Two-Dimensional Arrays of Self-Assembled Gold and Sulfur-Containing Fullerene Nanoparticles

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Two-dimensional (2D) arrays of gold nanoparticles with sulfur-containing fullerene nanoparticles were self-assembled through the formation of Au−S covalent bonds. Disulfide functional groups were introduced into the C_{60} molecule by reacting propyl 2-aminoethyl disulfide with C_{60}. The 2D arrays were formed at the interface of the aqueous phase of gold particles and organic phase of fullerene particles as a blue transparent film. Transmission electronic microscope images showed that the fullerene spacing between adjacent Au (∼10 nm) particles was about 2.1 ± 0.4 nm, which was consistent with the result of 2.18 nm by molecular molding calculations (MM^+). The UV−visible spectrum of this film showed a red shift and increased bandwidth due to the small spacing between gold nanoparticles. The arrays were deposited on the top of pairs of gold electrodes to form 2D colloidal single electron devices. The electrode pairs were made by electron beam lithographic techniques, and the separation between tips of the two electrodes in a pair was about 100 nm. Electron transport measurements at low temperatures exhibited Coulomb blockade type current−voltage characteristics due to the charge effects. The assembled arrays have potential applications as nanoelectronics.

Introduction

Nanomaterials are gaining importance in the development of nanosized and high-efficient electronic devices. The chemical and physical properties of nanomaterials have been studied for over a decade because of their interesting quantum effects. When the sizes of materials reduce to nanosize scale, their optical, electric, and magnetic properties are different from those of bulk materials.[1] These unusual properties are expected to be useful for the development of quantum devices such as single electron transistors (SETs).[2]

The single electron transistor is a potential candidate for the next generation of electronic devices. It possesses great advantages in low power consumption and high packing density. Since the operating temperature of a single electron transistor is determined solely by the geometrical size of the island(s) between the electrodes, the island(s) should be as small as only a few nanometers. This presents a challenge to modern nanofabricaton technology. Even with present day state-of-the-art electron beam lithographic technology, this is still a very demanding requirement. On the contrary, nanostructured materials with critical dimension smaller than few nanometers can be created through the control of matter at the level of atoms and molecules, but electrical contact to these materials is not at all trivial. Thus, self-assembly of nanostructured materials provides a potential process to fabricate high-temperature-operating nanodevices.

Many nanomaterials have been synthesized. However, finding a method to fabricate such materials in an organized fashion and on an appropriate location of circuitry effectively and efficiently is still a major challenge to scientists. There are numerous reports regarding the assembly of two-dimensional arrays of quantum dots by lithography and epitaxy depositions.[3] The self-assembly methodology has recently emerged as a useful technique. Many metal, insulator, and semiconductor nanoparticles have been assembled together with organic molecules such as alkyl dithiol,[4−6] surfactants,[7−9] organic polymers,[10] conjugated DNA,[11,12] or biomimic conjugated systems.[13] Two- or three-dimensional nanoparticles arrays have been constructed by the formation of covalent bonds, hydrogen bonds, or van der Waals forces.

Andres et al.[5] have observed an electrical conductance of a self-assembled array of gold clusters molecularly linked by aryl dithiols or aryl di-isonitriles. The self-assembled two-dimensional array of gold clusters exhibited nonlinear Coulomb charging behavior.

In this report, novel nanoparticle arrays were assembled and modified fullerene (C_{60}) derivatives were used for assembling nanoparticles. We introduced active functional groups (disulfide) to C_{60} molecules that formed two-dimensional arrays with gold nanoparticles by covalent

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Scheme 1. Synthesis Scheme of (a) Fullerene Derivative C$_{60}$-1, (b) Fullerene Derivative C$_{60}$-2, and (c) Gold Nanoparticles

C$_{60}$-1 (a)

bis-2-aminoethyl disulfide

C$_{60}$-2 (network structure) (b)

$$HAuCl_4 \ + \ \text{sodium citrate} \ \xrightarrow[\text{H}_2\text{O}]{\text{reflux}}$$

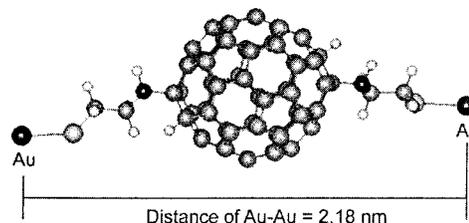aqueous solution of gold nanoparticles (c)

Figure 1. Molecular modeling calculations (MM$^+$) show the Au$-$Au space that is separated by a C$_{60}$-**1** molecule to be 2.18 nm. To simplify these calculations, gold atoms were used as gold nanoparticles.

