

## Preparation of echinoid-like aggregated hematite particles by forced hydrolysis with PEO-PPO-PEO triblock copolymers

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Sub-micrometre sized hematite particles with a controlled structure were prepared by forced hydrolysis of a  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  aqueous solution in the presence of poly(alkylene oxide) triblock copolymer (Pluronic P123). The resulting particles show an echinoid-like shape and a narrow size distribution. After removal of the polymer by calcination at 500 °C for 3 h, the resulting particles show a retained size and shape with disordered mesopores. Calcination also led to the complete transformation of crystallinity from ferric oxyhydroxide to hematite. Forced hydrolysis of the ferric ion solution in the presence of poly(ethylene oxide) (PEG) and poly(N-vinyl-2-pyrrolidone) (PVP) was also carried out to investigate the mechanism of the particle formation. Particles which resulted from PEG and PVP solutions have a different shape or a randomly aggregated form. The formation of micelles of Pluronic P123 copolymer and the hydrogen bonding between the exterior of micelles and inorganic precursors are responsible for the isotropic shape of particles.

**Key words:** hematite, forced hydrolysis, morphology, copolymer, Pluronic P123.

### Introduction

The synthesis of inorganic particles with a controlled structure have been attracting considerable research interest because their properties depend on the structure such as size and shape [1-5]. In recent years, various organic materials such as surfactants and polymers have been used to synthesize inorganic materials with a controlled structure [6-8]. Electrostatic and hydrophobic interaction and hydrogen bonding between the inorganic precursor and organics are key factors in the preparation of nanostructured inorganic particles. Teranishi et al. reported the control of size [9] and shape [10] of Pt nanoparticles using sodium polyacrylate and poly(N-vinyl-2-pyrrolidone) (PVP). In their studies, the size and shape of Pt nanoparticles were controlled by changing the amount of polymer and the reduction rate of  $\text{Pt}^{4+}$  ions. Caruso et al. prepared magnetic hollow particles using a LbL method in which a multilayer film is formed by the alternate adsorption of oppositely charged species ( $\text{Fe}_3\text{O}_4$  nanoparticles and polyelectrolyte multilayer) onto latex particles, followed by calcination to remove the template [11].

Poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide) (PEO-PPO-PEO) triblock copolymers are important practical polymers that are widely used in industrial fields because of their excellent properties such as nontoxicity, biodegradation,

and amphiphilicity. Numerous investigations of the behavior of PEO-PPO-PEO triblock copolymers in aqueous solutions and the adsorption of these copolymers at solid-liquid interfaces were carried out in the past decades [12-15]. Also, since the aggregated structure of PEO-PPO-PEO triblock copolymers is controlled depending on temperature, concentration, and the addition of additives, they have been used as structure-directing organic materials for the synthesis of inorganic materials with a controlled size, shape and structure. Bagshaw et al. prepared mesoporous silica molecular sieves using nonionic polyethylene oxide surfactants in a neutral condition [16]. The hydrogen bonding between the hydrophilic part of polymers and the inorganic precursor followed by molecular rearrangement involving the amphiphilic nature of polymers was the key factor for the preparation of this material. Zhao et al. reported on the synthesis of mesoporous silica structures using nonionic alkyl poly(oxyethylene) surfactants and poly(alkylene oxide) block copolymers in an acid media, which included cubic, three-dimensional hexagonal, two-dimensional hexagonal, and lamellar mesostructures [17].

Ferric oxyhydroxides or oxides have been used in many fields such as pigments, catalysts, gas sensors, and magnetic recording media [18-20]. Forced hydrolysis of  $\text{Fe}^{3+}$  ions in an aqueous solution is a simple method for the preparation of ferric oxyhydroxides or oxides. Matijevic and many other researchers have investigated the relation between the experimental conditions (pH, temperature, concentration of ferric ion, aging time, additives, etc) and the characteristics of the resulting particles such as shape, size, crystallinity [21-

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23]. Kandori et al. prepared nanoporous hematite by forced hydrolysis in the presence of polyethylene glycol (PEG) [24]. They discovered that hematite formed with PEG was hydrohematite with a distortion of the crystal lattice and that PEG acts as a prominent templating agent.

