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Use of the self-assembly of tyrosine-containing bolaamphiphile molecules as a reactive template for metal deposition

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ABSTRACT

A novel bolaamphiphile molecule exploiting biochemical functionality was synthesized and self-assembled to form a spherical reactive template for the preparation of composite metallic nanoshells. A tyrosine-containing bolaamphiphile, bis(N-alpha-amido-tyrosine)-1,7-heptane dicarboxylate, self-assembles instantaneously in an aqueous solution forming nanoscaled spheres. Instantaneous assembly of the prepared bolaamphiphile is driven by the polarity and stacking of phenol moiety in tyrosine. Through spectroscopic investigations, molecular interactions such as hydrogen bonding and π–π stacking of aromatic rings were found to induce the self-assembly of the molecule. The phenol moiety of tyrosine is exposed to the surface of the spherical assembly due to its polarity. Under basic conditions, the spherical assembly was used as a reactive template on which metal clusters were deposited. The surface-exposed phenol group reduced the silver ions to solid clusters, and these clusters were further exploited as catalysts for the gold layer deposition. This study illustrates that the bolaamphiphilic molecule with designed biochemical functionality provides a facile way to prepare supramolecular structures with chemical activity.

1. Introduction

Molecular self-assembly has attracted substantial interest for the preparation of complex supramolecular structures from discrete molecules. The prepared structures have been used as structural components for fabrication of novel biosensors, catalysts, and functional nanoparticles [1–8]. Self-assembly of the amphiphilic molecules is highly influenced by molecular structure as well as environmental conditions like pH and ion concentration such that proper design of the molecule is very important [9–12]. The characteristics of the functional group of the molecule as well as the hydrophilicity and hydrophobicity have profound influence on the self-assembly. For example, the aromatic ring in an amphiphilic molecule would promote assembly by planar stacking as well as the inherent hydrophobicity [13]. Recently, the bolaamphiphile molecule, an amphiphilic molecule containing a central hydrophobic chain and hydrophilic groups at both ends, has been studied for the construction of a self-assembled structure with diverse functionalities because it can contain more functional groups and make suprastructures easily [14–16]. Therefore, self-assembly of a bolaamphiphile molecule containing appropriate functional groups is a promising approach to construct supramolecular structures with designer functionalities.

Amino acids and peptides are biochemical molecules that can be conjugated with abiological organic substances. The peptide-containing amphiphiles have been studied in various applications using their assemblies as soft templates with distinct structures [17]. Many of peptides and amino acids are soluble in aqueous solvents and contain reactive functional groups which play key roles in most enzymatic functions. These functional groups have been utilized to mineralize inorganic substances as well as to decompose organic molecules. For example, the amine groups of poly(Lys) promote mineralization of Si and Ti precursor ions [18,19], and neighboring hydroxyl–imidazole groups of Ser-His combination mediate growth of crystalline metal oxides [20]. When synthesizing a novel amphiphile molecule, employment of a designer amino acid as a hydrophilic moiety is a promising approach allowing both self-assembly and catalytic function. Tyrosine is a polar amino acid containing a hydrophilic phenol group in the side chain. It is soluble in water and absorbs UV–vis light due to its aromatic structure [21]. Further, the hydroxyl group of the phenol moiety is reactive, allowing for conjugation with other molecules, and mediates the reduction of silver ions such that it can be used for the solidification of noble metal ions in aqueous solution [22,23]. In addition, the π–π staking of phenol rings may contribute to the self-assembly once they are properly positioned. All of the above properties make tyrosine attractive as a biological component of a bolaamphiphile molecule.

In this study, a novel tyrosine-containing bolaamphiphile molecule was synthesized, and its self-assembled structure was

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exploited as a reactive template for the preparation of gold and silver composite nanoshells. A novel bolaamphiphile molecule of bis(N-alpha-amido-tyrosine)-1,7-heptane dicarboxylate (Tyr-C7 hereafter) was synthesized which was composed of a central hydrophobic seven-carbon alkyl chain and tyrosines at both ends linked through amide bonds. The bolaamphiphile molecules instantly self-assembled to form spherical structures in the aqueous solution, exposing the tyrosine moiety to the outer surface. Exploiting the reactivity of the phenol groups, the spherical assembly reduced the silver ions to form solid silver clusters. The silver clusters were used as catalysts to lead to the subsequent deposition of a gold layer.

2. Experimental

2.1. Materials

For the synthesis of Tyr-C7, hydrophobic alkyl chain molecules of azelaic acid (98%, Aldrich) and a hydrophilic tyrosine source of L-tyrosine-benzylester-p-toluenesulfonate (98%, Fluka) were used as main chemicals. A crosslinker of N-[3-(diethylamino)propyl]-N′-ethylcarbodiimide hydrochloride (EDAC, commercial grade) was purchased from Sigma–Aldrich. 1-Hydroxybenzotriazole monohydrate (HOBT, 98%), methanol (99.5%) and triethylamine (TEA, 99%) were purchased from Dae-jung Chemical. The solvents N,N-dimethyl formamide (DMF, 99.5%) and chloroform were obtained from Duksan Chemical. All chemicals were used without further purification.

