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Decoration of Au and Ag Nanoparticles on Self-Assembling Pseudopeptide-Based Nanofiber by Using a Short Peptide as Capping Agent for Metal Nanoparticles

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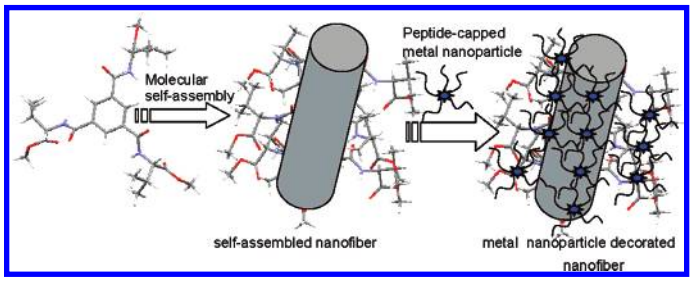
ABSTRACT



The surface of a nanofiber that is formed from a self-assembling pseudopeptide has been decorated by gold and silver nanoparticles that are stabilized by a dipeptide. Transmission electron microscopic images make the decoration visible. In this paper, a new strategy of mineralizing a pseudopeptide based nanofiber by gold and silver nanoparticles with use of a two-component nanografting method is described.

The shape and size of nanocrystals govern their catalytic, optical, and electronic properties.[1] To apply nanocrystals as building blocks for practical electronic, magnetic, and optical devices, the nanocrystals must be assembled in an ordered pattern. There are some recent examples of patterned deposition of various nanocrystals on flat surfaces.[2] Recent studies include the patterning of the nanocrystals on cylindrical nanotube surfaces.[3] Controlling diameter and packing densities of nanocrystals on the surfaces on which they are to be patterned is of utmost importance to produce nanodevices with tunable electronic properties from a single type of nanocrystal. Biological systems control the mineralization and nanocrystal synthesis of various metals in exact shapes and sizes with high accuracy.[4] There are many examples of using biological molecules as templates on which the

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monodisperse nanocrystals have been grown by biomineralization.[5] Oligomeric DNA, bacteriophages, and other biomecular components have been used to prepare various nanostructures.[6] Design and construction of supramolecular architectures of nanoscopic dimensions give access to entities of increasing complexity with distinct structural and functional properties. The use of intermolecular forces provides a rational and efficient method to position molecular components precisely in a well-defined supramolecular architecture. Self-assembly relies on a sequence of spontaneous recognition, growth, and termination steps to form the final equilibrium supramolecular entity (or a collection of such) through metal ion coordination, hydrogen bonds, or hydrophobic or electrostatic interactions. There are a few examples of mineralization on synthetic nanostructures by metal nanoperticles or nanocrystals, based on specific supramolecular intercations.[7,8] Matsui et al. made a template by immobilizing a histidine containing peptide on the surface of a nanotube that is made up of self-assembling bis(*N*-α-amido-glycylglycine)-1,7-heptane dicarboxilic acid and various metal nanoparticles including gold, silver, and platinum were stabilized on that nanotubular surface.[8a,b] Here, we report a new strategy of mineralizing pseudopeptide-based nanofiber by gold and silver nanoparticles using a two-component nanografting method exploiting the rationale of basic noncovalent interactions between the side chains of self-assembled pseudopeptides and the peptide capped gold/silver nanoparticles.

For obtaining an efficient capping agent for gold and silver nanoparticles, a cysteine containing C-terminally protected dipeptide (peptide **1**) has been synthesized (Figure 1). This peptide has been purified and characterized with conventional methods (Supporting Information). We have used methyl-ester protection at the C-terminus to lower the propensity of self-assembly of the dipeptide, so that it can be effectively used as a capping agent for gold and silver nanoparticles and to control the homogeniety in size of the metal

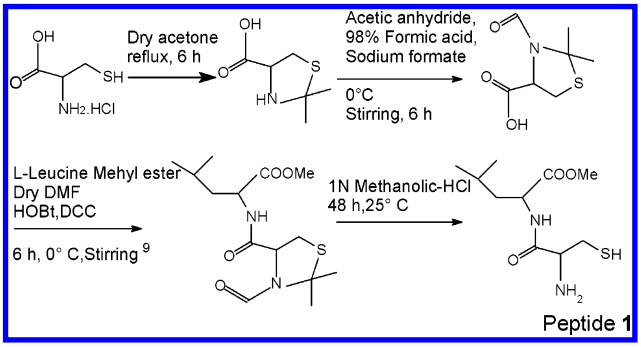

Figure 1. Schematic representation of the synthesis of peptide capping agent.