In this study, sub-micrometre hematite particles with a narrow size distribution and an isotropic shape were prepared by an economical and simple method. To obtain hematite particles, the ferric ion solution was aged at elevated temperature in the presence of poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide) (PEO-PPO-PEO) triblock copolymer EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub> (P123). The resulting particles also show disordered mesoporous structure and retain their shape after calcination. Other polymers whose molecular structure is different from PEO-PPO-PEO were used to investigate the formation mechanism of sub-micrometre hematite particles. In the proposed mechanism, the self-assembling behavior of the Pluronic P123 copolymer and the interaction between the particles and polymers are responsible for the formation of particles with a controlled size and shape.

## Experimental

### Materials

Poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide) copolymers (Pluronic P123, 99%), Poly(N-vinyl-2-pyrrolidone) (PVP Mw. 10000), poly(ethylene glycol) (PEG Mw. 2000) and sodium dodecyl sulfate (SDS) were purchased from Aldrich Chemical Company. Ferric nitrate nonahydrate (Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O) and ferric chloride hexahydrate (FeCl<sub>3</sub>·6H<sub>2</sub>O) as iron oxide source were purchased from Ducksan Pure Chemical. All chemicals were used in the as-received condition without further purification. The water used in this study was deionized and doubly distilled by a Milli-Q Plus system. (Millipore, France)

### Preparation Method

In a typical procedure, a PEO-PPO-PEO block copolymer or a PVP aqueous solution were prepared by dissolving 5 g of polymer in 200 ml of deionized water and kept in a water bath controlled to 40 °C with magnetic stirring. Then, 50 ml of iron salt aqueous solution was poured into the polymer solution. The concentration of ferric cations in the total solution was set to 0.1 M. After 1h of stirring, this solution was put into a polypropylene bottle and closed with cap. To induce precipitation of ferric oxyhydroxide, this solution was moved to a convection oven preheated to 80 °C. After 2 days of aging, brown precipitates were formed. After decantation of the supernatant solution, the collected particles were dried in a convection oven set to 80 °C. The dried powders were calcined at 500 °C for 3 hours and kept in glass vial.

### Characterization

The products were characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and nitrogen adsorption-desorption isotherms. XRD patterns were examined to investigate the crystallinity of resulting particles and were taken on a Rigaku D/MAX RINT 2500 X-ray diffractometer operated at 40 kV and 100 mA using CuK $\alpha$  radiation. The detector moved step by step ( $\Delta 2\theta=0.03^\circ$ ) between 10° and 80° with a scan speed of 5°/minute. The TEM images were taken using a JEOL 2000EX II electron microscope operated at 200 kV. For the preparation of the samples for TEM, as-prepared and calcined powders were dispersed in ethanol under sonication for 5 minute. A drop of a dispersed sample was placed on a carbon-coated TEM grid. A field emission scanning electron microscope (FE-SEM, JEOL Co. model JSM-6700F) was used to investigate the morphology of the prepared particles. The samples were coated with platinum by sputtering for 150 seconds. The nitrogen adsorption and desorption isotherms at 77 K were measured using a Micrometrics ASAP 2000 system after the samples were vacuum-dried at 110°C for 6 hours.

