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Journal of Colloid and Interface Science 348 (2010) 299–302

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

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$Mo_6S_3I_6$–Au composites: Synthesis, conductance, and applications

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ARTICLE INFO

Article history:
Received 6 January 2010
Accepted 20 April 2010
Available online 28 April 2010

Keywords:
$Mo_6S_3I_6$ nanowire
Gold nanoparticles
Nanocomposites
Synthesis
DNA sensing

ABSTRACT

A single-step, premixing method was used to directly deposit gold nanoparticles on $Mo_6S_3I_6$ (MSI) molecular wire bundles. Gold nanoparticles with different sizes and densities were coated on the MSI by changing the concentration of the gold containing salt, $HAuCl_4$. TEM, SEM, and EDX characterization showed deposition of gold nanoparticles on the MSI nanowire surface. The electrical resistance of these MSI–Au composites was more than 100 times lower than that for pure MSI, and was mainly dependent on the density of the deposited gold nanoparticles. Furthermore, we immobilized thiol group-labeled oligonucleotide on the composites and then hybridized with a fully matched sequence. The resistance of the MSI–Au composites increased during the thiol step, while it decreased by hybridizing, due to the conductance difference between single- and double-stranded DNA chains. These results indicate that this new kind of MSI–Au composite could be used as a platform for different applications, including biosensors.

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1. Introduction

Properties and applications of one-dimensional systems have received much attention during the last decade. The material most investigated is carbon nanotubes, including different composites [1–3]. However, carbon nanotubes have some problems such as difficulties in separating metallic and semiconducting tubes and the low solubility of the material [4–6]. One alternative of carbon nanotubes is $Mo_6S_{9-x}I_x$ molecular wires (MW) [7], which surpass some of the shortcomings of carbon nanotubes in particular the high solubility [4].

$Mo_6S_{9-x}I_x$ MWs are composed of Mo6 octahedral clusters and bridging anions, which can be fabricated using a single-step process [8,9]. These metal–chalcogenide–halide molecular wires have unique optical [10] and electronic properties [9]. $Mo_6S_{9-x}I_x$ MWs nanowires have a conductivity of about 1000 S/m [11], which is much lower than carbon nanotubes. The diameter of the single $Mo_6S_{9-x}I_x$ MWs is about 0.9 nm and these single wires are usually self-assembled during the synthesis into bundles with diameters typically a few hundred nanometers. They can be separated into single wires again by ultrasonication in several solvents [4].

One interesting application of these wires is the self-assembly of single $Mo_6S_{9-x}I_x$ wires (0.9 nm diameter) by attaching gold nanoparticles to the end of the wires using S atoms, which are terminating the wires, to covalently bond the particles and wires together [12]. This method has been used in an immunosensor applications [13].

Here, we take a different route using the thicker $Mo_6S_3I_6$ (MSI) molecular bundles and a single-step gold deposition method to decorate the side wall of the MSI bundles. This method was somewhat simpler than the previous reported one [12,13] and it allowed the resistance of the wires to be tuned by controlling the density of Au nanoparticles. We also show here a prototype biosensor using these composites based on DNA hybridization.

2. Experimental

2.1. Materials and synthesis of MSI–Au composites

MSI nanowires were from Mo6. $HAuCl_4$ and sodium citrate were purchased from Sigma. DNA sequences were purchased from DNA Technology (Denmark) without further purification. To obtain carbon nanotube composites, different methods have been used including direct [14] and indirect deposition [15]. Inspired by these works, we deposited gold nanoparticles on the MSI bundles using a simple direct method. First, 3.5 mg MSI bundles were dispersed in 4.0 ml 1.0 wt.% sodium citrate by ultrasonication [4]. Then the solution was diluted to 100 ml and boiled. The amounts of 0.25, 0.5, and 1.0 ml $HAuCl_4$ (1.0 wt.%) were added to the boiled solution separately to obtain different gold nanoparticle-coated MSI nanowires. The obtained MSI–Au composites were rinse three times with doubly distilled water and collected by centrifuge at 5000 rpm, and then diluted in 100 µl doubly distilled water.

