estimated from the ash weight by measurement of CHN elemental analysis and are shown in Table II. The difference among the content of TiO<sub>2</sub> containing cellulose/TiO<sub>2</sub> hybrid spherical microbeads was very small.

The three kinds of TiO<sub>2</sub> powders showed differences in their bulk gravities, as shown in Table I. In terms of bulk gravity, TiO<sub>2</sub>-1 was the lightest of all TiO<sub>2</sub> particles. Therefore, the hybrid spherical microbeads standing for CT-2-61 and CT-3-53 were prepared using TiO<sub>2</sub> powders amount corresponding to the volume of TiO<sub>2</sub> used for preparation of CT-1-30

hybrid spherical microbeads. Figure 3a and b show the diffuse reflectance spectra of the CT-2 and CT-3 hybrid spherical microbeads series. The photoabsorption in the visible region of CT-2-61 became less than that of CT-2-30 because of increase of adding of TiO<sub>2</sub>. This diffuse reflectance spectra is similar to that of CT-1-30. The reason CT-2-30 shows photoabsorption in the visible region is that the TiO<sub>2</sub> amount contained in CT-2-30 was so slight, the TiO<sub>2</sub> particles could not cover much of the surface of the sphere. The lack of photoabsorption in the visible region in CT-2-61 indicated that CT-2-61 could cover the surface of the sphere with TiO<sub>2</sub> particles. On the other hand, a decrease of photoabsorption of CT-3-53 was quite not observed for the visible region although a higher amount of TiO<sub>2</sub>-3 powder was added to the viscose. As a result, the degree of appearance of TiO<sub>2</sub> particles on the surface of CT-3-53 was smaller than that of CT-3-30. These phenomena were not attributed to TiO<sub>2</sub> amount but to other causes. It was considered that the distribution of TiO<sub>2</sub> particles on the hybrid



**Figure 5.** Zeta potential distributions of TiO<sub>2</sub> particles measured by laser Doppler method: (a) TiO<sub>2</sub>-1, (b) TiO<sub>2</sub>-2, (c) TiO<sub>2</sub>-3.

spherical microbeads might be related to electric repulsion between the CSS<sup>-</sup> group and TiO<sub>2</sub>.

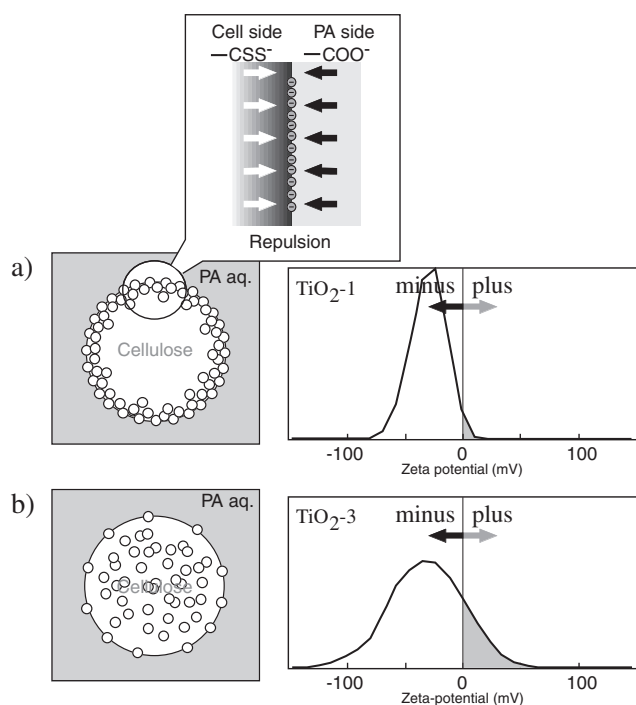
Figure 4a shows an SEM image of a section of CT-1-30. As a reference, an SEM image of a section of cellulose microbead is shown in Figure 4b. In the scanning electron micrograph, TiO<sub>2</sub> particles were brightly visible due to their electrostatic charge. Obviously, the SEM image of cellulose microbeads shows no TiO<sub>2</sub> particles. As expected, it was confirmed that TiO<sub>2</sub>-1 particles contained in CT-1-30 were located around the outline of the circle shape more tightly than inside the circle. In addition, it was confirmed that the hybrid spherical microbeads (stand for CT-1-15) in which the content of TiO<sub>2</sub>-1 is 15 wt %, had TiO<sub>2</sub>-1 particles only on the surface of sphere, because the section of CT-1-15 indicated that the TiO<sub>2</sub>-1 particles were located tightly only on the outline of the circle shape, as shown in Figure 4c. In contrast, as shown in the section of CT-3-30 of Figure 4d, TiO<sub>2</sub>-3 particles contained in CT-3-30 were situated a little on the outline of the circle shape, but relatively in the interior of the circle shape. This indicates that the CT-3-30 hybrid microbeads involved TiO<sub>2</sub> particles internally. In particular, the SEM image for the section of CT-3-30 indicated the presence of a phase-separation phenomenon between the TiO<sub>2</sub> and

viscous domains; as a result, their interface formed wide pores in the conversion from viscous droplet to cellulose microbead.

