Chemical Engineering Journal 166 (2011) 378–383

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

A novel method to prepare gold-nanoparticle-modified nanowires and their spectrum study

Zu-Fu Yao[a,b], Ke-Long Huang[a,*], Su-Qin Liu[a], Xiang-Zhi Song[a,**], Yan-Hua Li[a], Jun Guo[a], Jin-Gang Yu[a]

[a] College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, PR China
[b] Department of Pharmacy, Huaihua Medical College, Huai Hua 418000, PR China

ARTICLE INFO

Article history:
Received 26 January 2010
Received in revised form 6 June 2010
Accepted 10 June 2010

Keywords:
Silica nanowires
Gold
Sol–gel
3-Mercaptopropyltrimethoxysilane (MPTMOS)
Disulfide bonds
Solution
Large-scale preparation

ABSTRACT

In this paper, a practical and mild sol–gel self-assembly method was successfully developed for the synthesis of plain and gold-nanoparticle-modified silica nanowires (AuSiNWs). In this new method, the 3-mercaptopropyltrimethoxysilane (MPTMOS) was used as the key linker through disulfide bonds and mediated the reorganization of the particles into elongated clusters. The high surface strain energy of the silica nanoparticles, as a driving force, deformated the interconnected nanoparticles into nanowire. All the procedures were performed in solution and under mild conditions (below 100 °C at atmosphere pressure), and no special apparatus was needed. This promising method made it possible to synthesize the SiNWs in large scale. Transmission electron microscopy (TEM), energy dispersive X-ray (EDX) spectroscopy and scanning electron microscopy (SEM) were used to characterize the obtained nanostructures. The microscopy was used to investigate the products at each stage in the synthetic process and the formation mechanism of the new method was discussed. The investigated AuSiNWs displayed an intensive absorption at 528 nm, characteristic of gold nanoparticles, and a strong luminescence peak at 440 nm.

1. Introduction

One-dimensional (1-D) nanomaterials have attracted sustained interest in nanotechnology over recent decades due to their remarkable properties [1–3], fascinating geometries [4,5] and great potential applications in nanoscale electronics and optoelectronics [6–8], chemical and biological sensing [9,10], drug delivery [11,12], etc. A large number of these materials have been fabricated, such as nanowires [13], nanotubes [14], and helical nanospring [15,16]. Among them, people have paid special attention on silica nanowires (SiNWs) because they were hydrophilic and easy to form colloidal suspensions and had the good accessibility for surface functionalization. Recently, the SiNWs modified with biomolecule have shown potential applications in nanoscale sensors [17,18]. In addition, SiNWs are also promising dielectric materials to apply on nanoelectronics due to their relatively low dielectric constant. Furthermore, SiNWs are important photoluminescence and waveguide materials [19].

Thanks to their unique properties and potential applications, SiNWs are in demand in bulk quantities for the scientific study and industrial use. However, all the existing synthetic method for SiNWs including Vapor–Liquid–Solid (VLS) method [20], laser ablation [21], metal catalyst growths [22] and other methods were performed under relatively harsh conditions requiring high temperature (above 300 °C), high pressure or vacuum, and special instruments. And it is very difficult to synthesize SiNWs in large scale by these known methods. It is well known that most of chemical synthesis in solution is practical and can be enlarged for large-scale preparation. Therefore, it will be promising if a method to synthesize SiNWs in solution is developed.

Previous studies showed that gold-nanolayer-encapsulated SiO_2@Au core–shell nonoparticles were successfully prepared in solution at low temperature and atmosphere pressure [23,24]. In the procedures, the small gold particles (1–2 nm) were adsorbed on the silica nanoparticles modified with 3-aminopropyltriethoxysilane (APTEOS); and a subsequent reduction of chloroauric acid resulted in the formation of gold-nanolayer-encapsulated SiO_2@Au core–shell particles. It is well known the organic compounds with sulfhydryl group can form disulfide bonds to dimerize. Inspired by these facts, we expected that replacing APTEOS by 3-mercaptopropyltrimethoxysilane (MPTMOS) in the synthetic process would cause the silica nanoparticles reorganize and form ordered nanostructures through the disulfide bonds

---

[*] Corresponding author. Tel.: +86 731 88879850; fax: +86 731 88879850.
[**] Corresponding author.
E-mail addresses: huangkelong@yahoo.com.cn (K.-L. Huang), xzsong@pku.org.cn (X.-Z. Song).

