Self-organized Nanocomposites of Functionalized Gold Nanoparticles with Octa(3-aminopropyl)octasilsesquioxane

Xiaqin Wang, Kensuke Naka,* Hideaki Itoh, and Yoshiki Chujo*
Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto, 615-8510

Self-organized nanocomposites of functionalized gold nanoparticles with octa(3-aminopropyl)octasilsesquioxane were prepared via electrostatic interaction between carboxylate groups and ammonium cations under mild basic conditions. Subsequent chemical reaction between the reactive ion couples well-defined in the nanocomposites generated amide bonds between the two components.
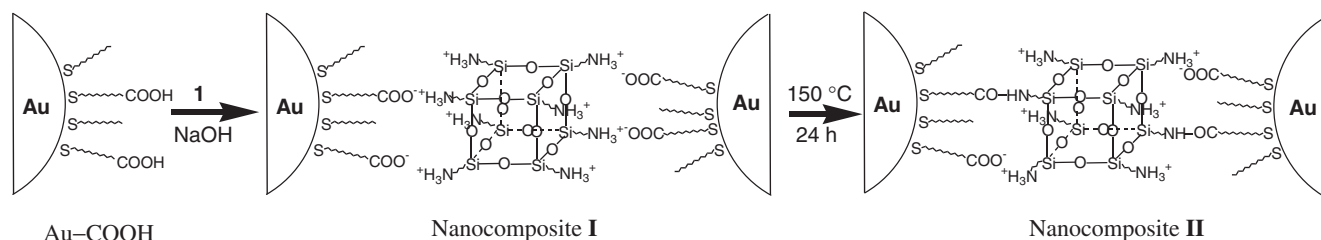
New class of nanocomposite materials with organized structures by manipulation of nanocrystals often lead to interesting chemical and physical properties distinctly different from those of their component parts.[1,2] Development of general methods for building and patterning 2-D or 3-D periodic structures of metal nanoparticles is a critical process and an important goal in materials chemistry for practical applications in nanotechnology as they provide a molecular-level control over the macroscopic properties.[3,4] A major challenge for such materials is the preparation of thermally and mechanically stable nanocomposites with high content of metal nanoparticles and preventing both phase separation and aggregation of the metal nanoparticles in the host matrices.

Polyhedral octasilsesquioxane has an inner rigid inorganic cubic core with the size of ≈0.5 nm containing silicon and oxygen. A series of cubic octasilsesquioxane based hybrid materials has been prepared in which the incorporation of the cubic cores provides hybrids with good thermal and mechanical properties, high transparency, and solvent-resistance.[5–9] Although several studies have been done on the self-organization of metal nanoparticles with monofunctionalized silsesquioxanes at a molecular level,[10,11] multifunctionalized cubic silsesquioxanes such as octa(3-aminopropyl)octasilsesquioxane (**1**)[12,13] have not been used to synthesize nanocomposites of metal nanoparticles. Recently, we have reported that coordination between ammonium groups of **1** and palladium assisted formation of palladium nanoparticles and concurrent self-assembly.[14] In this paper, we have developed a general and direct strategy of cross-linking functionalized nanoparticles with **1** via electrostatic interaction and subsequent covalent bonding to fabricate nanocomposites containing a large amount of metal nanoparticles without phase sep-

aration. Novel self-organized nanocomposites between gold nanoparticles coated with carboxyl groups (Au–COOH) and **1** were prepared, in which **1** acted as a rigid cross-linker of Au–COOH via electrostatic interaction between the carboxyl groups on Au–COOH and the ammonium groups on vortexes of the cubic silsesquioxane. Amide bonds were formed between the reactive ion couples well-defined in the nanocomposites during subsequent chemical reaction to generate nanocomposites with improved chemical properties (Scheme 1).

Gold nanoparticles protected by a mixed monolayer of dodecanethiol (DT) and 11-mercaptoundecanoic acid (MUA) were prepared by reducing $HAuCl_4 \cdot 4H_2O$ with $NaBH_4$ in a two-phase ($CHCl_3$–H_2O) system according to Brust reaction.[15,16] To a DMSO solution (64 mL) of **1** (80.0 mg, 6.8×10^{-2} mmol) and Au–COOH (8.0 mg, corresponding to 5.4×10^{-3} mmol of –COOH groups) was added dropwise 5.6 mL of 0.44 M NaOH aqueous solution. The dark red solution faded completely and Au–COOH precipitated out from the solution suddenly to form nanocomposite **I**. After **I** was washed with DMSO and separated by centrifugation for 3 rounds to remove unreacted Au–COOH and **1**, 5.0 mg of dried nanocomposite **I** was obtained. Nanocomposite **I** was insoluble in common solvents such as hexane, acetone, toluene, $CHCl_3$, EtOAc, THF, and H_2O. Thermogravimetric analysis (TGA) indicated that the nanocomposite **I** consisted of 11.0 wt % **1** and 89.0 wt % Au–COO^-. The molar ratio of –COO^- groups in Au–COO^- and –NH_3^+ groups in **1** was 1:1.3 for the nanocomposite **I**. According to an elemental analysis of N, the nanocomposite **I** consisted of 1.39 wt % of N and the calculated molar ratio of the –COO^- groups and –NH_3^+ groups was 1:1.0, in good agreement with that by the TGA analysis. Even a half amount of **1** (40.0 mg, 3.4×10^{-2} mmol) was added into a DMSO solution of Au–COOH (8.0 mg), the TGA results indicated that the resulting nanocomposite was of the same composition as that of the nanocomposite **I**. These results made it clear that the formed nanocomposites were not random aggregation between **1** and Au–COO^-.

