

## Synthesis and Assembly of Well-structured Hybrid Microgels

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We present the synthesis of organic/inorganic hybrid microgels. To obtain well-structured hybrid microgels, pre-formed polymer microgels were used as “templates” for synthesis and growth of several inorganic nanoparticles in situ. In addition, we present the assemble of colloidal crystals composed of various core/shell structured microgels and their hybrid microgel counterparts which contain localized Au nanoparticles.

Key words: microgel, nanocomposite, *N*-isopropylacrylamide, colloidal crystal, inorganic nanoparticle

### 1. Introduction

Over the past decade, inorganic nanoparticles have attracted much attention due to their potential use in optical, electronic, and magnetic devices.<sup>1</sup> For example, surface plasmon resonance (SPR) is one of the most attractive properties for Au nanoparticles.<sup>2</sup> This property depends on several factors such as their size, surface functionality, refractive index of medium, and interparticle interactions. In addition, the specifically designed structures such as core/shell, rod, and prism well determine the property.<sup>3</sup> For example, the color of the dispersion changes dramatically when Au or Ag layers are subsequently deposited on the seed particles, because the outermost layer interacts dominantly with incoming light.<sup>3</sup>

In general, these nanoparticles are synthesized with the aid of stabilizer such as surfactant to suppress aggregation. Herein, without surfactant, we report on a comprehensive study of synthesizing inorganic nanoparticles in polymer microgels. This methodology has several advantages: simple and easy synthesis, and addition of microgel properties such as stimuli responsiveness to nanoparticles.

First, we prepared *N*-isopropylacrylamide (NIPAm) and glycidyl methacrylate (GMA) copolymerized microgels (NG microgels). Then, using the microgels as templates for synthesizing inorganic nanoparticles, several types of hybrid microgels could be obtained.

In addition, we present the assemble of colloidal crystals composed of various core/shell structured microgels and their hybrid microgel counterparts which contain localized Au nanoparticles.

### 2. Experimental, Results, and Discussion

#### 2.1. Materials

Unless stated otherwise, all materials were purchased from Wako Pure Chemical Industries. NIPAm was kindly given by Kojin and recrystallized from hexane-toluene (1:1 on a volume basis). GMA was purified by distillation under a reduced pressure to remove inhibitors. *N,N*-methylenebisacrylamide (BIS) was used without further purification. Azobisamidinopropane dihydrochloride (V-50) was used without further purification. 3-Mercapto-1-propane sulfonic acid sodium salt (MPSA, Aldrich) and

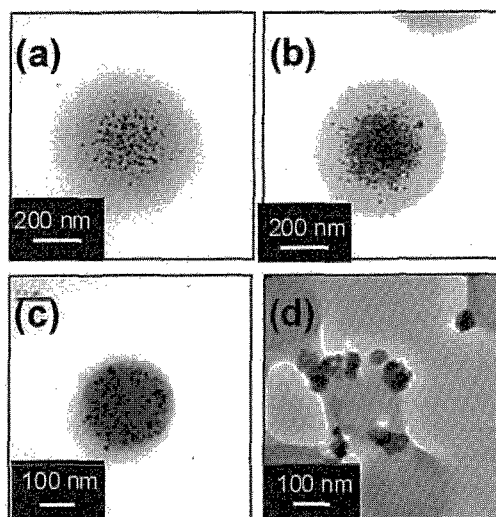


Figure 1. TEM images of the hybrid microgels deposited on a carbon coated copper grid dried at room temperature. Hybrid microgels using NG1-MPSA-Mag (a), NG2-MPSA-Mag (b), NG3-MPSA-Mag (c), NG4-MPSA-Mag (d) microgels. Monomer feed ratios for each template microgel (NIPAm/GMA); 2.8/0.2 for NG1, 2.0/1.0 for NG2, 1.5/1.5 for NG3, and 1.0/2.0 for NG4 microgel.

