

Synthesis and application of polymeric microspheres containing inorganic particles

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Structure controlled inorganic/polymeric composite microspheres could be prepared by in-situ formation of inorganic nanoparticle in microgel. Fine titania particle-containing composite microgels were prepared by referring to the methodology to prepare gold nanoparticle-containing microgels. First, amino group was introduced into poly(N-isopropylacrylamide). Then titania precursor anion was invited into the microgel. Precursor was converted in-situ to titania. Titania-containing microgels presented efficient and temperature-sensitive photocatalytic property.

Key words: Titania nanoparticle, Microgel, Poly(N-isopropylacrylamide), Stimuli-responsive polymer, In-situ nanoparticle formation

1. INTRODUCTION

A variety of novel functional composites have been prepared by combining organic and inorganic materials. Among them, polymeric microspheres containing inorganic nanoparticles gathered special attention because the characters and functions of inorganic and polymeric materials can be used effectively in dispersion for optical, catalytic, and biomedical applications. We developed a method to prepare composite particles in which inorganic nanoparticles distributed in polymeric microgel with designed manner [1,2]. In the preparation of magnetite-containing microgel, poly(N-isopropylacrylamide (NIPAM)-co-glycidyl methacrylate (GMA)) microgel having more GMA (or epoxy group) in the core and more NIPAM in the surface layer, which was prepared by soap-free emulsion copolymerization of NIPAM and GMA, was used as a template microgel. Into this microgel, sulfonic groups were introduced by the reaction of sulfonic compounds with epoxy groups in GMA inside of the microgel. Thus obtained sulfonic group-containing microgel successfully invited ferric and ferrous ions to the site where their counter ions were waiting and iron ions were oxidized in-situ to form magnetite nanoparticles. Resulting magnetite-containing composite microgels stably dispersed in aqueous medium at room temperature but coagulated and were easily collected above the lower critical transition temperature.

Learning from this methodology, that is, the method in which arrangement of host ions in microgel played an important role for the introduction of precursor ions, titania nanoparticle-containing thermosensitive microgels were prepared and their

photocatalytic property was examined.

2. EXPERIMENT

2.1 Materials

N-isopropylacrylamide (NIPAM) was recrystallized from hexane /toluene 1/1 (v/v). Acrylic acid (AAc) was distilled under a reduced pressure. Methylene-bis-acrylamide (BIS) was used as received. Potassium persulfate (KPS), was used after recrystallization from water. 3-Aminopropyltriethoxysilane (APS), a silane coupling reagent, was used for combine polymer and inorganic component with the aid of 1-(3-dimethylamino)propyl-3-ethylcarbodiimide hydrochloride (EDC). Titanium tetraisopropoxide (TTIP) was used as a precursor for the preparation of titania nanoparticles.

2.2 Microgel preparation

Precipitation copolymerization of NIPAM and AAc was adopted to prepare thermosensitive carboxyl group-carrying microgels. A typical polymerization recipe is; Monomer solution: NIPAM/AAc/BIS /water=1.44/x/0.06/155, $x = 0.20 - 2.0$ Initiator solution: KPS/water = 0.04 / 5.00 (gram), Initiator solution was added into monomer solution at 70°C under nitrogen with gentle stirring. NIPAM/AAc microgels were obtained after 4 hr polymerization and then cleaned up via repetitive centrifugation – decantation – redispersion.

2.3 Composite microgel formation

Titania-containing composite microgels were prepared by two methods; One is through silane-coupling reagent, APS, and the other is without using APS. In the former APS was bound to

microgels as follows; To 40ml aqueous dispersion of 0.3 g NIPAM/AAC microgel and 0.24 g EDC, 0.12ml APS was added and the dispersion was kept under mild stirring at room temperature for 2 days. The dispersion was cleaned by the same manner describe previously. Cleaned microgels (NA(K)A) were kept in dispersion. In the second method, ammonia was directly reacted with carboxyl group in AAC fragments to activate the microgels as Wang, et al. did [3]. The microgel cleaned was referred to as NA(K).

The same procedure was taken to introduce TiO^- ions into both of microgels, NA(K)A and NA(K). Microgels were added into ethanol solution of poly(vinylpyrrolidone) (PVP). Then catalyst, distilled water, and alcohol solution of TTIP were added to microgel dispersion in this order. The dispersion was kept under stairring for 24hrs. The clean^up was done in the same manner described above.

2.4 Characterization

Hydrodynamic diameter was measured by dynamic scattering using PSA III (Otsuka Electronics Co.) Microgels were observed in transmission and scanning electron microscope. The content of titania in microgel was analyzed by TG-DTA

Photocatalytic decomposition of methylene blue (MB) was determined from absorbance of titania-containing microgel/MB solution after UV irradiation.