Distance of Au-Au = 2.18 nm
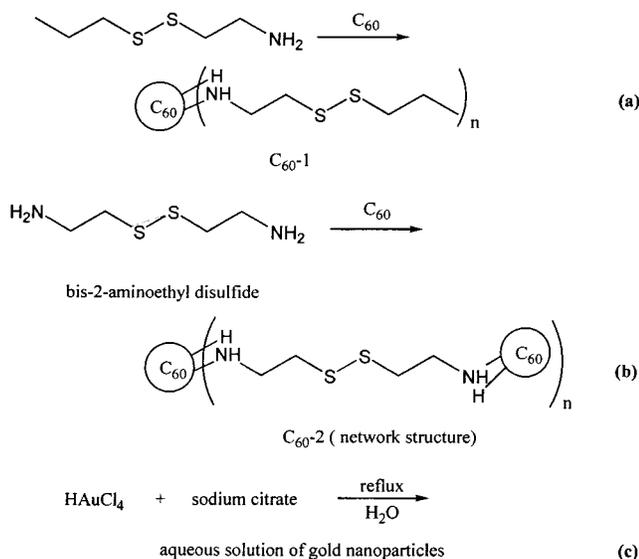
S$-$Au bonds. Then the arrays were placed on the electrodes to fabricate single electron devices.

By combining advanced electron beam lithography and nanophased material assembling techniques, we have successfully prepared single electron devices with gold colloidal islands. Their electrical properties have been characterized and are presented below. In this device configuration, the self-assembled array overcame the size limitations of lithography; thus it would provide a path for fabricating a single electron device operable at elevated temperature.

Experimental Section

Synthesis of Fullerene Derivative C$_{60}$-1. Ground C$_{60}$ (0.10 g) (Aldrich Chemical) was added to 3.4 g of propyl 2-aminoethyl disulfide. The propyl 2-aminoethyl disulfide was prepared from dipropyl disulfide and 2-mercaptoethylamine according to the procedure reported by Kitsuta.[14] The mixture was stirred for 3 days at room temperature until all C$_{60}$ had reacted. Methanol (20 mL) was added into the mixture, and brown precipitates were formed. The precipitates were collected by filtration and washed with methanol several times. The product was dried with a yield of 0.096 g (Scheme 1a). Anal. C, 71.34; H, 4.12; N, 4.22.

Synthesis of Fullerene Derivative C$_{60}$-2. In a 100 mL round-bottom flask, C$_{60}$ (20 mg) was dissolved in 15 mL of toluene. A solution (0.63 g of bis-2-aminoethyl disulfide dihydrogen chloride (Aldrich Chemical), 0.43 g of potassium dicarbonate, 30 mL of ethanol, and 10 mL of distilled water) was added to the C$_{60}$ solution. The mixture was refluxed for 20 h and then cooled to room temperature. The volume of the solution was reduced to 10 mL using a rotor-evaporator to remove solvent. The solution was then centrifuged twice with an addition of 20 mL of distilled water. Brown powder (22 mg) was produced after drying under vacuum (Scheme 1b). Anal. C, 69.36; H, 3.89; N, 4.41.

Self-Assembly of Gold Nanoparticles. An aqueous solution of gold nanoparticles was synthesized by reducing tetrachloroauric acid (Across Chemical) with trisodium citrate (Across Chemical) in distilled water (Scheme 1c). Fullerene derivatives (C$_{60}$-**1** or C$_{60}$-**2**, 1 mg) were dissolved (C$_{60}$-**1**) or suspended (C$_{60}$-**2**) in 10 mL of chloroform. When a gold solution (10 mL) was poured gently into 10 mL of fullerene solution, a film was formed at the interface of two solutions after 2$-$7 days. The film was transferred onto copper grid for transmission electronic microscopy (TEM, JEOL 100 CX II) study. Absorption spectra were performed by

directly examining the particle solutions or by transferring the films on quartz by using a UV$-$vis spectrometer (JASCO V550).

Fabrication of Nanodevice. A silicon chip containing gold electrodes was dipped into the interface of gold and C$_{60}$-**1** solutions. Thus a film of the two-dimensional array of C$_{60}$-**1** with gold nanoparticles was transferred on the chip to linked two electrodes. After the solvent was evaporated, the chip was washed with distilled water three times and dried by nitrogen. The electrodes are made by standard electron beam lithography and lift-off techniques. The gold electrodes were about 50 nm in width and 25 nm in thickness, and the gap between them was about 100 nm. The substrate was a standard Si wafer covered by a thermally grown 300 nm thick SiO$_2$ layer. To reduce the capacitance of the gold island further, the SiO$_2$ layer surrounding the junctions was etched away prior to place assembled array. This eliminated the capacitance of the island to the ground and helped to increase the operating temperature.