2-aminoethanethiol (AET, Tokyo Kasei Kogyo) were used without further purification. Sodium nitrate ( $\text{NaNO}_3$ ), iron sulfate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , Junsei Chemical), and ammonia solution (28%  $\text{NH}_4\text{OH}$ , Junsei Chemical) were used as received. Chloroauric acid ( $\text{HAuCl}_4$ ), sodium borohydride ( $\text{NaBH}_4$ ), and hydroxylamine hydrochloride ( $\text{NH}_2\text{OH}\cdot\text{HCl}$ ; Junsei Chemical Co., Ltd.) were used as received. The water used in all experiments was from a Milli-Q reagent water system (Millipore).

#### 2.2. Synthesis of the Hybrid Microgels

To get template microgels for hybrid microgels, NIPAm and GMA copolymerized microgels (NG microgels) were prepared by surfactant free emulsion polymerization with different feed ratios of monomers using BIS as a cross-linker. (Experimental details can be

found in our previous manuscripts<sup>4-8</sup>). Because of the different reactivity ratios of NIPAM and GMA (0.39 and 2.69, respectively)<sup>9</sup>, GMA tended to be consumed faster than NIPAM. In addition, each polymer's hydrophilicity was not very different at 70 °C; the most outer layer of each NG microgel was supposed to be rich in polyNIPAM.

GMA can be modified to introduce functional groups of materials such as proteins. In this study, MPSA, and AET were introduced, respectively. Using the MPSA modified NG microgels, magnetic nanoparticles were synthesized *in situ*.<sup>7</sup> Magnetic nanoparticles were synthesized by co-precipitation method reported previously<sup>10</sup>. Figure 1 presents TEM images of four types of the hybrid magnetic microgels. We found from TEM views that the magnetic nanoparticles were formed only in the template microgels except NG4-MPSA-Mag microgels. The almost same average diameters (~ 13 nm) of the magnetic nanoparticles from TEM views were obtained for NG1-, NG2-, and NG3-MPSA-Mag microgels although that of NG4-MPSA-Mag microgel was ~ 66 nm. This difference of NG4-MPSA-Mag microgel might be due to less effect of polymer chain networks for generating nanoparticles. TGA measurements revealed that each magnetic nanoparticle content was 11.1, 32.9, 10.1, and 6.2 wt% for NG1-MPSA-Mag to NG4-MPSA-Mag microgels, respectively. The highest value of magnetic nanoparticle content was obtained from NG2-MPSA-Mag microgels. This was due to the template structure and composition. Taking reactive ratios of NIPAM and GMA into consideration, the core/shell structure in which core has the space for generating magnetic nanoparticles and localizes sulfonate groups attaching precursor iron ions—whereas only shell has thermosensitivity—should be formed. But, we assumed, such structure is formed effectively only when monomer feed ratio is well balanced. Compared to NG1-MPSA and NG3-MPSA template microgels, NG2-MPSA microgel was the best candidate template that satisfied above-mentioned requirement and can hold large amounts of inorganic nanoparticles. The hybrid core/shell microgels have potential magnetic and biomedical applications. Because all magnetic nanoparticles are localized in the core, the outer shell layer prevents the hybrid particle from aggregation.

Next, we developed thermosensitive hybrid core/shell microgels via *in situ* Au nanoparticle formation using thermosensitive core-shell microgels as a template.<sup>5</sup> The proposed method here for the *in situ* synthesis of Au nanoparticles with microgel interiors offers the advantage of eliminating or significantly reducing particle aggregation. In addition, by using thermosensitive microgel structures in which the shell has thermosensitive and gel properties in waters whereas the core itself is a water-insoluble polymers, we were able to synthesize gold nanoparticles only at the surface of the core, which had reactive sites to bind metal ions (Figure 2(a)). After the Au nanoparticles were synthesized, electroless gold plating was carried out to control the thickness of the gold nanoshells (Figure 2(b)). These types of hybrid microgels have potential biomedical and optical applications. For example, theoretical calculations indicate that a colloidal crystal,