3. Results and Discussion

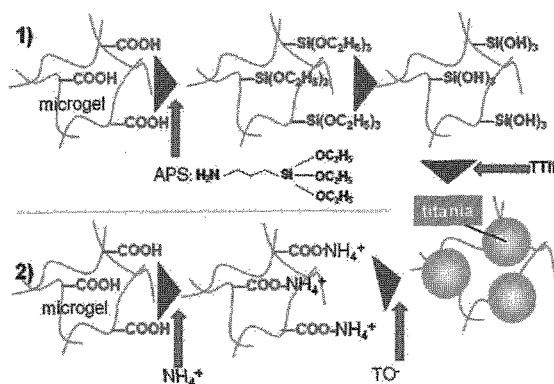
3.1 Thermosensitiveness of microgels

Precipitation polymerization of NIPAM with a small amount of AAC resulted in the formation of monodisperse microgels with diameter in the range from 200nm to 300nm. Hydrodynamic size of the microgels decreased showing their own transition with increasing temperature in the range of 25 to 45°C. The transition temperature of microgels increased and became unclear with increasing AAC content.

3.2 Composite microgel formation

Introduction of titania precursor, TiO^- , into the poly(NIPAM-co-AAC) microgel was carried out by two ways. One used APS to invite titania precursor into the microgel whereas the other used carboxylic group of AAC unit as shown in the lower case of Scheme 1. The same chemistry was applied to both for the in-situ formation of titania from the precursor.

The transmission electron micrographs of composite microgels of both systems showed similar views which indicated successful introduction of fine titania particles (Figs.1 and 2). The right-side micrographs of figures show enlarged microgel's appearance, on which a number of nanoparticles of titania can be observed.



Scheme 1 Two reaction processes for the preparation of composite microgels

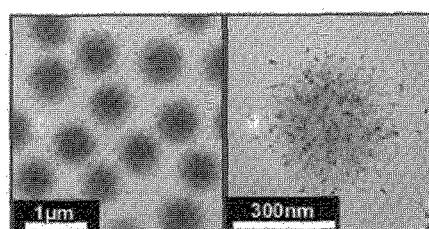


Figure 1 FE-TEM views of NA(K)A-titania particles.

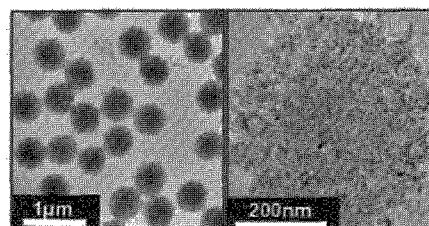


Figure 2 FE-TEM views of NA(K)-titania particles.

Fig. 3 shows the effects of microgel modification on hydrodynamic size. Starting microgel (NA(K)3/2.0) exhibited the sharpest transition around the native transition temperature of PNIPAM (31°C). The transition got dull and the temperature shifted higher through modifications of the microgel. But, even after composite formation (NA(K)3/2.0A-titania), thermo- sensitivity of microgel was retained.

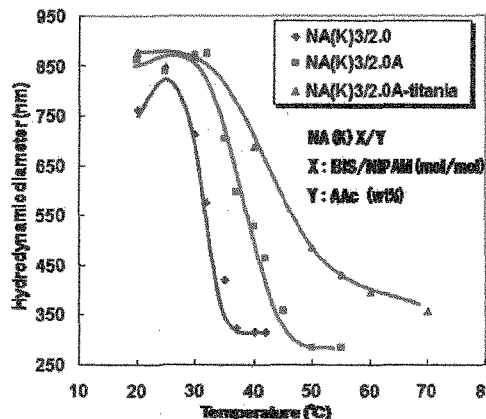


Figure 3 Hydrodynamic diameter of N(K)3/2.0A-titania particles as a function of temperature.

The most promising application of titania-containing composite is the use of them for photocatalytic reaction [4]. The photocatalytic property of the titania-containing composite microgels was examined using methylene blue (MB) as a decomposed material. The degree of MB decomposition was measured by direct spectrometry as a function of time. The results are shown in Fig. 4. Microgels containing no titania exhibited negligible catalytic property as same as water. In contrast, microgels containing titania showed an appreciable photocatalytic property in MB decomposition, which was higher than that of bare titania particles when the same weight of titania. This is perhaps due to the higher specific surface area of titania in composite microgel than of bare one. Bare titania used here was obtained by the same procedure in the absence of microgel and has ten times larger diameter than titania in microgel.

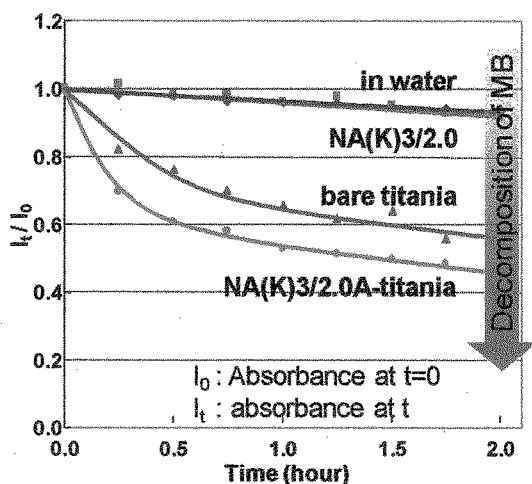


Figure 4 Photocatalytic degradation of MB

Fig. 5 shows the rate of MB decomposition by a series of titania-containing composite microgels which were prepared using different amounts of AAc. The rate of decomposition increased with increasing AAc content in microgel. This was attributed to the high content of titania nanoparticles in microgels with high content of AAc. The relation between the amount of AAc used for polymerization and the amount of titania nanoparticle in microgel is shown in Table 1.