Results and Discussion

In order for assembling gold nanoparticles by fullerene nanoparticles, we synthesized two fullerene derivatives with disulfide functional groups as shown in Scheme 1. The molecule of C$_{60}$ is a buckyball of carbon, covered on its surface with unsaturated conjugated double bonds. This molecule can be attacked by more than one nucleophile. We have used two kinds of nucleophiles: (1) propyl 2-aminoethyl disulfide (Scheme 1a) and (2) bis-2-aminoethyl disulfide, which has two amino groups (Scheme 1b).

The amino group attacks fullerenes and links onto their surfaces; this has been extensively studied and is well understood.[15-18] We initially used 2-mercaptoethylamine to introduce thiol groups onto C$_{60}$. However, the reaction of 2-mercaptoethylamine with C$_{60}$ was complicated. Both the amino and thiol groups were active toward fullerene molecules. As a result, we obtained an insoluble polymeric product and that was inactive toward gold nanoparticles. Therefore, we tried to react propyl 2-aminoethyl disulfide with C$_{60}$.

The disulfide group of this compound did not react with fullerene, and it was reactive toward gold. The reaction of propyl 2-aminoethyl disulfide with C$_{60}$ proceeded as expected. The amino group attached C$_{60}$ to form C$_{60}$-**1** and the resulting disulfide group of C$_{60}$-**1** reacted with gold. The structure of C$_{60}$-**1** is a ball with tentacles as shown in Figure 1. The exact positions of amino groups on the surface of C$_{60}$ are not identified. Four tentacles were found on the molecule of C$_{60}$-**1** from elemental analysis.

The reaction of bis-2-aminoethyl disulfide with C$_{60}$ was more complicated than that of the reaction of propyl 2-aminoethyl disulfide with C$_{60}$. Both amino groups of bis-2-aminoethyl disulfide reacted with C$_{60}$ and formed

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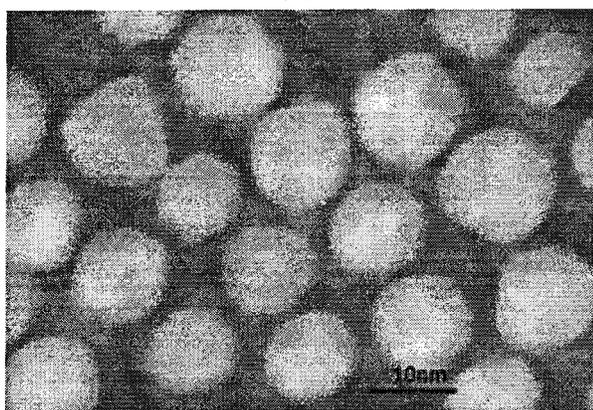(16) Geckeler, K. E.; Hirsch, A. *J. Am. Chem. Soc.* **1993**, *115*, 3850.
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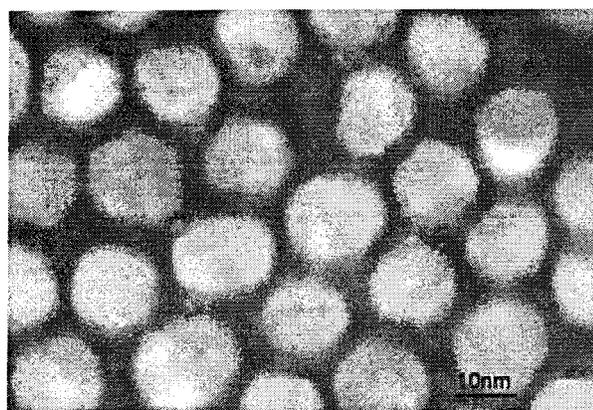
Figure 2. Micrographs of transmission electronic microscopy of (a) self-assembly of gold nanoparticles and C_{60}-**1**. The average size of gold particles is 14.5 ± 2.3 nm and average space between gold particles is 2.1 ± 0.4 nm. The length of scale bar is 10 nm. (b) Self-assembly of gold nanoparticles and C_{60}-**2**. The average size of gold particles is 10.8 ± 1.5 nm and average space between gold particles is 3.3 ± 0.8 nm. The length of scale bar is 10 nm. Some larger gold particles were found in both photos. They are small defects from three-dimensional arrays.

an insoluble polymeric product C_{60}-**2**. The exact structure of C_{60}-**2** has not been resolved.