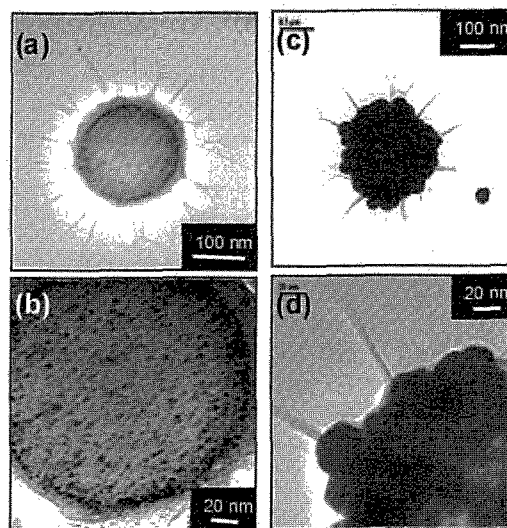


Figure 2. TEM images of thermosensitive hybrid core/shell microgels deposited on a carbon coated copper grid dried at room temperature. (a,b) Before and (c,d) after electroless gold plating treatment. b and d are close up images of a and c, respectively.

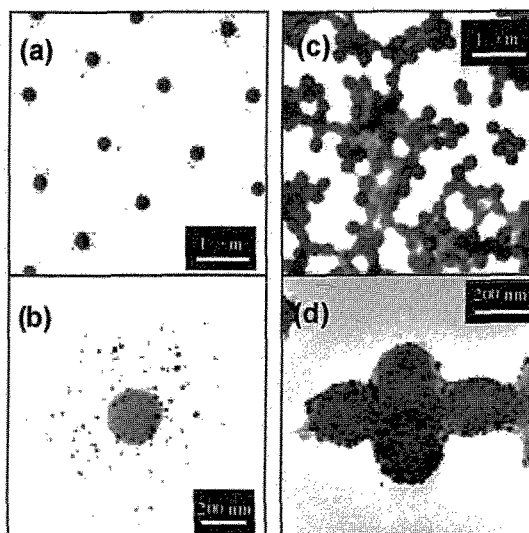


Figure 3. TEM images of thermosensitive hybrid core/shell microgels deposited on a carbon coated copper grid. (a,b) Dried at 25 °C. (c,d) Dried at 50 °C. b and d are close up images of a and c, respectively.

composed of metalodielectric spheres, can have a full photonic band gap.<sup>11</sup>

Furthermore, we also developed thermosensitive hybrid core/shell microgels having Au nanoparticles in the shell. The shell was composed of the cross-linked polyNIPAM hydrogel. The amino or thiol groups were immobilized in the polyNIPAM shell to hold the Au nanoparticles effectively. We designed the template structures and compositions so as to yield a variety of hybrid microgels whose properties would respond to temperature changes. Figure 3 shows TEM images of the core/shell hybrid microgels having Au nanoparticles in the shell dried below and above a lower critical

solution temperature (LCST) of polyNIPAm (polyNIPAm has LCST around 32 °C)<sup>12</sup>. The hybrid microgels were uniformly distributed on the substrate when they were dried at 25 °C (Figure 3(a)). The close-up (Figure 3(b)) shows that Au nanoparticles were located around the hard core and were well isolated from each other. We also confirmed that the area containing the Au nanoparticles coincided with the area covered by the hydrodynamic diameter of the hybrid microgels at 25 °C. In contrast, the microgels dried in the shrunken states at 50 °C were distributed randomly on the substrate, and the Au nanoparticles were localized on the hard core. Interestingly, they showed reversibly color change just by changing the temperature. This behavior is mainly due to the change of the interparticle distance among Au nanoparticles. In order to improve the color change property of the hybrid microgels, we controlled the structures of the hybrid microgels. Interestingly, the hybrid microgels were able to exhibit multiple brilliant colors by attaching Au/Ag multiple core/shell bimetallic nanoparticles in the microgels, and the color change reversibility of each hybrid microgel was accomplished by adjusting the nanoparticles' sizes. Obtained microgels will find important applications such as in biomedical and electronic devices.