In order to examine the mechanism of hybridization of TiO<sub>2</sub> and cellulose, the zeta potentials of TiO<sub>2</sub> used were respectively measured by the electrophoresis using Laser Doppler method in pH 13 aqueous solution. The pH of zeta potential measurement corresponded to that of the viscous phase separation spherulization system. The zeta potentials of TiO<sub>2</sub>-1, TiO<sub>2</sub>-2, and TiO<sub>2</sub>-3 all had minus potentials. Figure 5a–c show the zeta potentials distribution of each type of TiO<sub>2</sub> particle. As shown in Figure 5, the zeta potential distribution of TiO<sub>2</sub>-1 was equal to that of TiO<sub>2</sub>-2. However, the zeta potential distributions of both were much narrower than that of TiO<sub>2</sub>-3. This indicates that the surface electric potentials of TiO<sub>2</sub>-1 and TiO<sub>2</sub>-2 particles, respectively, are comparatively homogeneous. The distribution of TiO<sub>2</sub> particles on the hybrid spherical microbeads must be related to electric repulsion between the CSS<sup>-</sup> group and TiO<sub>2</sub>. Figure 6a and b show the mechanism of hybridization of TiO<sub>2</sub> and cellulose xanthate. TiO<sub>2</sub>-1 and TiO<sub>2</sub>-2 particles possessing the minus potential uniformly were driven out by the CSS<sup>-</sup> group of cellulose xanthate and the COO<sup>-</sup> group of polyacrylic acid. Therefore, TiO<sub>2</sub>-1 and TiO<sub>2</sub>-2 particles localized at the interface between the cellulose xanthate phase and the PAA aqueous solution phase, as shown in the speculation on Figure 6a. In contrast, the zeta potential distribution of TiO<sub>2</sub>-3 was the broadest of all given TiO<sub>2</sub> particles. This indicates that the surface electric potential of TiO<sub>2</sub>-3 is inhomogeneous. As shown in the speculation of Figure 5b, TiO<sub>2</sub>-3 particles were located within the cellulose xanthate phase, because of the diffusion to plus electric potential (around +60 mV) of its zeta potential. The fact that the content of TiO<sub>2</sub> particles of CT-3-53 was more than that of CT-1-30 indicates that the CT-3 hybrid microbeads series involved TiO<sub>2</sub> particles internally but did not have a great amount of TiO<sub>2</sub> particles on the surface. In addition, the shape of hybrid microbeads obtained using TiO<sub>2</sub>-3 was most irregular. This phenomenon is attributed to the fact that the surface electric potential of TiO<sub>2</sub>-3 was so inhomogeneous, the interface condition of phase separation between the cellulose xanthate phase and the polyacrylic acid phase was not stabilized.

## CONCLUSIONS

Various types of cellulose/TiO<sub>2</sub> hybrid spherical microbeads were obtained by using several kinds of TiO<sub>2</sub> particles. It was confirmed that the distributions of TiO<sub>2</sub> particles contained on hybrid spherical microbeads depend on the composition of TiO<sub>2</sub> parti-



**Figure 6.** Schematic illustration of mechanism of hybridization between TiO<sub>2</sub> particles and cellulose: (a) Cellulose/TiO<sub>2</sub> spherical beads hybridized TiO<sub>2</sub> particles possessing homogeneous potential: narrow zeta potential distribution. (b) Cellulose/TiO<sub>2</sub> spherical beads hybridized TiO<sub>2</sub> particles possessing inhomogeneous potential: broad zeta potential distribution.

cles. Based on the finding that TiO<sub>2</sub> particles possessing the minus potential uniformly were driven out by the CSS<sup>-</sup> group of cellulose xanthate and the COO<sup>-</sup> group of polyacrylic acid, TiO<sub>2</sub> particles localized at the interface between the cellulose xanthate aqueous solution phase and the PAA aqueous solution phase. The narrower the zeta-potential distribution of TiO<sub>2</sub> particles in the sphering pH condition (*i.e.*, in pH 13 aqueous solution) is, the more TiO<sub>2</sub> particles were driven out from the cellulose xanthate domain. Thereby, we could prepare cellulose/TiO<sub>2</sub> hybrid spherical microbeads that were covered densely with TiO<sub>2</sub> particles on the surface and were also involved TiO<sub>2</sub> particles. The data gathered here are not only useful for the preparation of photocatalysis adsorbent, but also

for preparation of ion exchanger adsorbent<sup>7,8</sup> composed from cellulose/TiO<sub>2</sub> composite matrix, cellulose/inorganic materials hybrid-fiber<sup>14</sup> and hybrid materials for cosmetic materials<sup>5</sup> from viscose.

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