The aqueous solution of gold nanoparticles was synthesized by reducing tetrachloroauric acid with trisodium citrate in water[19] (Scheme 1c). Uniform size and shape of spherical gold nanoparticles was obtained. By this method, we can synthesize aqueous solution of gold nanoparticles ranging from 5 to 13 nm.

A two-dimensional array was prepared by reacting an aqueous solution of gold nanoparticles with an organic solution of sulfur-containing fullerene nanoparticles. A thin transparent film was obtained at the interface of these two solutions. When the disulfide group of fullerene derivatives reacted with gold nanoparticle, the S—S bond broke and two covalent S—Au bonds formed immediately.[20] We may view the arrays as superlattices that consist of gold nanoparticles and C_{60} nanoparticles. The gold particles were spaced by fullerene derivatives. The molecular modeling calculations (MM^+) showed that the spacing occupied by C_{60}-**1** between two Au nanoparticles was 2.18 nm as shown in Figure 1. This distance is the sum of the

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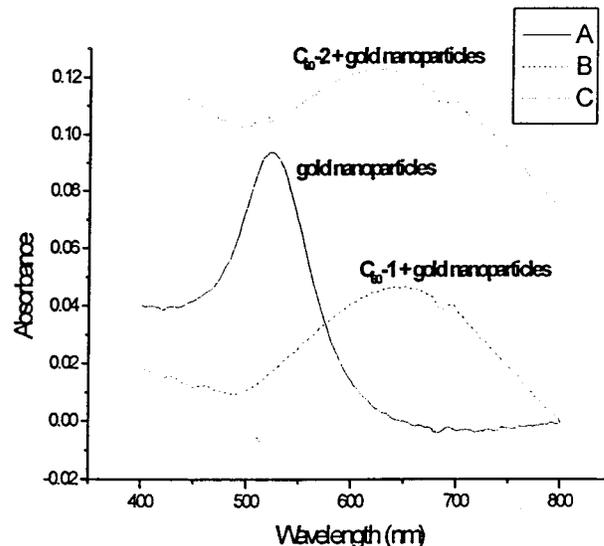(20) Nuzzo, R. G.; Zegarski, B. R.; Dubois, L. H. *J. Am. Chem. Soc.* **1987**, *109*, 733.

Figure 3. Ultraviolet—visible spectra of (a) gold nanoparticles solution, line A. $\lambda_{max} = 525$ nm. (b) Nanoparticle arrays of gold and C_{60}-**1**, line B. $\lambda_{max} = 649$ nm. (c) Nanoparticle arrays of gold and C_{60}-**2**, line C. $\lambda_{max} = 632$ nm.

diameter of one molecule of C_{60} and the length of two molecules of 2-mercaptoethylamine. Transmission electronic microscopy studies of the two-dimensional array made from C_{60}-**1** and gold nanoparticles indicate that the spacing between two Au particles was an average of 2.1 ± 0.4 nm (Figure 2a). This result indicated that the disulfide group of C_{60}-**1** reacted with gold particles, as expected, by breaking the disulfide bond into two sulfur groups that reacted with gold particles individually.

The TEM study of C_{60}-**2** assembled gold nanoparticles showed spacings with an average of 3.3 ± 0.8 nm between gold particles (Figure 2b). Spacings from 2.1 to 5.1 nm were observed; a broad distribution was found. Also, the results show that there were more than two molecules of C_{60} inserted between gold particles. The fullerene derivative of C_{60}-**2** is suspected to be a polymer because bis-2-aminoethyl disulfide contains two active amino groups. The gold particles have to insert into the polymeric matrix to form two-dimensional arrays. When the first gold particle breaks and the disulfide bond of C_{60}-**2** and forms covalent bonds with it, the second gold particle faces steric hindrance from the bulky neighboring molecule of C_{60}. This steric hindrance effect retards the reaction of the gold particle with the second disulfide group. Consequently, disulfide groups did not react completely, especially the ones close to the reacted gold particles.

The solution of gold nanoparticles appeared dark red because of the surface plasma resonance of gold particles. The ultraviolet—visible spectrum of gold nanoparticles shows a sharp peak at 525 nm (visible region) (Figure 3a). When gold nanoparticles were assembled into arrays, the plasmon peak shifted toward low energy and the bandwidth increased[21] (lines B and C of Figure 3). The red shift was attributed to a decreasing of spacing between gold nanoparticles. The increasing of bandwidth was due to the coagulation of gold nanoparticles. Insomuch, a blue film was obtained when red gold nanoparticles were assembled by fullerene derivatives.