More stable and solvent-resistant nanocomposite **II** was produced after the nanocomposite **I** underwent a subsequent chemical reaction at 150 °C for 24 h. The size of the gold nanoparticles in the nanocomposite **II** was ≈3.0 nm estimated from an XRD

Scheme 1.

pattern of the nanocomposite (Figure 1), which means no phase separation and aggregation of the gold nanoparticles occurred. The Fourier transform infrared (FTIR) spectra (Figure 2) showed that the majority –COOH groups were changed into –COO⁻ in the nanocomposite **I**. After the chemical reaction, a characteristic absorption for –CONH– bonds appeared, and traces of the cations and anions are hardly detected in the FTIR spectra, suggesting a high conversion of amide bonds. From the TGA results the weight loss before 200 °C disappeared for the nanocomposite **II** compared with TGA weight loss for the nanocomposite **I** (Figure 3). Electrostatic interaction between negatively charged Au–COO⁻ and positively charged **1** is the driving force of the formation of the nanocomposite **I**. Deprotonation of Au–COOH under mild basic condition facilitated effective coupling of the carboxylate anions and ammonium cations and rapid aggregation of the gold nanoparticles with **1**. Further chemical reaction occurred between the reactive ion couples, similarly as synthesis of polyamide 6,6. Large surfaces of the gold nanoparticles provided great areas for high-level ion coupling and increased reactivity of the ion couples.
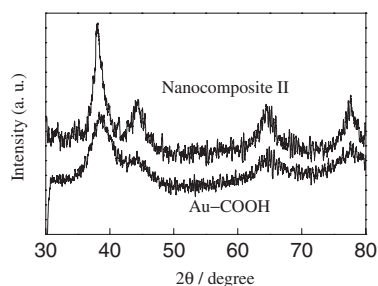

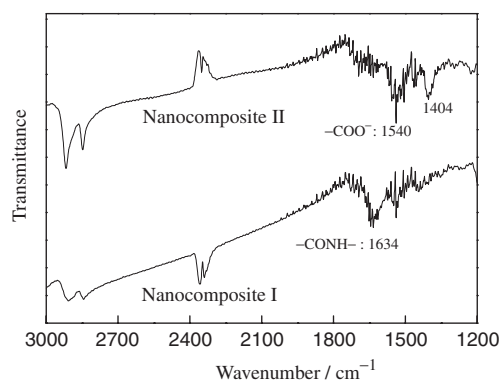**Figure 1.** XRD patterns for Au–COOH and nanocomposite **II**.

Figure 2. FTIR spectra of nanocomposite **I** and **II**.
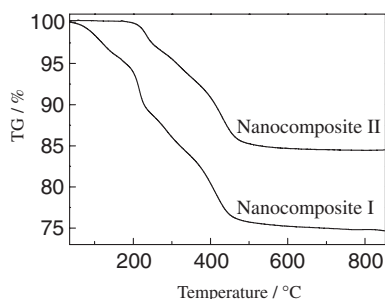

Figure 3. TGA thermograms of nanocomposite **I** and **II**.

In conclusion, we have developed a general and direct approach by which the negatively charged gold nanoparticles self-assembled with positively charged **1** into nanocomposites. The coupling of the ammonium cations radiated out from the cores of **1** with the carboxylate groups coated on Au–COO⁻ was strong enough to form networks of the gold nanoparticles. Further chemical reaction between the ion couples transformed electrostatic interaction into amide bonds. In brief, the organic/inorganic hybrid nanocomposites without phase separation and aggregation of the metal nanoparticles were produced with a well-designed strategy using functionalized **1** as a rigid linker of the gold nanoparticles via electrostatic interaction and subsequent formation of covalent bonds. Our current results provided a new field to organize metal, semiconducting, and magnetic nanoparticles with rigid linkers to create nanocomposite materials with customizable chemical and physical properties.

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16   Gold nanoparticles stabilized by DT were prepared by reducing $HAuCl_4 \cdot 4H_2O$ with $NaBH_4$ in a two-phase ($CHCl_3$–H_2O) system. DT monolayer-protected gold nanoparticles were precipitated from the separated $CHCl_3$ layer via adding a large quantity of CH_3OH. MUA was employed to exchange with the DT layer coated on the gold nanoparticles in a $CHCl_3$ solution, and thus carboxyl groups were introduced into outmost portion of the monolayer. The mixed monolayer-protected gold nanoparticles (Au–COOH) precipitated out from $CHCl_3$ during exchange reaction. After washing and drying, the as-prepared Au–COOH was soluble in polar solvents, such as CH_3OH, CH_3CH_2OH, and DMSO. XRD pattern of the product showed the presence of diffraction peaks corresponding to the (111), (200), (220), and (311) planes, which indicates the formation of metallic gold. ^{1}H NMR spectrum of the resulting Au–COOH colloid showed the molar ratio of ω-thiol carboxylic acid to dodecanethiol was 1:1 by comparing the peaks at δ 2.2 (–CH_2–COOH), and 0.9 (–CH_3). On the basis of the ^{1}H NMR results and the fact that the organic content in Au–COOH was 20 wt % by thermogravimetric analysis (TGA), it was determined that 1.0 mg of Au–COOH has 6.69×10^{-4} mmol of –COOH groups. The average size of Au–COOH was 2.7 ± 0.3 nm measured from a transmission electron microscopy (TEM).