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Nanohybrid polymer prepared by successive polymerization of methacrylate monomer containing silver nanoparticles in situ prepared under microwave irradiation

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Abstract

The well-dispersed silver nanoparticles were prepared in reactive methacrylate monomers under microwave irradiation without polymerization. In contrast to conventional heating, the synthesis of Ag nanoparticles proceeded uniformly throughout the reaction vessel only under microwave irradiation, reaching the completion of the reaction simultaneously in the whole reaction solution. Successive polymerization of the monomer containing the resulting nanoparticles has successfully produced a monohybrid of the silver nanoparticles dispersed in polymer matrix.

Keywords: Microwave; Nanohybrid; Silver nanoparticles

1. Introduction

Recently, organic–inorganic nanohybrids have attracted much attention due to their potential properties which are far superior to those of individual components [1–6]. For example, nanohybrids of polymers containing silver nanoparticles are of great interest because they are good candidate of materials applied for optics [2] and electronics [7]. Properties of these nanohybrids are dependent on particle size [3,4], particle distribution [2,4,8,9] and particle density [4], therefore controls of these parameters in a deterministic way are under intensive investigation.

Generally, two main approaches are employed to prepare nanohybrids: first, previously prepared nanoparticles are dispersed in polymers [2,5,6] and second, nanoparticles are generated in situ in polymers or their monomers by external stimulation such as heating or UV light irradiation [7,10–13]. It is very difficult to obtain good dispersion of nanoparticles in the former method. Then the latter seems more promising than the former, but a critical problem to be solved therein is to achieve uniform generation of nanoparticles in organic matrices. For other approaches such as substrate act as a reagent to synthesize nanoparticles thereby it itself transforms to a template to hold the particles, there is no effective approaches to prepare the nanohybrids (polymer/nanoparticles) [14].

Microwave dielectric loss heating is rapidly emerging as a newly accepted heating technology for a variety of organic and inorganic syntheses. It has been reported that microwave heating can effectively control the size distribution in a narrower

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range within a shorter reaction time than the conventional heating due to the homogeneous and rapid heating in the preparation of nanoparticles [15,16]. Furthermore, microwave heating would provide its direct heating mode independent of heat conduction and convection.

In this paper, the well-dispersed silver nanoparticles were prepared in methacrylate monomers under microwave irradiation. Rapid heating mode of microwave heating has enabled us to in situ synthesize nanoparticles without polymerization of the reactive monomer, which cannot be avoided under conventional heating. Successive polymerization of the monomer containing the resulting nanoparticles has successfully produced a nanohybrid of the silver nanoparticles dispersed in polymer matrix.

Silver myristate $C_{13}H_{27}COOAg$ was selected as a precursor, because silver nanoparticles prepared from $C_{13}H_{27}COOAg$ were capped with a moiety of long-chain carboxylic acid, which acts as a stabilizer of the colloidal dispersion, promoting dispersibility of the nanoparticles [16–19].

2. Experimental

2.1. Synthesis of polymer film containing silver nanoparticles

MW irradiation experiments were performed using a multimode MW apparatus (Micro Denshi MMG-213VP, 2.45 GHz). A fiber optic sensor (Anritsu SP-SM5176FL) was inserted into the reaction solution and the reaction temperature was controlled by the repeated on–off MW irradiation. In a typical experiment, the powder of $C_{13}H_{27}COOAg$ (0.634 g, 1.9 mmol) was added to cyclohexyl methacrylate (CHMA, 10.0 g, 59.4 mmol) containing triethylamine (NEt_3, 0.191 g, 1.9 mmol) in a three-necked quartz flask. $C_{13}H_{27}COOAg$ was not dissolved totally, giving a suspended solution. The solution stirred by a Teflon magnetic stirrer was heated up to 413 K under MW (200 W) irradiation within 1 min. The color of the solution changed to dark brown. The solution was maintained for 5 min at 413 K under the repeated on–off MW (200 W) irradiation. After the MW irradiation, the solution was cooled down immediately by an air blower. After a photoinitiator, 1 wt% Irgacure 907 (Ciba), was added to the solution, the solution was spread on a slide glass substrate using adhesive tapes as a spacer. The solution was subjected to ultraviolet light for 30 min under a nitrogen atmosphere with a high pressure mercury lamp. The dark brown film of thickness ~100 μm was obtained after the UV irradiation.