2.2. Synthesis and self-assembly of Tyr-C7

The bolaamphiphile Tyr-C7 was synthesized through carbodiimide-based conjugation. Azelaic acid and 1-hydroxybenzotriazole monohydrate were mixed in DMF to be concentrations of 5.0 and 6.5 g/L, respectively. 4.8 mol of N-[3-(diethylamino)propyl]-N′-ethylcarbodiimide hydrochloride in chloroform was added to the above mixture to induce carbodiimide. Later, 2.1 g of the tyrosine source, L-tyrosine-benzylester-p-toluenesulfonate, and a catalyst of triethylamine were added. The mixture was stored in a refrigerator (4 °C) overnight to conjugate the reactants. After partial removal of the solvent by evaporation, intermediate products were obtained through crystallization. The intermediate crude product was filtered, washed with acetone, and dried in a vacuum at 40 °C. This dried intermediate was re-dissolved in DMF. Volumes of 40 ml of 0.1 N sodium hydroxide and 1 N hydrochloride solutions were added to the DMF solution for the subsequent base hydrolysis/acidification reaction. After the reaction, the Tyr-C7 product was further purified by repeating crystallization and acetone washing. The chemical structure of bis(N-alpha-amido-tyrosine)-1,7-heptane dicarboxylate is shown in Fig. 1(a). ^{1}H NMR spectra (Advance 600, 600 MHz High Resolution NMR Spectrometer, Bruker) were recorded for structure confirmation.

Tyr-C7 molecules self-assemble instantaneously in an aqueous solution. The produced Tyr-C7 powder dissolves in pH-controlled water easily and forms spherical self-assemblies quickly. The pH of the solution was adjusted to 5–7 by adding 50 mM citric acid solution. The self-assembled Tyr-C7 was allowed to settle down and was separated by centrifugation at 14,000 rpm.

2.3. Use of Tyr-C7 assembly as a template for Ag/Au shell formation

Exploiting the activity of surface-exposed tyrosine, reduction of silver ions was performed producing silver clusters on the self-assembled system. A volume of 1.5 ml of $AgNO_3$ solution (30 mM) was added to the suspension containing a spherical assembly of Tyr-C7 (prepared from 8.9 mg of Tyr-C7), and the pH of the suspension was adjusted to pH 10–11 using a 1 N NaOH solution. The mixture was stirred for 24 h to complete the reaction at room temperature while keeping in the dark to prevent photoreduction. Reduction of the silver ions to solid clusters was monitored using UV-vis spectroscopy. The mineralized silver clusters on the spherical Tyr-C7 assembly were further exploited as catalysts, reducing gold precursor ions to form a gold particle layer on the self-assembled template. A volume of 1.0 ml $HAuCl_4$ solution (10 mM) was added to the above silver decorated Tyr-C7 assembly suspension to form the gold particle layer. A schematic of the whole templating process is shown in Fig. 1(b).

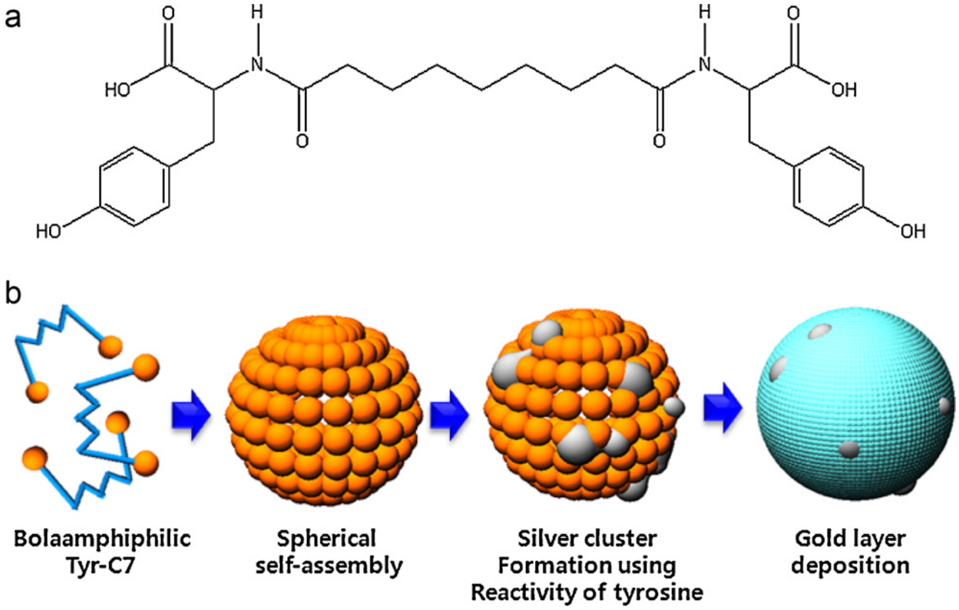

Fig. 1. (a) Chemical structure of the synthesized peptide-containing bolaamphiphile molecule, Tyr-C7, and (b) schematic process of the preparation of the Tyr-C7 spherical self-assembly and its subsequent usage as a template for the Ag/Au composite deposition.