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doi:10.1016/j.jcis.2010.04.047

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2.2. DNA modification and hybridization

Twenty microliters of the obtained composites solution was mixed with 50 μl –SH-labeled oligonucleotide (original concentration 48 nmol/ml) and incubated for 30 min at room temperature. After that, 50 μl fully matched sequence (original concentration 60 nmol/ml) and 50 μl hybridization buffer were added. The hybridization was reacted at 37 °C for 12 h, and then it was rinsed three times with doubly distilled water and centrifugation. In controlled experiments, (A) 20 μl obtained composites was incubate with 50 μl –SH-labeled oligonucleotide (original concentration 48 nm/ml) and incubate for 30 min, then 50 μl hybridization buffer and 50 μl doubly distilled water were added; (B) 20 μl obtained composites was mixed with 50 μl hybridization buffer and 100 μl doubly distilled water. Both these two controlling samples were treated at 37 °C for 12 h together with the hybridization sample and collected with the same procedure as above.

2.3. TEM characterization

For TEM characterization, a 400 M gold grid without carbon film was put under the gold film, and then deposited by retracting the grid from the solution. The grid was dried at room temperature for 20 min. TEM imaging was done using a JEOL 2000FX transmission electron microscope at 160 kV accelerate voltage.

2.4. Current/voltage (I/V) measurements

To measure the conductance, 2 μl of each solution was dropped on 40 × 3000-μm channels between two gold electrodes on an oxidized silicon wafer and let to dry at room temperature. These samples were made in a very simple way: a gold film of 40 nm was evaporated on the oxidized Si wafer and then the patterning was made by simply scratching the gold film using the stainless-steel needles and moved by the probe station micromanipulator. *I*/*V* measurements were performed on a micromanipulator 1800 wafer probe station (Micromanipulator).

3. Results and discussion

Fig. 1 shows the TEM (JEOL 2000FX) images of the synthesized MSI–Au composites. The surfaces of pure MSI nanowires were very clean. After the synthesis procedure, gold nanoparticles were deposited on the MSI nanowires with different densities depending on the amount of added $HAuCl_4$. The highest density of gold nanoparticles was obtained by adding 0.25 ml $HAuCl_4$ solution into the reaction system, and the diameters of gold nanoparticles were then around 10 nm (Fig. 1B). When the amount of $HAuCl_4$ increased to 0.5 ml, the diameters of gold nanoparticles increased to around 20 nm, but the density of gold nanoparticles decreased (Fig. 1C). When we increased the amount of $HAuCl_4$ to 1.0 ml, gold nanoparticles around 30 nm were obtained on the MSI nanowires with good order (Fig. 1D), while the density of gold nanoparticles was further decreased. Fig. 2 shows the SEM-EDX of the obtained MSI–Au composites. As expected, the elements from the wires (Mo, S, I) and the nanoparticles (Au) as well as from the sodium citrate (Na, O, C) were detected. The high C atom peak was due to the carbon paste used for SEM-EDX study.

Fig. 3 shows the *I*/*V* curves of the three synthesized MSI–Au composites. A higher density of gold nanoparticles gave lower