## Results

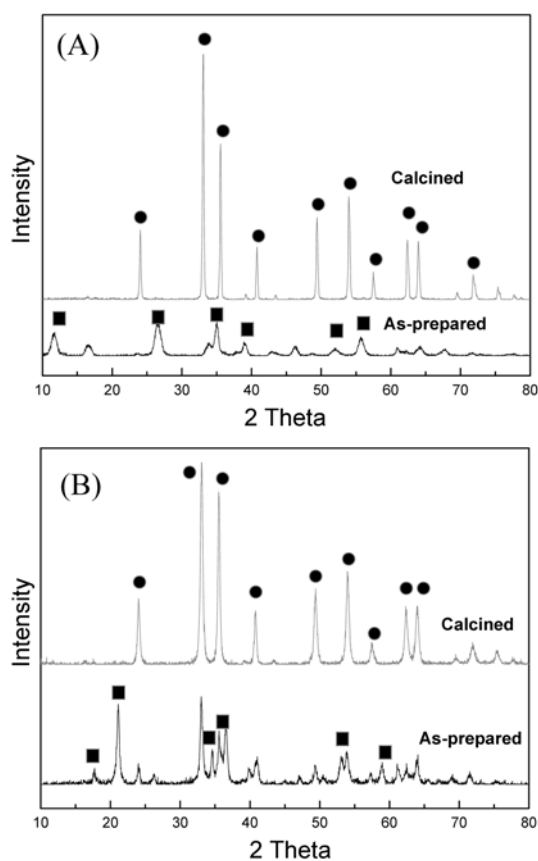
### Crystallinity

The crystallinity of the resulting particles was investigated using XRD patterns (Fig. 1). XRD patterns of the as-prepared particles from the Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O solution showed that two phases ( $\alpha$ -FeOOH (goethite) and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (hematite)) were formed. By contrast to this result, only  $\beta$ -FeOOH (akaganeite) was detected in the XRD patterns of powders prepared from the FeCl<sub>3</sub>·6H<sub>2</sub>O solution. After calcination at 500 °C for 3 hours,  $\alpha$ -FeOOH (goethite) and  $\beta$ -FeOOH (akaganeite) particles were completely transformed to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. These results are the same as those in the literature that investigated the forced hydrolysis of ferric cation solutions [25, 26].

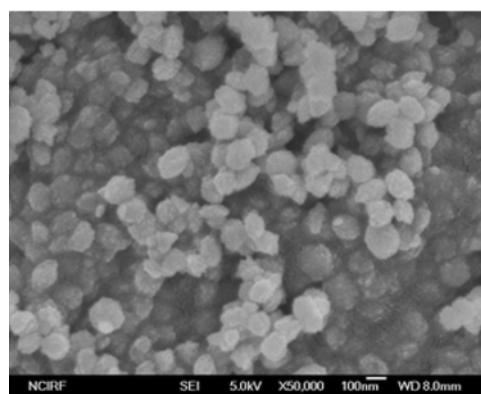
### Particle morphology

SEM images of particles synthesized by thermo-hydrolysis in the presence of Pluronic P123 are presented in Fig. 2. When Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O was used as an iron source, aggregated particles with an ehinoid-like shape and a relatively narrow size distribution were formed. The unique shape of aggregated particles was retained after calcination at 500 °C for 3 hours.

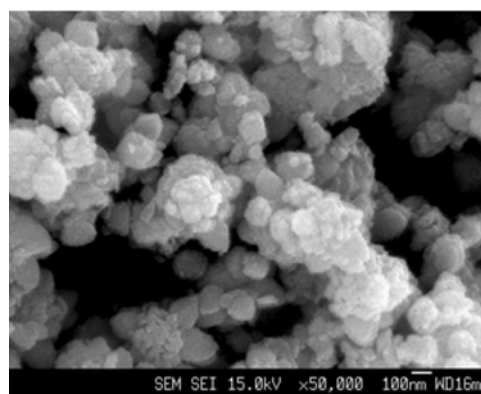
Figure 3 shows the SEM images of particles synthesized from the PVP and PEG systems. Particles prepared with PVP also show an ellipsoidal shape, but aggregated forms shown in the case of P123 do not appear. The different aggregation behavior of particles prepared from the two types of polymer solutions indicates that the difference of molecular structure of polymers induces different formation mechanisms of



**Fig. 1.** XRD patterns of particles prepared by 2 days aging of ferric salt solutions in the presence of Pluronic P123 tri-block copolymer: (A)  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  solution, (B)  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  solution.