nanoparticles. The capping agent is bidentate in nature with a free amine ($-NH_2$) and free sulfahydryl group ($-SH$) at the same terminus of the molecule, and this has made it an efficient capping agent for metal nanoparticles. The peptide **1** was separately stirred with the aqueous solution of $HAuCl_4$ and $AgNO_3$ and then it was reduced with aqueous $NaBH_4$ solution, which produced a purple and light gray solution stabilized by the peptide **1** capping agent. The plasmon band appeared at 537 and 462 nm (broad) (Figure 2, parts c and

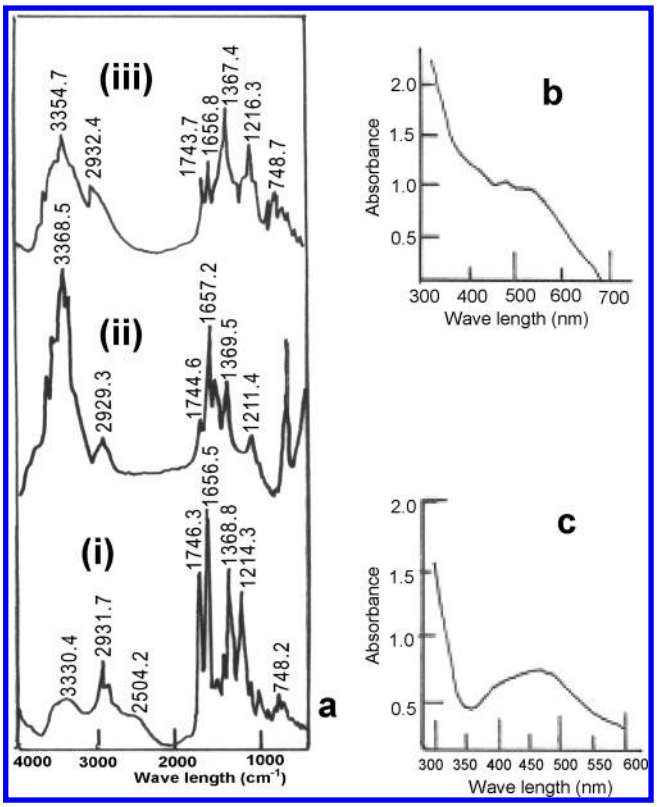

Figure 2. (a) Infrared spectra of (i) peptide **1**, (ii) peptide **1** capped gold nanoparticle, and (iii) peptide **1** capped Ag nanoparticle. (b) Plasmon band of peptide **1** capped gold nanoparticle solution and (c) plasmon band of peptide **1** capped silver nanoparticle.

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d, respectively) and transmission electronic microscopic images (Figure 3a,b) showed the presence of gold/ silver

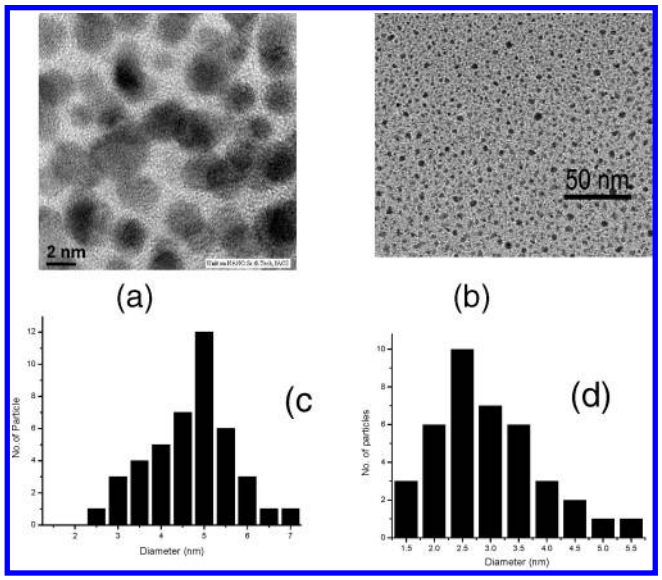

Figure 3. Transmission electron microscopic (TEM) images of peptide **1** capped (a) gold nanoparticles and (b) silver nanoparticles. Size distribution of peptide **1** stabilized (c) gold nanoparticles and (d) silver nanoparticles.

nanoparticles and their size distributions (Figure 3c,d) which were stabilized by the peptide **1** capping agent. FT-IR studies clearly indicate the participation of the side chain thiol group (−SH) and the terminal amino group ($-NH_2$) of the peptide **1** for capping the gold and silver nanoparticles (Figure 2). Bonding of both amine and sulfydryl groups with gold/silver nanoparticles was evident from the FT-IR spectra (Figure 2a). In the solid state (KBr), the FT-IR spectrum of peptide **1** indicates a broad band centered at 3330.4 cm^{-1} due to the N−H streching vibrations of the terminal amino group. However, the N−H streching frequency of peptide **1** capped gold and silver nanoparticles appeared at 3368.5 and 3354.7 cm^{-1}, respectively.