### 2.3. Assembly of the Hybrid Microgels

In this section, we present the assembly of colloidal crystals composed of various core/shell microgels and their hybrid microgel counterparts that contain localized Au nanoparticles. Our main purpose in this study is to demonstrate that complex, nanostructured microgels that are the product of multiple synthetic steps can be crystallized into highly ordered 3D crystals. Notably, these microgels can be assembled as such without fractionation or purification aimed at narrowing the size polydispersity. All particles are obtained with a high degree of size uniformity and can be crystallized as prepared. To obtain nanostructured microgels, we conducted a three-stage polymerization. First, core microgels composed of cross-linked polyNIPAm were synthesized by free-radical precipitation polymerization. By using these microgels as cores or "seeds", a shell of polyNIPAm copolymerized with a cationic comonomer was added by seeded polymerization, which provided a functional site for Au nanoparticle nucleation. Finally, another polyNIPAm shell was formed onto the preformed core/shell microgels. This second shell was added to maintain colloidal stability and prevent aggregation during Au nanoparticle synthesis and crystallization. With use of these hierarchal core/shell/shell microgels as templates, Au nanoparticles were synthesized in situ, using the cationic sites in the inner shell to nucleate particle growth. To control the optical properties of the Au nanoparticles, electroless Au plating was carried out with the preformed Au nanoparticles in the microgel as seeds. Each type of microgel was assembled into three-dimensional colloidal crystals by centrifugation and thermal annealing, as described previously.<sup>13</sup> The colloidal crystals that were obtained were characterized by optical microscopy and reflectance spectroscopy (Figure 4). Optical microscopy confirmed the crystalline order of these 3D structures by the observation of the 111 plane, typically found for the

fcc lattice structure. In addition, Bragg diffraction peaks were observed in the visible or near-infrared region for all samples, indicating a high degree of order in these assemblies. In particular, a colloidal crystal that exhibited distinct optical properties was fabricated with use of the hybrid microgel (core/Au+Au@shell/shell hybrid microgel) building blocks, by taking advantage of both the "softness" of the microgel network and the ability to localize the Au nanoparticles. These results suggest that this approach could be expanded to enable the creation of complex tunable optical materials containing refractive index periodicity on multiple length scales.

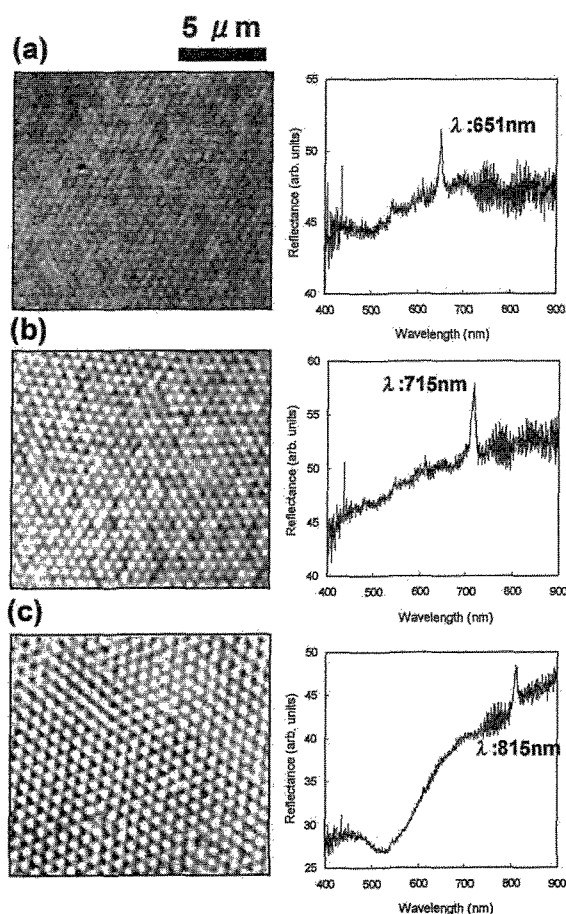


Figure 4. Differential interference contrast microscopy images (left) and reflectance spectra (right) of microgel colloidal crystals assembled from core (a), core/shell/shell (b), and core/Au+Au@shell/shell (c) microgels in deionized water at room temperature. Insets are photographs of each microgel crystal in the rectangular capillary tube.

### 4. Acknowledgement

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