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Top-down synthesis of polyaspartamide morphogens to derive platinum nanoclusters

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ABSTRACT

Metallic nanoparticles are widely used in various applications, and their successful uses depend on the size and stability. In this study, we present a method to synthesize platinum nanoparticle clusters with tunable size and spatial organization. These nanoparticle clusters were synthesized by conducting sol-gel polymerization of platinum precursors in aqueous solution of poly(amino acid)s' derivative substituted with both particle precursor-binding amine groups and particle-binding thiol groups. Control experiments displayed that poly(amino acid)s' derivative tuned the morphology of nanoparticles and also induced organized association between the particles. Therefore, this study serves to provide novel method to synthesize a wide array of nanoparticles and clusters along with novel polymers to tune morphology and organization of the nanoparticles.

1. Introduction

Metallic nanoparticles are being extensively studied to improve performance of various photonic, catalytic, bio-imaging, and therapeutic modalities while reducing particle loadings [1–3]. The functionality of nanoparticles is known to greatly rely on its diameter and spatial organization [4,5]. Specifically, several computational modeling often suggested that nanoparticle clusters resulting from controlled association between multiple nanoparticles should display significantly enhanced performance of single nanoparticles [6,7]. However, there are few successes in preparing nanoparticle clusters, because the large surface area of nanoparticles leads to uncontrollable crystallinity resulting from interparticle agglomeration. Organic templates with defined molecular architecture or self-assembled morphologies are used to control the size of nanoparticles, but no template is available to prepare the nanoparticle cluster.

This study presents a new method to prepare electrocatalytic nanoparticle and clusters with controllable crystallinity *via* simultaneous sol-gel polymerization of nanoparticles and subsequent self-assembly between the particles. In addition, this study demonstrates that the resulting nanoparticles and clusters carry more significant electrocatalytic activities than nanoparticles separated from each other. We used polyaspartamides substituted with varying numbers of thiol and amine groups to control the morphology and spatial organization of nanoparticles. Platinum particle is extensively being used as catalysts in several energy and environment-related fields, such as fuel cells, oil refining process and car exhaustion [8–10]. Therefore, we implemented the sol-gel polymerization of platinum (Pt) clusters in the solution of polyaspartamide variants and demonstrated the individual and combined functionality of amine and thiol groups of polyaspartamide to controlling the size and spatial organization of Pt nanoparticles. The degrees of substitution of thiol and amine groups to polyaspartamide were independently controlled *via* top-down nucleophilic substitution of poly(succinimide), polymerized by acid-catalyzed polycondensation of aspartic acid.

2. Experiments

Poly(succinimide) (PSI) was synthesized by acid-catalyzed polycondensation of aspartic acid (Sigma) [4]. The molecular weight of PSI was determined by gel permeation chromatography (Breeze 2 GPC, Waters), with Styragel® HT column (Waters). Then, the designated amounts of cysteamine (Sigma) and ethanolamine (Sigma) were sequentially added to the synthesized PSI to prepare poly(2-hydroxyethyl-2-mercaptoethyl aspartamide) (PHMA, Fig. 1a). In parallel, poly(2-amino-2-hydroxyethyl-2-mercaptoethyl aspartamide) (PAHMA, Figs. 1a and 2) were prepared with the designated amounts of cysteamine and ethylene diamine (Aldrich), and then ethanolamine. The resulting chemical structures of PHMA and PAHMA were confirmed with ^{1}H NMR (Avance II,

