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Metal-coated microcapsules with tunable magnetic properties synthesized *via* electroless plating

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ABSTRACT

Metal-coated microcapsules with tunable magnetic properties, which contained liquid cores and metallic Ni–P alloy shells, were synthesized *via* electroless plating. The fabrication process consisted of emulsification, phase separation, and electroless Ni plating stages. The material composition and sizes of Ni single crystals in the obtained metallic shells depended on the pH of the plating solution. It was found that the microcapsules prepared at high pH values (8.0 and 10.0) were characterized by ferromagnetic properties, whereas those synthesized at low pH values (4.7 and 6.0) were superparamagnetic. The produced microcapsules have potential applications as magnetic responsive carriers of phase change materials, which can be easily transferred to a desired place by applying external magnetic field.

1. Introduction

During the last decades, microcapsules have attracted significant attention because of their wide applications, which include fragrances [1], pesticides [2], self-healing materials [3], drug delivery systems [4], and suspensions containing phase change materials (PCMs) [5]. They can be synthesized by various methods such as interfacial polymerization [6], layer-by-layer (LbL) assembly of polyelectrolytes [7], phase separation [8], colloidosome preparation [9,10], and coacervation [11]. Among different types of microcapsules, polymer/metal composite ones are of particular interest since they are responsive to magnetic and optical stimuli and exhibit enhanced catalytic properties and structural stability [12,13].

The advantage of magnetically responsive microcapsules is their ability to be controllably delivered to a targeted location by applying external magnetic field [14,15]. Among various techniques for the fabrication of microcapsules with magnetic properties, embedment of magnetic nanoparticles onto the capsule wall during LbL has been most widely utilized [16–18]. However, the magnetization of a material surface *via* LbL requires using multiple complex steps, which results in relatively low loading efficiency of magnetic nanoparticles.

Meanwhile, electroless plating (ELP) is also a wet chemical process, during which a metal film is deposited onto the substrate surface through the in-situ chemical reduction of metal ions [19]. It is widely used for the preparation of various surface-modified colloidal materials such as core-shell particles and composite fibers [20–22]. In particular, electroless Ni plating was utilized for fabricating films of composite particles, which possessed enhanced magnetic and catalytic properties as well as high corrosion resistance due to their controlled functionalities [23–25]. Thus, Tierno and Goedel successfully prepared composite microparticles consisted of poly(methyl methacrylate) cores and various types of metallic shells (NiP, CoP, CoNiP, NiFeP, and CoFeP) with magnetic properties ranging from superparamagnetic to ferromagnetic ones [26]. Sanles-Sobrido et al. synthesized Ni-coated submicron-sized polystyrene particles with tailored magnetic properties, which could be adjusted by varying the amount of deposited metal species [27].

In addition, several articles have recently reported fabrication of functional microcapsules *via* ELP. In one study, Patchan et al. demonstrated encapsulation of a moisture-sensitive liquid (isophorone diisocyanate) inside a metallic shell [28]. It was achieved by Ni-coating of polymeric microcapsules, which preserved the sensitive content of their interior for a long period. Hitchcock et al. also reported retention of volatile oil species inside microcapsules with impermeable metal shells [29]. On the other hand, Alshannaq et al. demonstrated a significant increase in the heat conductivity of PCM-containing microcapsules, which significantly improved their heat exchange properties [30]. Hence, metal-coated microcapsules can be potentially utilized in a wide range of practical applications.

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In this study, hexadecane, a typical liquid PCM, was successfully encapsulated inside metallic microcapsules with tunable magnetic properties through the preparation of crosslinked polymelamine microcapsules by phase separation [31], and subsequent electroless Ni plating. As far as we know, this is the first paper presenting the synthesis of magnetic-tunable microcapsules that contains PCM using electroless plating. The magnetic properties of the resulting microcapsules were switched from superparamagnetic to ferromagnetic ones by varying the pH of the plating solution during the electroless Ni plating process. In addition, the morphology and material composition as well as the crystalline and magnetic properties of the fabricated microcapsules were characterized.