The increase in wavenumber can be justified by the interaction of lone pair of electrons of the free amine group ($-NH_2$) with the suitable vacant orbital of Au and Ag in their neutral states.[10] Peaks that appeared due to carbonyl stretching of amide and ester functionalities do not show significant shifts as they do not involve capping of the metal nanoparticles. Another broad band centered at 2504 cm^{-1} was also observed in case of peptide **1** and this peak disappeared in the spectrum of gold and silver tagged nanoconjugates. This vividly demonstrates the role of the −SH group in stabilizing the gold and silver nanoparticles.[11] Pseudopeptide **1** was prepared by a conventional solution-phase DCC-HOBt coupling method.[12] A good quality single crystal of pseudopeptide **1** was obtained from solution of MeOH−H_2O (2:1) by slow evaporation and single-crystal X-ray diffraction study of this pseudopeptide **1** was done.[12] The self-assembling nature of the pseudopeptide **1** in methanol−water can be assessed from its crystal structure in the same solvent system. The crystal structure of the pseudopeptide **1** reveals that the molecule has crystallographic 3-fold symmetry within a hexagonal unit cell, space group $P6_3$ (Supporting Information, Figure S10). This facilitates the formation of supramolecular columnar packing along the axis parallel to unique crystallographic *c*-axis. These supramolecular columns are regularly aligned via non-hydrogen bonding, noncovalent interactions to form hierarchical supramolecular arrays along the equivalent crystallographic *a* and *b* axes (Supporting Information, Figure S11) to produce a straight nanofiber, which was observed in the TEM image (Figure 4c) of pseudopeptide **1** nanofiber. Figure

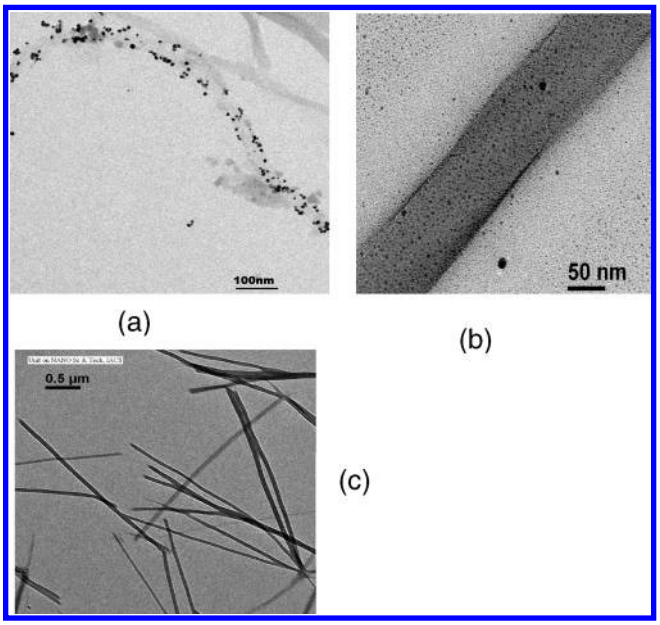

Figure 4. Transmission electron microscopic images of (a) nanofiber of pseudopeptide **1** decorated with peptide **1** stabilized gold nanoparticles, (b) nanofiber of pseudopeptide **1** decorated with peptide **1** stabilized silver nanoparticles, and (c) nanofiber of pseudopeptide.

5 shows the mechanism of formation of nanofiber in light of crystallography and self-assembly.

Transmission electronic microscopic (TEM) studies were carried out with the methanol−water (2:1) solution of pseudopeptide **1** to obtain the information about the nanodimensional insight of the pseudopeptide **1** in solution. From the TEM images (Figure 4c), it was evident that pseudopeptide **1** molecules form nanofibers with a width ranging from

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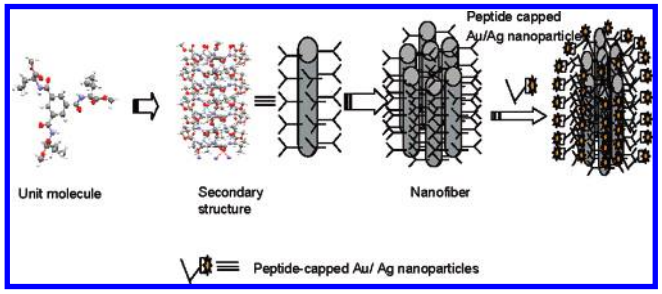

Figure 5. Schematic representation of immobilization of dipeptide capped metal nanoparticles on the self-assembling pseudopeptide **1** based nanofibers.