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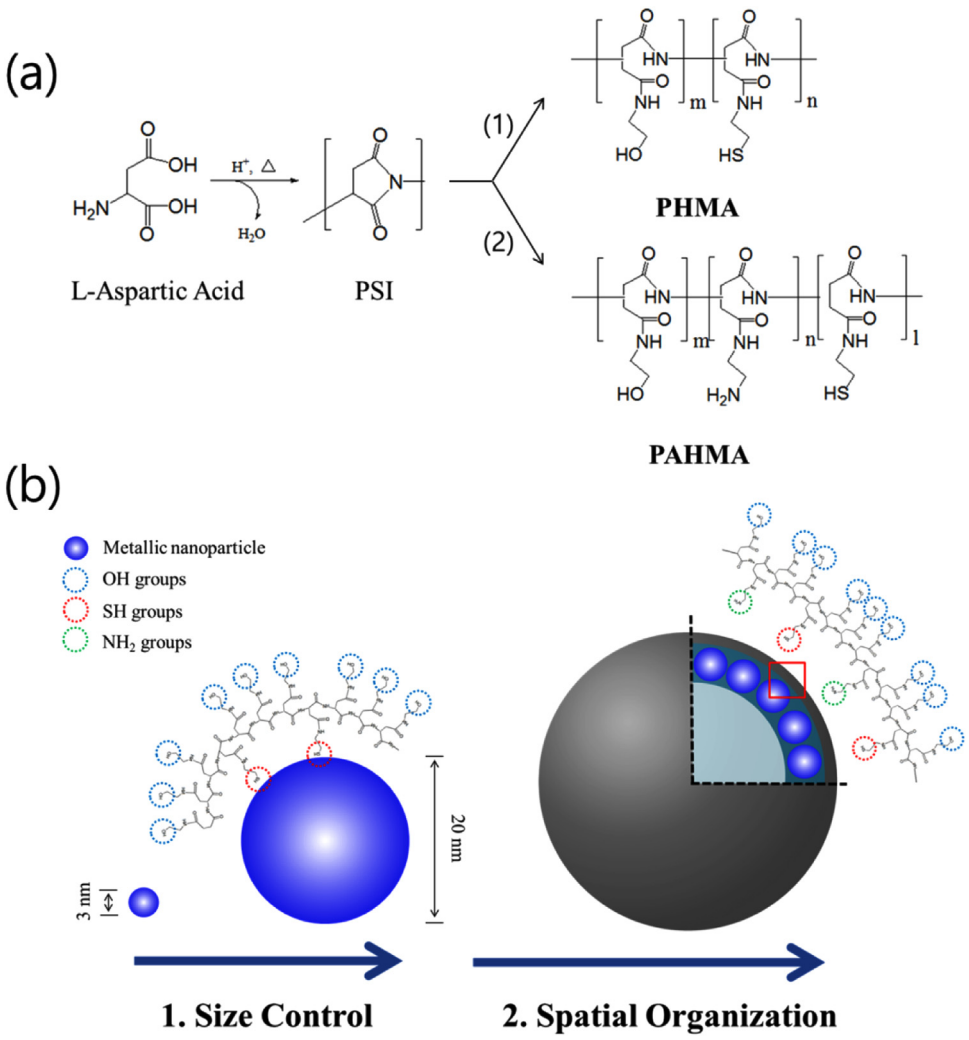

Fig. 1. (a) Top-down synthesis schemes of PHMA (1) and PAHMA (2) *via* nucleophilic substitution of PSI from L-aspartic acid. (b) Schematic description of the poly-aspartamide morphogens to control the size and spatial organization of metallic nanoparticles.

Bruker Biospin), and the degree of substitution of thiol and amine groups were measured with Ellman [11] and TNBS (trinitrobenzensulfonic acid) assay [12].

The predetermined amount of Pt precursor, potassium tetrachloroplatinate (K_2PtCl_4, Sigma), was preloaded into the PAHMA solution. Then, the mixture was incubated for 24 h to ensure the complete ligand-exchange reaction between Pt precursors and amine groups of the PAHMA. The binding between PAHMA and K_2PtCl_4 was confirmed with a shift of the UV absorbance peak from 215 nm to 245 nm. The 0.5 M sodium tetraborohydrate

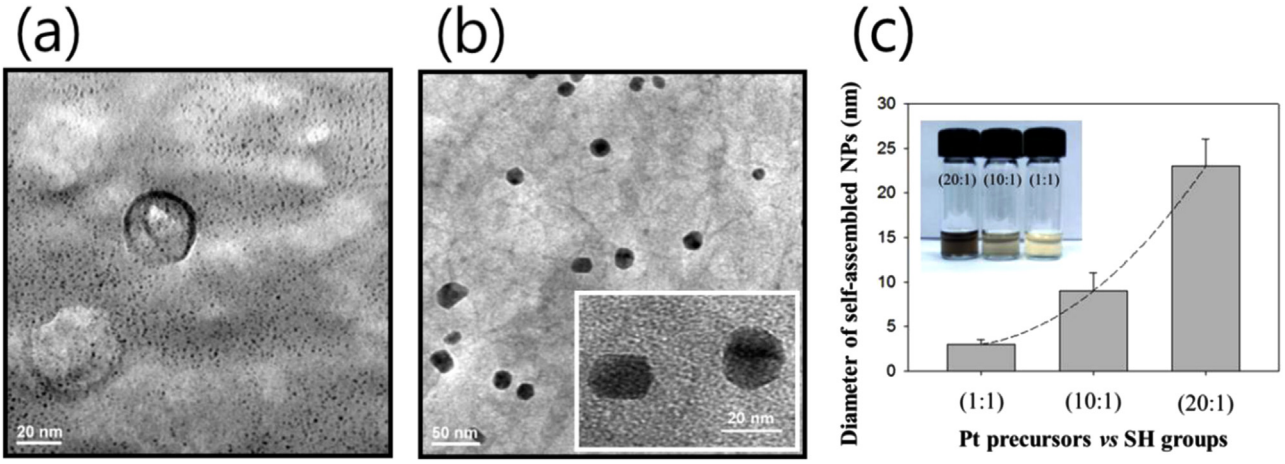

Fig. 2. TEM images of Pt nanoparticles at varied molar ratios between precursors and thiol groups of PHMA of 1:0 (a), and 20:1 (b). Inset represents the magnified Pt nanoparticles in TEM image. (c) Diameter of poly(amino acid)s derivative-mediated Pt nanoparticles, according to the mole ratio of Pt precursors and thiol groups in PHMA.