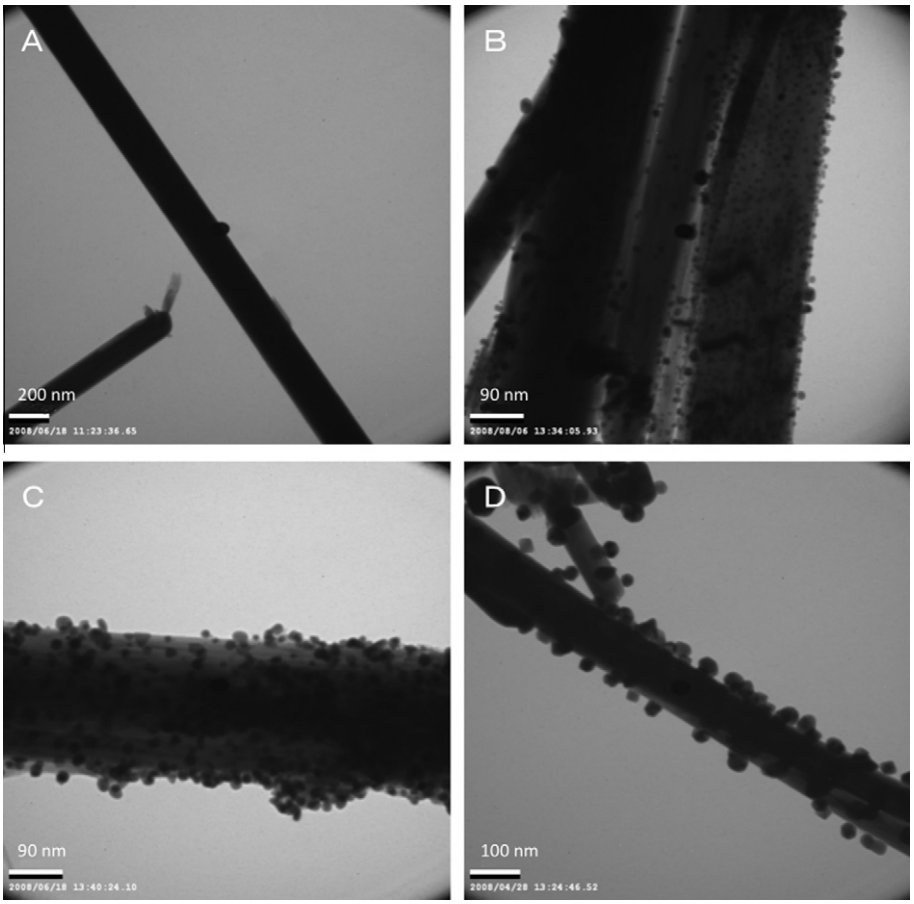

Fig. 1. TEM of MSI nanowires (A) and MSI–Au nanocomposites synthesized at $HAuCl_4$ amounts of 0.25 (B), 0.5 (C), and 1.0 ml (D).

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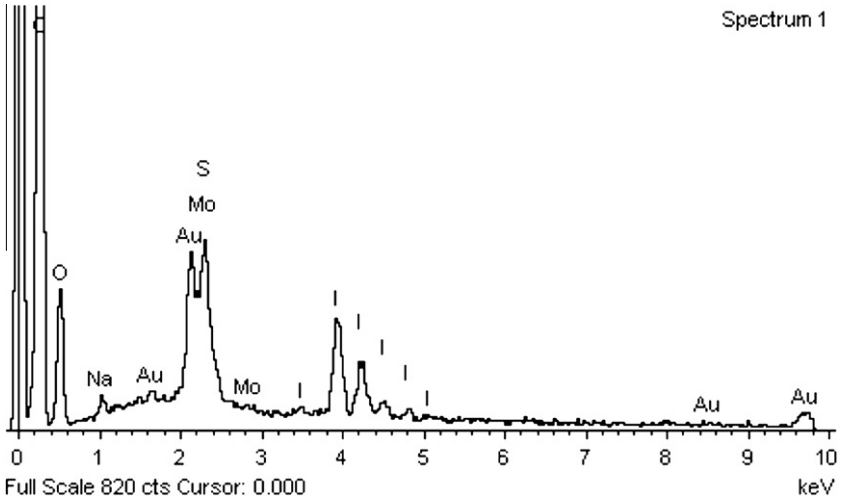

Fig. 2. SEM-EDX of MSI–Au nanocomposites.