108 to 140 nm. To assess the efficiency of the method of grafting of peptide stabilized gold and silver nanoparticles on the pseudopeptide nanofiber, transmission electron microscopy was carried out. The solution of the pseudopeptide **1** in methanol−water (2:1) was then mixed with the solution of peptide capped gold/silver nanoparticles and the mixture was then incubated at 30 °C for 2 h. After that TEM studies were carried out with these two solutions separately on a carbon-coated copper grid (300 mesh) by slow evaporation and vacuum drying at 30 °C for 2 days. The transmission electron microscopic images showed that gold and silver nanopaticles (capped with the dipeptide) were uniformly deposited on the pseudopeptide nanofiber to form gold and silver nanoparticle decorated nanofibers (Figure 4a,b).

From the above result, it is clear that the metal nanoparticle coated nanofiber can be made by using this technique, based on the noncovalent interactions between the peptide capped Au/Ag nanoparticles and the interacting groups anchored on the surface of the nanofiber. From crystallography and higher order packing it is evident that the hydrophobic isopropyl side chain and hydrophilic methyl carboxylates (−COOMe) of the valine residues (attached to each of the centrally positioned aromatic rings) are present at the periphery of the supramolecular assemblage (Supporting Information, Figure S9).

Because of this unique positioning of the hydrophilic and hydrophobic groups along the surface, the pseudopeptide-based nanofiber adopts a very high recognizing behavior at the supramolecular level. Here, we used a cysteine-containing dipeptide (peptide **1**) as a stabilizer for Au/Ag nanoparticles. This capping agent contained a hydrophobic part consisting of the side chain of the amino acid leucine and a hydrophilic group (−COOMe) too. The terminally located free amine group ($-NH_2$) and the sulfahydryl group (−SH) were involved in capping the metal nanoparticles. The dipeptide molecule (peptide **1**) capped with the metal (gold/silver) nanoparticle forms a nanoconjugate in such a way that the hydrophobic (isopropyl) and hydrophilic (−COOMe) groups were positioned on the surface of the nanoconjugate (Supporting Information, Figure S11). Peptide capped metal (gold/silver) nanoparticles come in contact with the pseudopeptide **1** based nanofibers involving the non-hydrogen bonding noncovalent interactions among the anchoring groups present in both interacting surfaces (one suface from the peptide−metal nanoconjugate and the other from the nanofiber) to form the gold/silver nanoparticle decorated pseudopeptide based nanofiber (Figure 5). In this method peptide stabilized gold or silver nanoparticles are immobilized on the surface of the pseudopeptide based nanofiber by suitable non-hydrogen bonding noncovalent interactions between the interacting groups of the pseudopeptide nanofiber and the metal nanoparticle−peptide **1** nanoconjugate. We have used the peptide **1** molecule as a capping agent and the peptide **1** is a bidentate ligand in which −SH and $-NH_2$ groups are in appropriate juxtraposition to stabilize the nascent Au/Ag nanoparticles to prevent further aggregation of these nanoparticles and thus the size of GNPs and SNPs is somewhat controlled. Our method differs from the previously reported method of mineralization on synthetic nanostructure by metal nanoparticles, as in our method freshly prepared nanoparticles are first capped by a bidentate ligand (peptide **1**) and then the nanoconjugate comes in contact with the interacting groups situated on the surface of the pseudopeptide nanofiber.

This is different from Matsui's method, in which the metal ions are first stabilized on the surface of the nanotubes and subsequent reduction of the metal ions by suitable reducing agent produces the mineralization of metal nanoparticles on nanostructures.

Our result describes a new method of fabricating a metal nanoparticle coated nanofiber based on the rationale of supramolecular chemistry, involving the noncovalent interactions between the interacting groups present in the nanofibers (isopropyl and −COOMe from valine residue) and peptide capped nanoparticles. This method can be utilized for making new hybrid nanomaterial from synthetic nanomaterials obtained from self-assembling building blocks and peptide stabilized metal nanoparticles. The functional nature of the metal nanoparticle grafted nanofiber is yet to be explored.

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Supporting Information Available: Experimental details, synthesis,^{1}H NMR and HRMS of all compounds, TEM studies, EDX profiles of gold/silver nanoparticles, and packing pictures from crystal data of all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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