Fig. 6 shows that, when the amount of titania was increased in photochemical reaction, the amount of decomposed MB increased in composite microgel system as expected. But, in the case of bare titania system, the decomposition was rather delayed with increasing amount of titania. The unexpected result of the latter was attributed to the aggregation progress of bare titania with increasing amount. Here, we can confirm the merit of inclusion of

titania in polymeric microgels. That is, inclusion of titania in microgel enabled to disperse titania stably without losing high specific surface area of titania nanoparticle in the microgel.

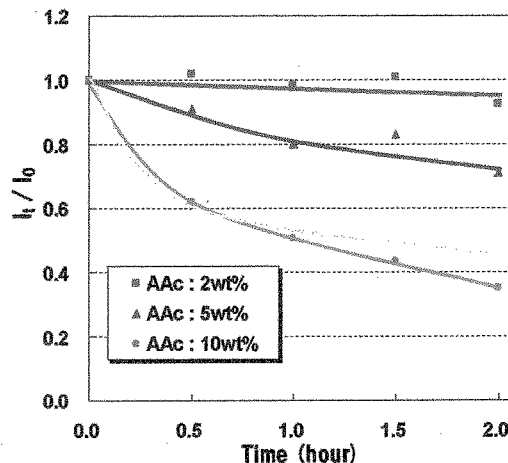


Figure 5 Dependence of decomposition on AAc content in microgel

Table 1 Amount of titania in microgel

Code	AAc (wt%)	TTIP (ml)	Titania in gel (w%)
NA(K)3/2.0-titania	2.0	0.050	2.1
NA(K)3/5.0-titania	5.0	0.125	12.8
NA(K)3/10.0-titania	10.0	0.250	29.2

NA(K)X/Y X: BIS/NIPAM (mol/mol) Y: AAc (wt%)

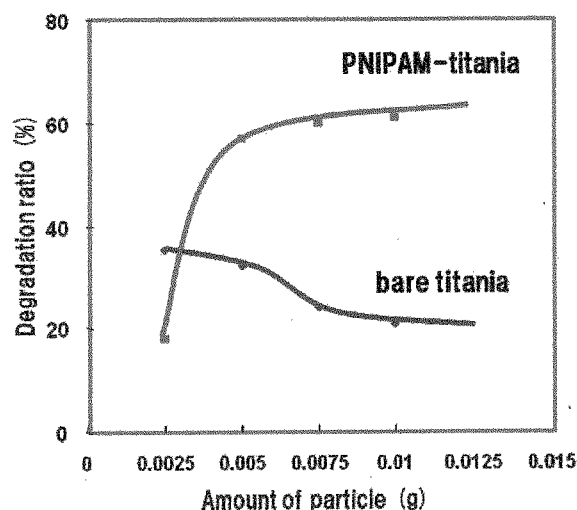


Figure 6 MB Degradation as a function of amount of titania used

Photocatalytic decomposition of MB by composite microgel was carried out at 25 and 70°C which were lower and higher than LCST, respectively. As presented in Figure 7, the decomposition of MB was almost shut down at 70°C. One of possible reasons for this would be that shrunken microgel put out water molecules from the inside and titania missed free water molecules which are necessary for

photocatalytic reaction. Another reason might concern with suppressed permeation of UV wave into shrunken microgels which had high refractive index.

Repeated use of composite microgel as photocatalyst was examined and the result indicated the second and more use exhibited slightly lower efficiency in catalytic activity. The polymer surrounding titania nanoparticles might suffered some degradation by UV irradiation in the presence of titania.

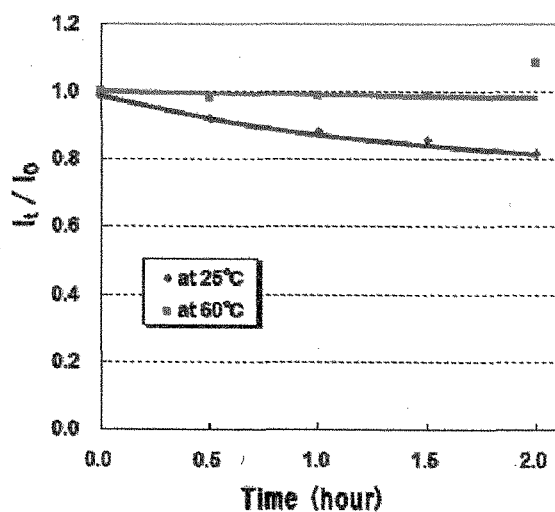


Figure 7 Degradation of MB at temperatures lower and higher than LCST of PNIPAM.

Conclusions

In-situ formation of functional nanoparticles after inviting precursor ion in microgels is one of very promising methods to prepare functional composite microgel. This method was applied for the formation of titania nanoparticle-containing microgels. Composite microgels thus obtained were superior to bare titania nanoparticles in the dispersion stability and photo-catalytic ability.

References

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