Monodisperse Pickering emulsions using Au nanoparticles for bioencapsulation

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INTRODUCTION

Emulsions have been widely applied in various fields such as foods, pharmaceuticals, and cosmetics. Emulsions stabilized by solid particles adsorbed at a liquid-liquid interface are called as ‘‘Pickering emulsions’’ (Pickering, 1907). Recently, these have been expected to be used pharmaceutical, cosmetic, and food media because this emulsion system can reduce the use of artificial surfactants that could cause several problems such as irritation, especially for sensitive skins. In the preparation of Pickering emulsions, particles of inorganic materials such as metal oxide (Stiller et al. 2004) and silica (Giermanska-Kahn, et al. 2005) have been most frequently used as emulsion stabilizers; organic latex particles have also been utilized (Binks and Lumsdon 2001). An oil-in-water (O/W) Pickering emulsion stabilized by a biobased material bacteria-chitosan network was also developed (Wangkongkatep et al. 2012). Recently, Pickering emulsions stabilized by nanoparticles have been anticipated to serve as templates for new functional materials (Ikem et al. 2010) and as bioencapsulation media for enzymes and microorganisms (Wu et al., 2011; Keen et al., 2012).
Nanoparticles of metals and semiconductors exhibit characteristics different from those of the corresponding bulk material. Owing to these features nanoparticles are anticipated to serve as new materials and tools in various fields. Gold (Au) nanoparticles are the most attractive metal nanoparticles since they exhibit fascinating aspects such as various types of assemblies having new functions in the field of material science. Here, we report the preparation of monodisperse Pickering emulsions using Au nanoparticles as solid particles and their preparation conditions for bioencapsulation.

MATERIALS AND METHODS

Au nanoparticles were prepared by phase transfer method based on the synthetic method by Brust et al. (1994). Typically, the phase transfer method consists of the transfer of Au ions to an organic phase with a phase transfer reagent Tetrakis(decyl)ammonium bromide (TDAB), the addition of a stabilizing agent 15-mercaptopentadecanoic acid (MPDA), chemical reduction reaction by a reducing agent $NaBH_4$, and washing. Transmission electron microscopy (TEM) images of Au nanoparticles were obtained using a JEOL JEM-3100 FEF. From TEM image, size distributions were calculated by measuring nanoparticles for each sample. Ultraviolet-visible (UV-vis) spectroscopy was used to monitor the dispersed Au nanoparticles using a Shimadzu UV-2400PC. The Au nanoparticle aqueous solution with NaCl was added to toluene (aq. soln./toluene = 1: 1 vol.), and the mixture was homogenized by using an homogenizer (IKA Ultra-Turrax T25, 1 cm head) operating at various rotation speeds for 2 min. The ultrasonication to the mixture of the Au nanoparticle aqueous solution and toluene solution was conducted for 1 min using a Kenis US-3 ultrasonication cleaner bath (oscillation frequency: 36 kHz, power output: 150 W).

RESULTS AND DISCUSSION

Water-soluble Au nanoparticles were prepared by using MPDA as a stabilizing agent in the phase transfer method. After washing, the collected precipitates were dispersed in water. The color of the aqueous solution was wine-red, which is the specific color of Au nanoparticles due to local surface plasmon resonance absorption at around 520 nm. The prepared Au nanoparticle solution was stable for a long time, for more than 12 months. From the TEM images the average size of the metal core of MPDA-Au nanoparticles was 2.0 nm with a size distribution of 16.2% (Fig. 1).

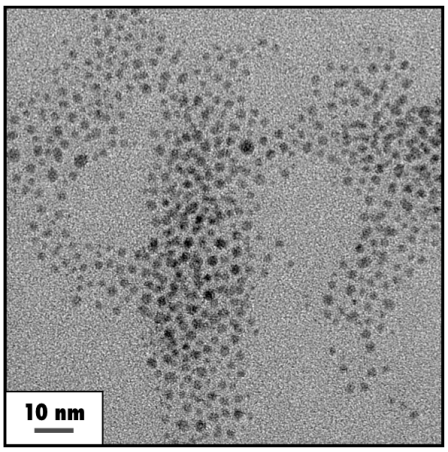

Figure 1: TEM image of MPDA-Au nanoparticles.

A mixture of the Au nanoparticle aqueous solution containing NaCl and toluene solution (aq. soln./toluene = 1: 1 vol.) was homogenized for 2 min. After homogenization, monodisperse emulsions with diameters in the size range of 0.5 to 1.2 mm in the oil phase were successfully prepared without any surfactants (Fig. 2). The color of the emulsion droplets is a light shade of wine-red, indicating that the emulsions would be stabilized by the Au

nanoparticles. The drop and conductivity tests confirmed that this was a W/O emulsion. The emulsions were very stable for a long time, for more than 12 months. The emulsion size and size distribution depend on the rotation speed of the homogenizer, the NaCl concentration, and the Au nanoparticle concentration. There was an optimal condition for obtaining highly monodisperse emulsions with a size distribution of 9.2% (Fig. 2B). Re-formation of Au nanoparticle-stabilized emulsions after demulsification was possible by re-homogenization using homogenizer.

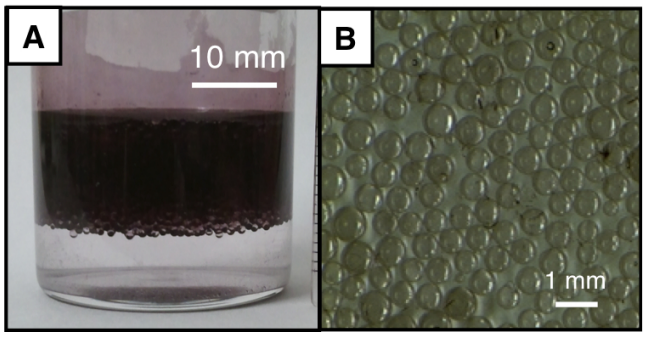

Figure 2: Photographs of MPDA-Au-nanoparticle-stabilized W/O emulsions prepared by a homogenizer (A and B).

Ultrasonication conducted to the mixture of toluene/aqueous solution containing MPDA-Au nanoparticles also produced W/O emulsions (Fig. 3), which was confirmed by the conductivity test. The emulsions in the size range of 0.8-3.2 μm were obtained. The prepared emulsions will be useful for an encapsulation of enzymes, and especially its use as micro-bioreactors for the bio-catalytic conversion of hydrophobic substrates.

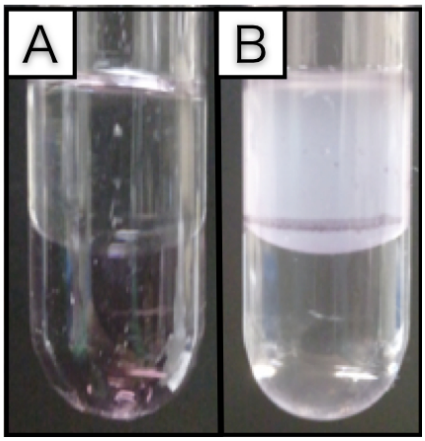

Figure 3: Photographs of toluene/aqueous solution containing MPDA-Au nanoparticles (A) before and (B) after ultrasonication.

CONCLUSIONS

Highly uniform and stable Pickering W/O emulsions in the size range of 0.5 to 1.2 mm were successfully prepared using 2 nm Au nanoparticles coated with mercaptocarboxylic acid as a stabilizing agent. The emulsion size and size distribution depend on the rotation speed of the homogenizer, the NaCl concentration, and the Au nanoparticle concentration.

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