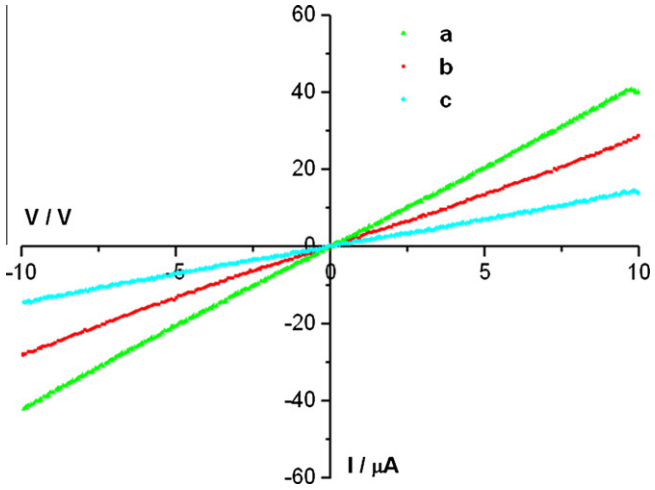

Fig. 3. *I*/*V* curves of the synthesized MSI–Au nanocomposites at $HAuCl_4$ concentrations of 0.25 (a), 0.5 (b), and 1.0 (c) ml.

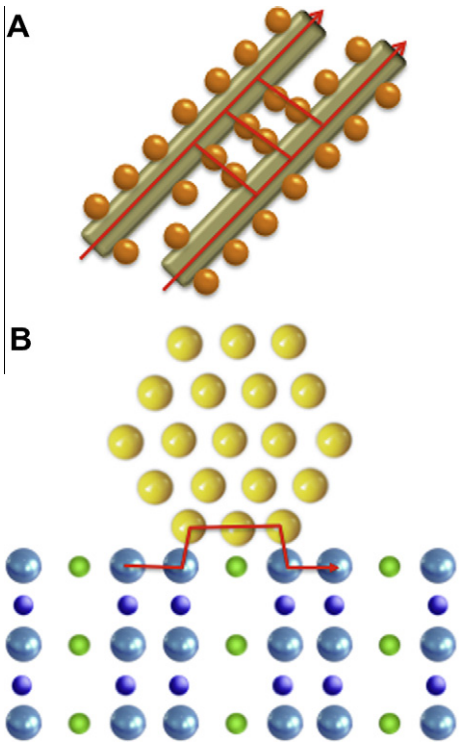

Fig. 4. Schematic drawing of possible mechanisms for the conductance increase of the MSI–Au nanocomposites.

resistance. The resistances for the MSI–Au composites synthesized at $HAuCl_4$ concentrations of 0.25, 0.5, and 1.0 ml were about 250, 480, and 1100 kΩ, while it was about 30 MΩ for pure MSI nanowires (see the *I*/*V* curves in Supplementary data).

There are several possible mechanisms for the increase in conductivity for samples with higher densities of gold. One explanation is a higher degree of interconnections between wires, which will lead to parallel connection of resistances leading to a decrease of resistance by 2 for every ideal connection between two wires ($R_{connected} = R * R/(R + R) = R/2$, where R is the resistance of the interconnected section of the wire). See Fig. 4A. The same interconnection argument can be used for imperfect wires, where some sections of the wire have a larger resistance due to some scattering centers. For this kind of imperfection, an interconnection will allow the current to pass the path with lowest resistance, resulting in an overall decrease in resistance; the electron percolation path will be the one with lowest resistance [16]. Another possibility is that the gold nanoparticles on the surface will stick to the S atoms on the wire surface and thereby decrease the resistance (Fig. 4B). The MSI nanowires consist of Mo, S, and I atoms. When gold nanoparticles are deposited on the nanowire surface, they will more easily be deposited at the S position due to the high affinity between S and Au [12]. The gold particle will then short circuit the S atom, leading to an increase in conductivity. However, even though it might be possible to address the problem to determine the mechanism using in situ TEM probing techniques [17–19], it will require a new carefully designed study. For the first possible mechanism, such an investigation might be done by connecting one gold decorated wire with an undecorated one, and compare the resistance with two undecorated wires, while imaging at high resolution inside a TEM. For the second possible mechanism a comparison of the conductance between single decorated and undecorated wires should be done. However, because each wire is an individual, the conductance property will be shifting from wire to wire, requiring a large statistical set for both types of experiments.