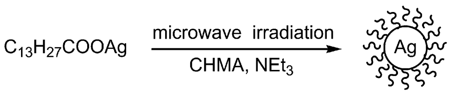
2.2. Measurements

For characterization of silver nanoparticles and films, transmission electron microscopy (TEM), UV–vis and FT-IR were employed. TEM analyses were performed with Hitachi H-9000 operating at 300 kV. The *n*-hexane solution dispersing silver nanoparticles was dried slowly on an amorphous carbon supported on a copper mesh TEM grid. The particle sizes of nanoparticles were determined by directly measuring the particle sizes randomly chosen over 400 nanoparticles on the TEM images. Samples were prepared for cross-sectional TEM observation by embedding the films in epoxy resin followed by curing and cutting the films perpendicular to the film surface using microtome with a diamond blade. UV–vis absorption spectra were measured using Jasco V-570 at room temperature. FT-IR measurements were performed at room temperature by a Perkin–Elmer system 2000 FT-IR spectrometer with an ATR equipment over the frequency range of 600–3500 cm^{-1}.

3. Results and discussion

Silver nanoparticles were prepared in a monomer under microwave irradiation as shown in Scheme 1. Fig. 1 shows a TEM image, an electron diffraction pattern and size distribution of silver nanoparticles prepared in CHMA under microwave irradiation. The particles were spherical in shape with a narrow size distribution ranging from 1.0 to 5.5 nm. The mean diameter was 2.8 nm. The nanoparticles consisted of face-centered cubic (fcc) metal silver according to the diffraction pattern. The distances between the nanoparticles were evaluated to be 2.8 nm from the TEM image (Fig. 1a), suggesting that the nanoparticles should be surrounded by a myristate moiety [16,18,19]. From UV–vis spectrum of the silver nanoparticles in *n*-hexane solution, an absorption peak at 416 nm was observed, attributed to the surface plasmon resonance of silver nanoparticles.

For comparing the preparation under microwave irradiation with conventional heating, the experiments were carried out using an oil bath. A flask containing a CHMA solution of $C_{13}H_{27}COOAg$ and NEt_3 was immersed for 6 min in an oil bath previously heated to 413 K. The photographs shown in Fig. 2a and b demonstrate the difference in the appearance of the solutions after the reactions between microwave irradiation and conventional heating. The color change to dark brown was observed for the whole solution under microwave irradiation, but the color change of only the solution in proximity to the reactor wall was observed under conventional heating. Fig. 2c shows FT-IR spectra obtained from the samples before and after microwave irradiation. The spectrum of the reaction mixture before microwave irradiation showed the absorption bands attributed to CHMA and $C_{13}H_{27}COOAg$. The carbonyl asymmetric stretching band [$\nu_{as}(COO^-)$] of $C_{13}H_{27}COOAg$ at 1515 cm^{-1} disappeared after microwave irradiation, indicating that reduction of $C_{13}H_{27}COOAg$ completed. The FT-IR spectra of the samples of the dark brown part and the yellow part collected from the proximity to the wall and from the center, respectively, in the oil bath experiment showed that the $\nu_{as}(COO^-)$ of $C_{13}H_{27}COOAg$ at 1515 cm^{-1} remained intact at the center (Fig. 2d).



Scheme 1. Preparation of the silver nanocrystallites in a monomer under microwave irradiation.