Figure 4 shows the SEM photo of two-dimensional array of gold and C_{60}-**1** nanoparticle that was transferred to the gap between two gold electrodes by the dipping method. Figure 5 shows the current—voltage characteristics of the

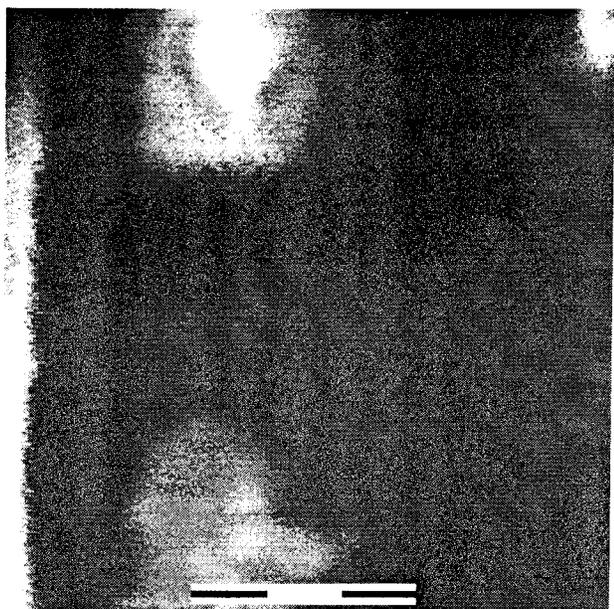(21) Huang, Y.; Freiser, B. S. *J. Am. Chem. Soc.* **1991**, *113*, 9418.

Figure 4. Micrograph of scanning electronic microscopy of two-dimensional array on the chip. This array of gold and C_{60}-**1** nanoparticle was transferred to the gap between two gold electrodes. The gold electrode was about 50 nm in width and 25 nm in thickness, and the gap between them was about 100 nm. The length of the scale bar is 100 nm.
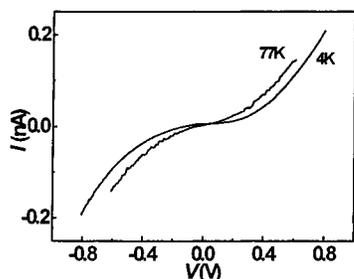

Figure 5. Current−voltage characteristics of the two-dimensional array of gold and C_{60}-**1** nanoparticles in the gap between two gold electrodes. The device exhibited a Coulomb gap at 4 K.

two-dimensional array. This nonlinear behavior is more pronounced at lower temperature, which is a sign of Coulomb blockade of electron tunneling. The lower the temperature, the more Coulomb blockade was pronounced. The device exhibited a Coulomb gap of about 0.8 V at 4 K. This device is very stable because the shape of the current−voltage characteristics was reproducible for repetitive traces of measurement at a fixed temperature.

The successful fabrication of fullerene-based two-dimensional arrays offers a new class of materials with tunable electronic properties for nanodevice applications. The C_{60} is electrically conducting due to the conjugating double bonds on its molecular surface. This electronic property is expected to be tunable by doping different ions or atoms into the C_{60} buckyball or onto its surface[22−26] When this phenomenon works in coordination with changing the size or elements of particles, there exists an enormous potential for fabrication of different type quantum devices. In our future work, we would like to fabricate a single electron device with a one-dimensional array of gold and C_{60} nanoparticles.

Conclusions

Sulfur-containing fullerene nanoparticles were synthesized by reacting amino disulfide with C_{60}. They were self-assembled with gold nanoparticles through the formation of Au−S covalent bonds. The 2D arrays were formed at the interface of aqueous phase of gold particles and organic phase of fullerene particles as a blue transparent film. Transmission electronic microscope images showed that the fullerene spacing between adjacent Au (~10 nm) particles was about 2.1 ± 0.4 nm, which was consistent with the result of 2.18 nm by molecular molding calculations (MM$^+$). The UV−visible spectrum of this film showed a red shift and increased bandwidth due to the small spacing between gold nanoparticles. The arrays were deposited on the top of pairs of gold electrodes (spaced by 100 nm) to form 2D colloidal single electron devices. Electrons transport measurements at low temperatures exhibited Coulomb blockade type current−voltage characteristics due to the charge effects. The assembled arrays have potential applications as nanoelectronics.

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