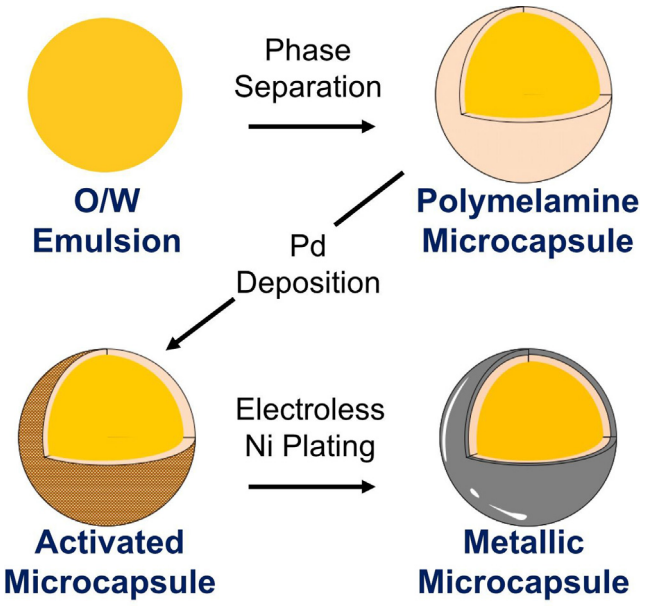
2. Materials and methods

2.1. Materials

Melamine [CAS: 108-78-1], formaldehyde solution [CAS: 50-00-0], NaOH aqueous solution [CAS: 1310-73-2], $SnCl_2$ [CAS: 7772-99-8], $PdCl_2$ [CAS: 7647-10-1], $NiSO_4{\cdot}6H_2O$ [CAS: 10101-97-0], $Na_2HPO_2{\cdot}H_2O$ [CAS: 10039-56-2], *DL*-malic acid [CAS: 6915-15-7], sodium acetate [CAS: 127-09-3], *DL*-lactic acid [CAS: 50-21-5], and ammonia solution [CAS: 1336-21-6] were purchased from Wako Pure Chemical Industries. Poly(ethylene-*alt*-maleic anhydride) (Poly(E-MA); average Mw = 100,000–500,000) [CAS: 9006-26-2], hexadecane [CAS: 544-76-3], and tergitol NP-9 [CAS: 127087-87-0] were purchased from Sigma-Aldrich. Ultrapure water obtained by using a Millipore Milli-Q purification system (EMD Millipore Corporation) was used in all experiments.

2.2. Synthesis of polymelamine microcapsules

Crosslinked polymelamine microcapsules were prepared through a combination of emulsification and phase separation methods (Scheme 1). During emulsification, 200 mL of 5 wt% poly (E-MA) aqueous solution with pH = 4.3 (adjusted *via* the addition of aqueous NaOH solution) was used as the continuous phase. Oil-in-water emulsion containing the aqueous solution of poly(E-MA) and 10 mL of hexadecane was prepared *via* vigorous homogenization at a rotation speed of 2000 rpm using a POLYTRON PT3100 disperser (KINEMATICA AG). Crosslinked polymelamine microcapsules were synthesized by the addition of a melamine–formaldehyde solution through phase separation, which was stirred at a rotation speed of 300 rpm and temperature of 60 °C using an impeller. The melamine–formaldehyde solution was obtained by mixing 2.5 g of melamine monomer, 6.25 g of formaldehyde solution, and 16.25 g of water with 1 drop of 1 mol/L sodium hydroxide solution. After 30 min of microencapsulation, the prepared polymelamine microcapsules were washed with deionized water.



Scheme 1. A schematic describing the synthesis of metallic microcapsules.

2.3. Electroless plating

Metallic shells for the synthesized crosslinked microcapsules were prepared *via* Pd deposition with subsequent electroless Ni plating (Scheme 1). The produced polymelamine microcapsules were gently stirred in an acidic $SnCl_2$ aqueous solution (containing 10 g/L of $SnCl_2$ and 5 mL/L of HCl) for 10 min. Afterwards, the solution was decanted, and the microcapsules were washed with water, placed into an acidic $PdCl_2$ solution (containing 0.5 g/L of $PdCl_2$ and 4 mL/L of HCl), stirred for 2 min, and then washed again 3 times. The activated microcapsules were placed into an electroless Ni plating bath and stirred for 1 h at 60 °C. The composition of the utilized plating solution was as follows: 22.4 g/L of $NiSO_4{\cdot}6H_2O$, 25 g/L of $Na_2HPO_2{\cdot}H_2O$, 4 g/L of *DL*-malic acid, 8.5 g/L of sodium acetate, 21 mL/L of *DL*-lactic acid, and 3 mg/L of nonionic surfactant tergitol NP-9 (the pH of the plating solution equal to 4.7 was adjusted by adding an appropriate amount of the ammonia solution) [32]. After electroless plating, the prepared metal-coated microcapsules were washed with deionized water 3 times followed by decantation. The material composition of the produced metal shells was controlled by adjusting the pH of the plating solution to 6.0, 8.0, and 10.0, which was achieved *via* the addition of the specified amounts of the ammonia solution.

2.4. Characterization

2.4.1. Optical microscopy and SEM studies

The morphology of the synthesized polymelamine and metal-coated microcapsules was studied using a BX51 optical microscopy system (OLYMPUS) and a field emission scanning electron microscopy (FE-SEM) instrument (S4700, Hitachi). All samples were freeze-dried to remove any traces of liquids (such as water and hexadecane) before SEM measurements. During SEM studies, the applied voltage was equal to 1.0 kV.

2.4.2. Elementary analysis

The elemental surface composition of the prepared microcapsules was conducted after each ELP step using an accurate and non-destructive X-ray photoelectron spectroscopy (XPS) technique. XPS measurements were performed after Ar-ion sputtering of the freeze-dried samples for 10 s using an S-Probe ESCA apparatus (Fusion Instruments) equipped with a monochromated *AlKα* X-ray source. A quantitative energy dispersive X-ray spectroscopy (EDX) analysis of the metal-coated microcapsules was conducted using an FE-SEM S4300 instrument (Hitachi) equipped with an EDAX-Genesis (AMETEK) detector at an applied voltage of 20.0 kV. To evaluate the material composition of the produced metal shells, the presence of multiple elements on the sample surface (including C, N, O, Na, P, S, Cl, Sn, Pd, and Ni) was confirmed, and fractions of each component were estimated. Mapping images of Ni and P elements were also obtained for the synthesized metal-coated microcapsules *via* EDX.