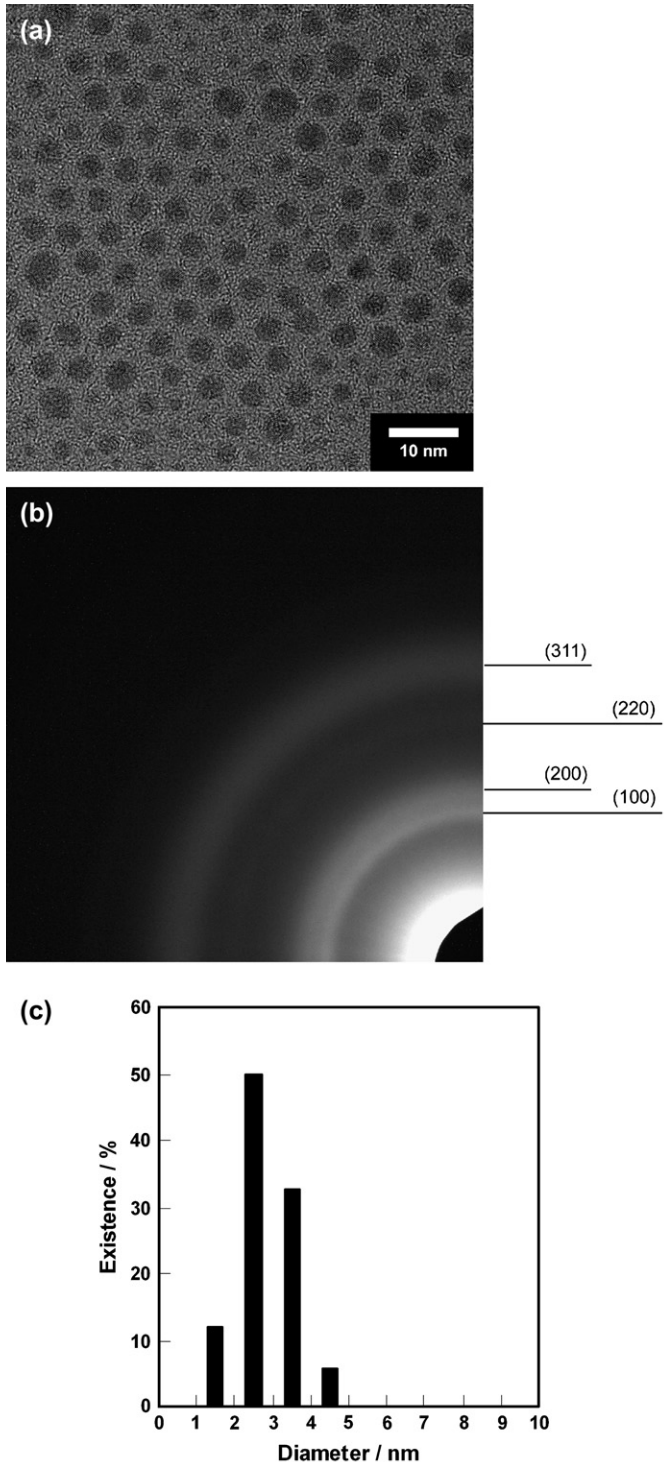


Fig. 1. (a) TEM image, (b) electron diffraction pattern and (c) size distribution of silver nanoparticles prepared in CHMA under microwave irradiation.

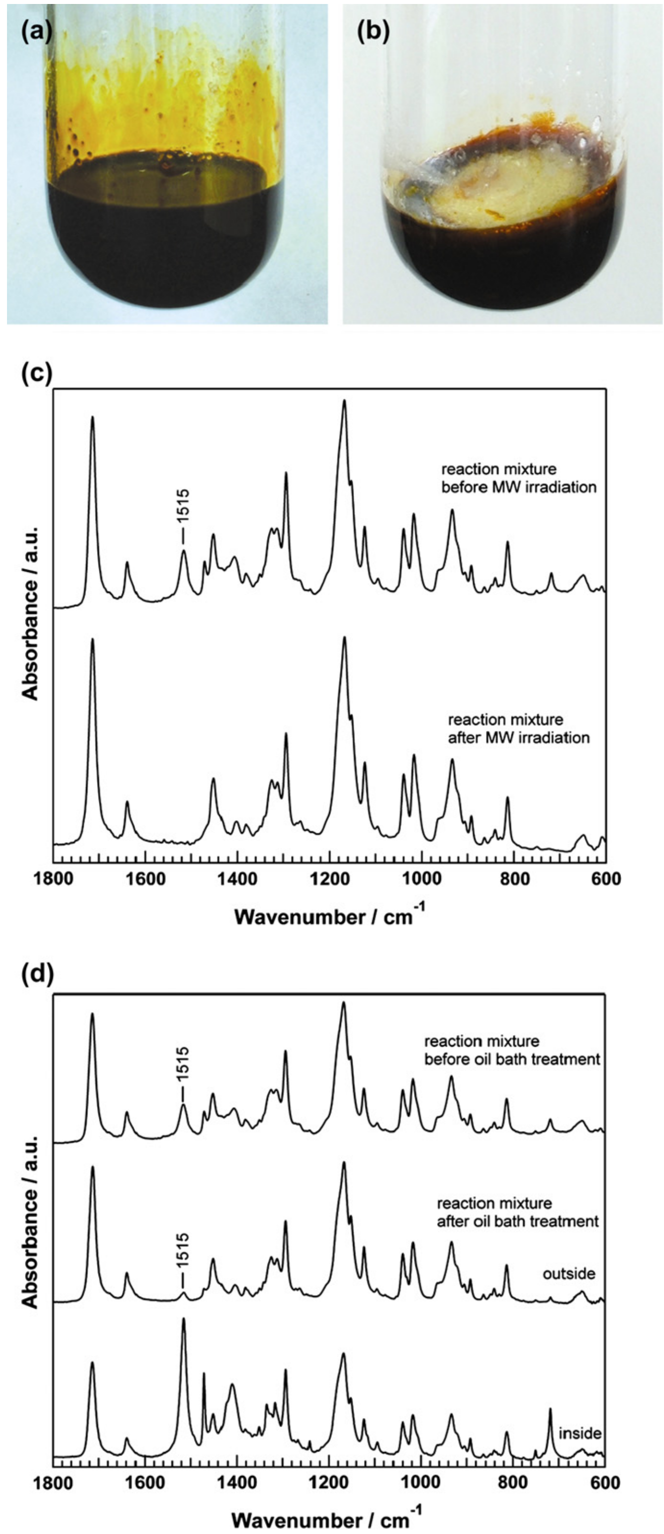


Fig. 2. Photographs of the reaction mixtures heated (a) under microwave irradiation and (b) in an oil bath. FT-IR spectra of the reaction mixtures (c) before and after microwave irradiation and (d) before and after oil bath treatment.