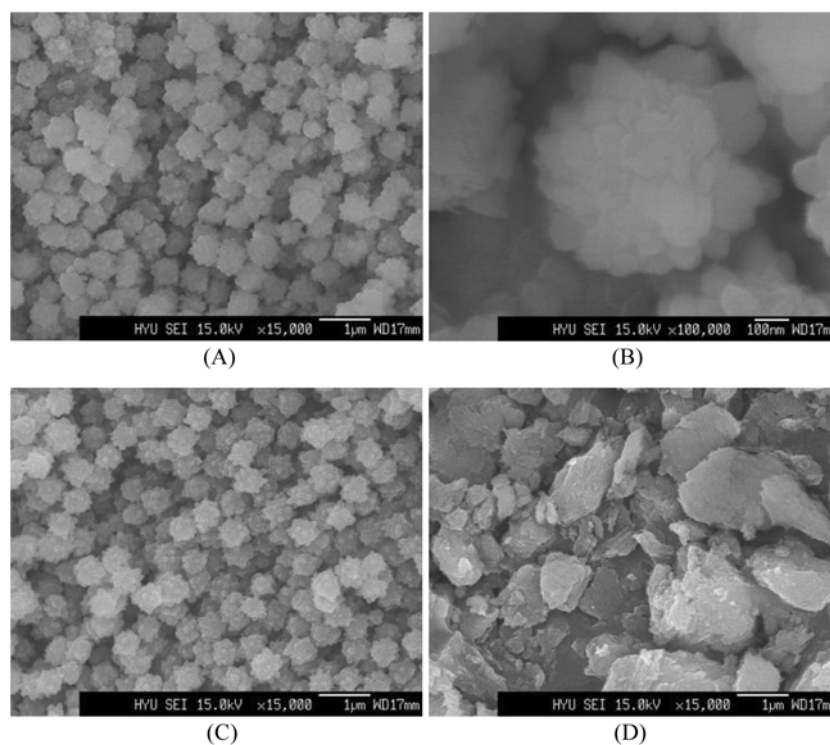


(A)

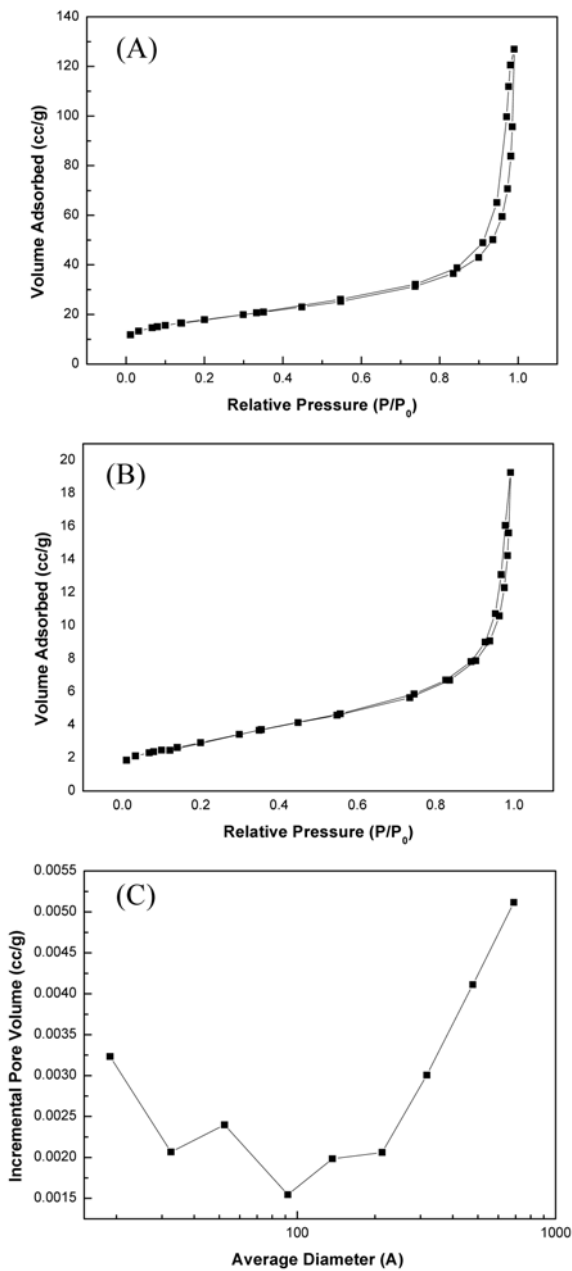


(B)

**Fig. 3.** SEM images of particles prepared by thermohydrolysis of 0.1 M of iron nitrate aqueous solution in the presence polymer: (A) PVP (Mw 10000), (B) PEG (Mw 2000)