These MSI–Au composites can serve as substrates for further modification since gold nanoparticles easily form Au–S bonds with

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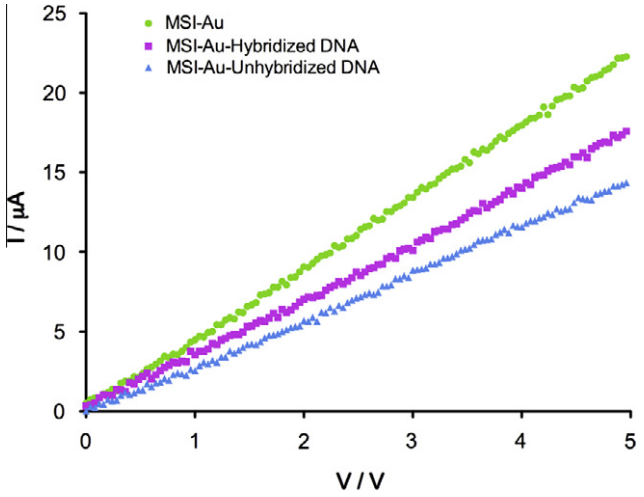

Fig. 5. *I*/*V* curves of MSI–Au nanocomposites. MSI–Au nanocomposites linked with single-stranded DNA before and after hybridize with a fully matched sequence.

molecules that contain –SH groups. The composites can therefore be a platform for sensor applications, for example, a biosensor. Here we used the synthesized composites for oligonucleotide hybridization biosensing. –SH-labeled oligonucleotide (5′SH-TGA GAT AAG GAT GGT) was first immobilized on the MSI–Au composites, and then, fully matched oligonucleotide (3′ ACT CTA TTC CTA CCA) was hybridized. Here, we chose the composites synthesized at $HAuCl_4$ concentrations of 0.25 ml as the materials for hybridization.

The same procedure for resistance measurements was used as for the MSI–Au composites. Fig. 5 shows current versus voltage (*I*/*V*) curves for MSI–Au composites, composite–oligonucleotide, and composite–oligonucleotide after being hybridized with fully matched sequence. The resistances for these three samples were about 240, 360, and 290 kΩ, respectively.

One possible mechanism for the resistance changes before and after DNA hybridization is that when the single-stranded DNA (ssDNA) molecules are attached to the gold, the particles will somewhat be separated leading to a higher resistance. After the hybridization, the ssDNA are now double-stranded DNA, which is known to have a lower resistance than ssDNA [20–22]. Although many theoretical models for this charge transfer have been discussed in the literature, the exact mechanism is not yet clear. After many contradictory results, the consensus today is that DNA molecules longer than 40 nm in a dry state are insulators [23], while short DNA duplexes (8–26 bp) demonstrate significant conductance [22,24–28]. One direct evidence, using break-junction techniques in vacuum, for the conductance between single-stranded and double-stranded 15-bp DNA sequences, which is the same length as those used in our experiment, is reported by Guo and co-workers, where the well-matched duplex DNAs have five times higher conductance [24].

The resistance changes before and after DNA hybridization suggest that this kind of new MSI–Au composites could serve as a platform for biosensing. Moreover, since the gold nanoparticles on the composites are easily functionalized, the application of MSI–Au composites could be extended to a wider set of applications, such as electrochemical immunodetection [13].

4. Summary

In summary, we have synthesized a new kind of MSI–Au composite using a simple single-step method, with a high density of gold nanoparticles. Resistance measurements showed that the density of gold nanoparticles on MSI–Au composites influenced the conductance between the MSI nanowires. Application of MSI–Au composites in DNA hybridization detection suggested that this composite could be used for biosensing. Also the results of this paper indicate that the unique structure of MSI nanowires could be used to construct other kind of composites and thus a wider set of applications of this nanowire.

Acknowledgments

We thank Sundsvall Community for financial support, and Göran Tungström for the silicon dioxide wafers.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcis.2010.04.047. Supplementary data include the IV curve of MSI nanowire networks, and experimental data of IV measurements.

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