The inhomogeneity observed for the reaction carried out under conventional heating should be due to low thermal conductivity of the reaction mixture. On the other hand, microwave irradiation can raise the temperature of the whole reaction volume simultaneously via interaction with CHMA. Now we have reached an important conclusion that the synthesis of Ag nanoparticles proceeds uniformly throughout the reaction vessel only under microwave irradiation, reaching the simultaneous completion of the whole reaction solution.

FT-IR measurement of the reaction solution also showed that the band assigned to the carbon–carbon double bond stretching band [ν(C═C)] of CHMA at 1640 cm^{-1} was

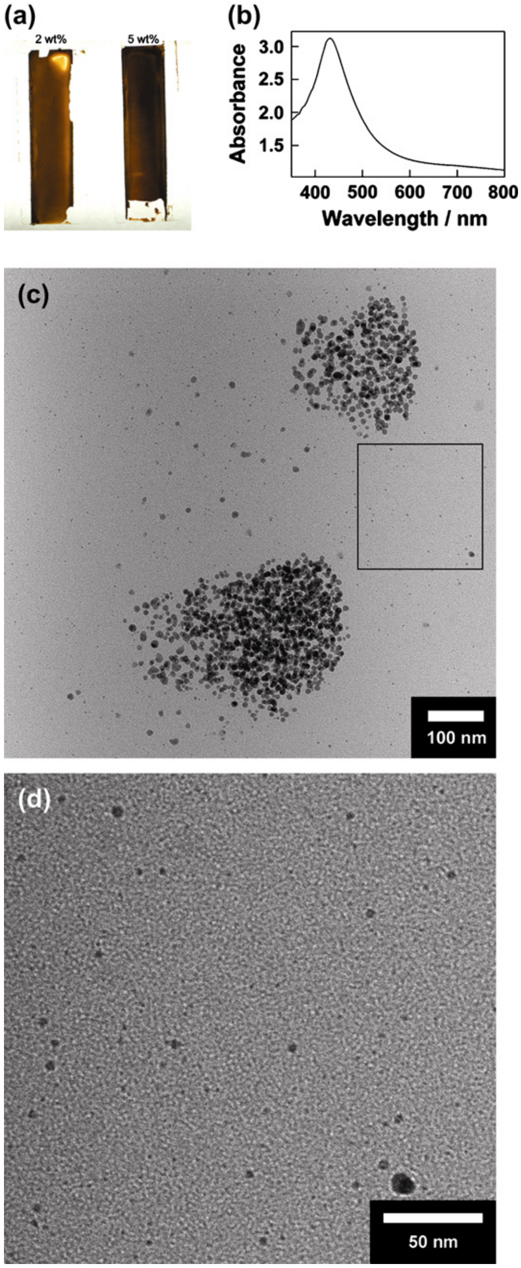


Fig. 3. (a) Photographs of the PCHMA films containing dispersed silver nanoparticles. (b) UV–vis spectrum of silver nanoparticles dispersed in PCHMA. (c) Cross-sectional TEM images of the PCHMA films containing dispersed silver nanoparticles and (d) enlargement of the square field in (c).

disappeared after UV irradiation, ensuring the completion of polymerization under UV irradiation.

Fig. 3a shows the photographs of the PCHMA films containing dispersed silver nanoparticles (Ag contents of 2 and 5 wt%). The films had transparency with dark brown color. Fig. 3b shows UV–vis spectrum of the poly-cyclohexyl methacrylate (PCHMA) film containing dispersed silver nanoparticles (Ag content 2 wt%), which displayed the surface plasmon resonance at 432 nm shifting to the long wavelength compared to that observed in the monomer.

The morphological information on silver nanoparticles in PCHMA has been obtained from cross-sectional TEM images (Fig. 3c and d). The well-dispersed nanoparticles were observed in the wide area of the photograph and the formation of aggregated silver nanoparticles was also recognized. The silver nanoparticles possessed larger size ranging from 10 to 30 nm compared with those before UV irradiation (1.0–5.5 nm), suggesting the size growth during the polymerization process. Kell et al. [20] reported that gold particles modified with thiol derivative underwent particle size growth in the presence of photogenerated radicals. In the present case, the photogenerated radicals should also induce the particle growth of silver nanoparticles due to abstracting of the surface-modifying layer consisting of myristate.

In conclusion, we have developed a novel method for the preparation of inorganic–organic nanohybrid in which reactive monomer containing silver nanoparticles in situ synthesized under microwave irradiation is successively photopolymerized. Our new method would open a novel methodology for nanohybrid chemistry.

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