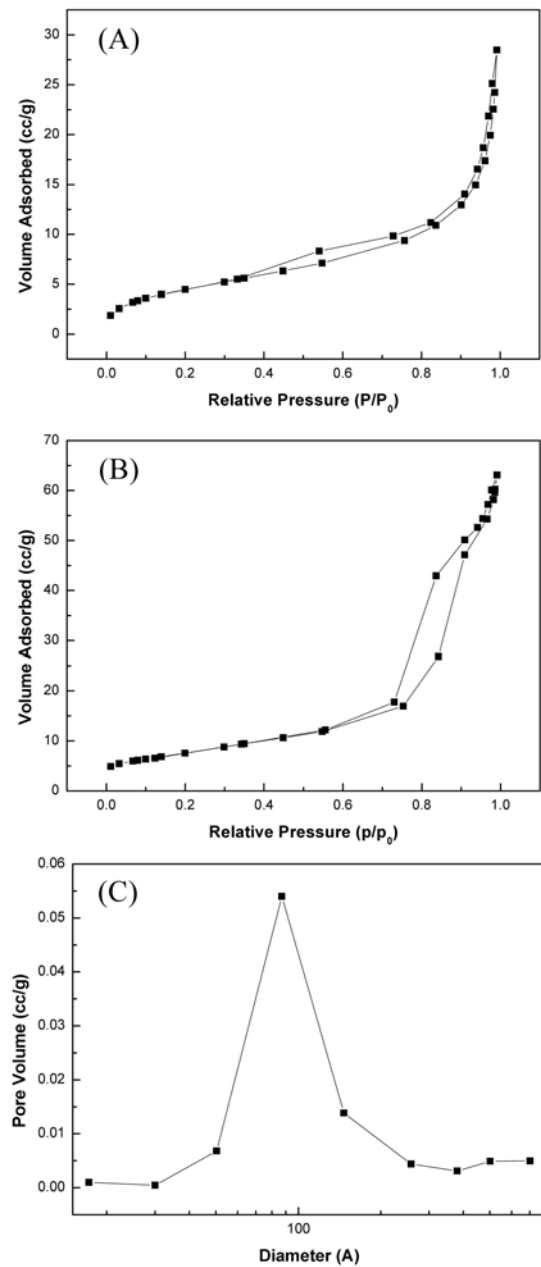
**Fig. 2.** SEM images of particles prepared by forced hydrolysis at  $80^\circ\text{C}$  in the presence of Pluronic P123 triblock copolymer: (A), (B) as-prepared particles using  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  as iron source; (C) calcined particles at  $500^\circ\text{C}$  for 3 hours; (D) as-prepared particles using  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  as iron source.



**Fig. 4.**  $N_2$  adsorption-desorption isotherms and BJH pore diameter distribution of (A) the as-prepared and (B), (C) calcined particles prepared in the absence of PEO-PPO-PEO copolymer.

particles. By contrast to these results, when  $FeCl_3 \cdot 6H_2O$  was used as an iron source, the resulting particles were irregularly aggregated with an amorphous shape.

In the case of PEG, aggregated particles resulted but the shape of the particles was not well-defined (Fig. 3-(B)). The formation of aggregated particles results from the dehydration of PEO induced by the increase of temperature [27]. Dehydration of PEO leads to the micelle-like aggregates of PEG polymer in the aqueous solution and then aggregated particles are formed by interaction between these aggregates and particles. However, compared to the case of Pluronic P123, these aggregated particles have an ill-defined shape because



**Fig. 5.**  $N_2$  adsorption-desorption isotherms and BJH (Barrett-Joyner-Halenda) pore diameter distribution of (A) the as-prepared and (B), (C) calcined particles prepared in the presence of PEO-PPO-PEO copolymer.

of an indefinite hydrophobic interaction between dehydrated PEO blocks by which isotropic aggregates of polymer can not be formed.

### Internal structure

Figure 4 and 5 show nitrogen adsorption-desorption isotherms and pore diameter distribution of the particles prepared in the absence and presence of PEO-PPO-PEO copolymer, which is measured by BJH (Barrett-Joyner-Halenda) method. The isotherms in Fig. 4 correspond to type II, which indicates that both the as-prepared and the calcined particles synthesized in the

**Table 1.**

Pluronic P123	Sample	BET surface area (m <sup>2</sup> /g)	Pore Volume (cc/g)
Absence	As-prepared	62.6633	0.1296
	Calcined	9.8833	0.0220
Presence	As-prepared	15.3471	0.03488
	Calcined	25.4919	0.09220

absence of Pluronic P123 are a nonporous solid [28]. The isotherm of the as-prepared particles resulting from the Pluronic P123 copolymer solution also shows a similar shape (Fig. 5-(A)). However, when the particles synthesized in the Pluronic P123 copolymer dissolved solution are calcined, their isotherm is changed from type II to type IV, which is associated with capillary condensation in mesopores.

BET surface area and pore volumes are presented in Table 1. In the presence and the absence of Pluronic P123 copolymer, the change in tendency of the BET surface area and pore volume is contrary before and after calcination. When Pluronic P123 copolymer is not used in the synthesis process, the surface area and total volume of prepared particles are prominently decreased after calcination. On the other hand, when it is present in the solution, they are increased after calcination. Moreover, this trend appears in the BJH pore size distribution of hematite particles. While particles prepared in the absence of Pluronic P123 copolymer do not have a particular size distribution peak, particles synthesized in the presence show a narrow pore size distribution of which the maximum peak is located surrounding about 9 nm. Based on the above results, it can be inferred that Pluronic P123 copolymers obstruct the collapse of the pore structure and relatively control the pore size and the pore size distribution, which exist in the particle aggregates before calcinations. As a

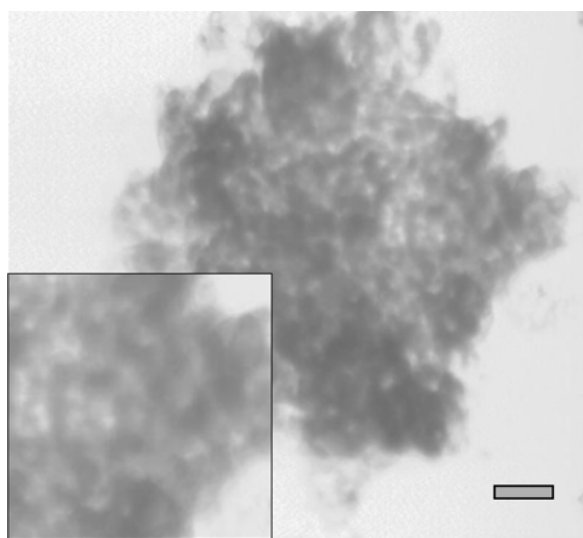
result, it is shown that the PEO-PPO-PEO triblock copolymer acts as an agent that can control the morphology and the structure in the forced hydrolysis of ferric oxyhydroxide.

A TEM image of the resulting particles is presented in Fig. 6. Bright regions in the image show pores in aggregated particles and the size of pores is approximately matched with the result from BJH pore size distribution, though measuring the precise pore diameter is difficult because of the limitation of the resolution.

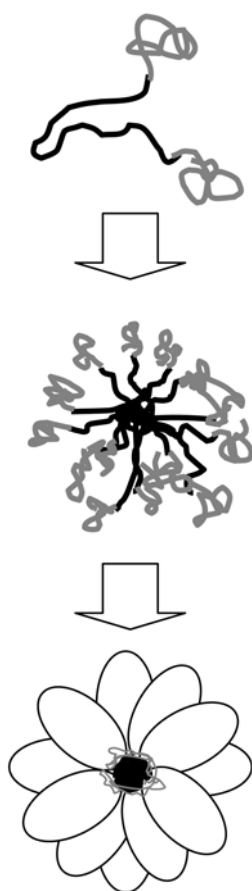
## Discussion

Zhao et al. prepared highly ordered mesoporous silica using self-assembly of nonionic alkyl-ethylene oxide surfactant and/or poly(alkylene-oxide) triblock copolymer in aqueous solution [17]. They suggested a mechanism for the interaction between nonionic surfactants or polymers and silica surface. According to their proposed mechanism, in acidic conditions, protonated ethylene oxide (EO) units and the cationic silica species are assembled together by electrostatic hydrogen bonding and van der Waals interactions which can be designated as  $(S^0H^+)(X^-T^+)$ , where R=alkyl or poly(propylene oxide) and  $X^- = Cl^-$ . However, when iron oxide particles are synthesized, it is shown that chloride ions do not influence the interaction between the EO units of P123 copolymers and the surface of particles because particles synthesized from  $FeCl_3 \cdot 6H_2O$  aqueous solution are nonporous and agglomerated with a random shape, as shown in Fig. 2-(D). Lee and Somasundaran [29] investigated the adsorption of nonionic macromolecules on the surface of oxide particles from a different point of view. In contrast to Zhao et al.'s proposed mechanism, they reported that hydrogen bonding between hydroxyl groups of ferric oxyhydroxide and oxygen atoms in the ethylene oxide segment is responsible for this adsorption under a wide range of pH [29].

On the basis of our results and two research groups' discussion, the formation mechanism of hematite sub-micrometre particles is suggested with a schematic diagram in Fig. 7 as follows. When Pluronic P123 copolymer is dissolved in the aqueous solution, it forms micelles because P123 triblock copolymer is composed of a hydrophobic chain in the center of a polymer chain and two hydrophilic chains on the side of polymer. Inorganic materials hydrolyzed by forced hydrolysis on the aqueous solution interact with the two hydrophilic PEO chains, which compose the exterior of the preformed micelles. Continuous hydrolysis and condensation of inorganic precursors during the aging time result in the formation of hematite particles with echinoid-like shapes. The echinoid-like shape formed at the initial stage is larger, up to 500 nm scale, through further agglomeration without deformation. In addition, the fact that particles prepared with PVP do not have



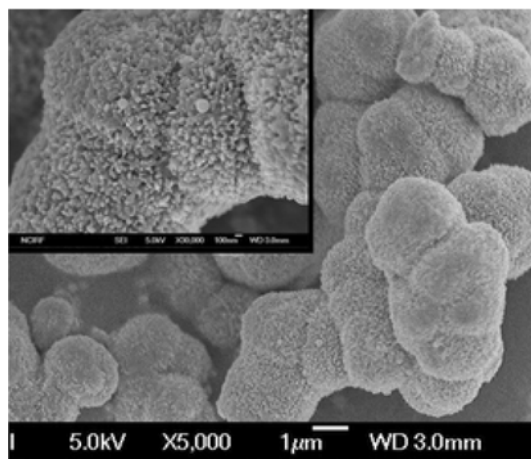
**Fig. 6.** TEM image of hematite particles prepared with Pluronic P123 copolymer. (Scale bar : 50 nm)



**Fig. 7.** Schematic diagram of the formation of aggregated particles in PEO-PPO-PEO aqueous solution.

an aggregated shape as shown in Fig. 3-(A) supports this mechanism. Since the PVP polymer has long hydrophobic alkyl chains and a hydrophilic pendant, it cannot induce micelle formation. Although the PVP polymer influences the morphology of hematite particles due to its amphiphilic property, aggregates of isotropic shape cannot be formed because micelle formation is impossible.

Figure 8 shows an SEM image of particles obtained by forced hydrolysis of ferric nitrate solution in the presence of Pluronic P123 copolymer and sodium dodecyl sulfate (SDS). Hecht and Hoffmann reported the influence of SDS on the self-assembly behavior of Pluronic F127 [30]. Their study shows that Pluronic F127 copolymers have a straight-extended configuration because the SDS binds to unimers of F127 and completely suppresses the formation of copolymer micelles. Since the formation of isotropic particle aggregates were due to the micelles formation of PEO-PPO-PEO copolymer micelles, the particles synthesized in the mixed surfactants system of Pluronic P123 copolymer and SDS anionic surfactant should not result in isotropic particle aggregates. As expected, particles obtained from the mixed surfactant system did not form the particle aggregates with an isotropic shape. However, unusually, the surface of particles resembles corallite,



**Fig. 8.** SEM image of particles prepared with CTAB and SDS.

as shown in the inset of Fig. 8.

## Conclusions

Aggregated hematite particles with a narrow size distribution, an isotropic shape and mesopores have been synthesized by forced hydrolysis of ferric nitrate aqueous solution using Pluronic P123 triblock copolymers. Formation of aggregated particles is associated with the micelle formation of Pluronic P123 copolymers and the hydrogen bonding between copolymers and particles. These ferric oxide particle aggregates with unusual structures may have important applications especially as absorbants and this method can be extended to prepare aggregated particles of other metal oxides. Also, although the formation of particle aggregates is difficult through mixed surfactant systems, it is thought that the surface modification of metal oxides is possible through further research.

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