1385-8947/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2010.06.015

between MPTMOS molecules; and the SiNWs might be prepared by the same procedure. Therefore, we conducted the research and successfully obtained SiNWs in solution, below 100 °C and at atmosphere pressure. The new method processed through the following sequential steps: (1) the modification of silica nanoparticles with MPTMOS; (2) the disulfide bonds formation between MPTMOS molecules reorganized the nanoparicles and made elongated clusters; (3) adsorption of the small gold particles on the elongated clusters, and the elongated clusters were deformated into SiNWs with gold nanoparticles attachments by the driving force, the high surface strain energy of the colloidal particles. Also, gold–silica core–shell nanoparticles were used to produce gold-nanoparticle-embedded SiNWs in the same method. In order to understand the mechanism of SiNW formation and prove our thought, the microscopy was used to investigate the products at each stage in the synthetic process. Importantly, in the new method all experiments were performed in solution and under mild conditions (below 100 °C at atmosphere pressure), and special apparatus was avoided. Therefore, the new synthetic method was very practical and efficient, and could open a new route for the synthesis of novel SiNWs in large scale.

2. Materials and methods

2.1. Materials

3-Mercaptopropyltrimethoxysilane (MPTMOS) and tetramethoxysilane (TMOS) were purchased from Sigma. $HAuCl_4$ was obtained from Yunnan Haitai Chemicals Reagent Co., Ltd. Sodium silicate, sodium citrate, 25–28% $NH_3{\cdot}H_2O$, $NaBH_4$, potassium carbonate and absolute ethanol were purchased from Shanghai Shi Yi Chemicals Reagent Co., Ltd. All chemicals were used as received. Water used in all experiments was purified with a three-stage Millipore Milli-Q Plus 185 system and had a resistivity higher than 18.2 MΩ cm.

2.2. Preparation of gold–silica core–shell nanoparticles

A colloidal dispersion (30 mL 5×10^{-4} M $HAuCl_4$) of gold nanoparticles with about 17 nm diameter was firstly prepared according to the standard sodium citrate reduction method [25]. At room temperature, the gold nanoparticles were modified with organosilane molecules, MPTMOS, by adding its ethanol solution (1 mL 2×10^{-4} (v/v)). After 15 min, 1 mL of 0.02% sodium silicate solution (pH ≈ 7.5) was added under vigorous magnetic stirring and the resultant mixture was allowed to stand overnight. After centrifugating (8000 rpm, 1 h) to remove excess silicate and redispersing in ethanol (30 mL), extensive growth of the silica shell was performed by addition of 1 mL of 25–28% ammonium hydroxide and 30 μL of TMOS during 12 h. After centrifuging (8000 rpm, 1 h) and redispersing three times in ethanol, finally the prepared core–shell nanoparticles were suspended in 30 mL ethanol.

2.3. Formation of gold-nanoparticle-modified SiNWs

To the above prepared core–shell nanoparticles ethanol solution was added 10 μL MPTMOS. After standing for 2 h at room temperature, the mixture was boiled for 4 h, keeping the volume of the solution constant by periodically adding additional ethanol. After three cycles of centrifugation and redispersion in pure ethanol to remove residual reactants, the products were redispersed in 10 mL water. Under mild magnetic stirring, 5 mL of the products were then added to 40 mL of 3.5 ± 0.7 nm gold nanoparticle solution prepared according to the $NaBH_4$ reduction method [26]. After 1 h, the mixture was centrifuged (5000 rpm, 30 min) many times until the solution was clear. The sediment was subsequently dispersed in 30 mL water. Then, a one-day-old K-gold solution (25 mg potassium carbonate in 5 mL of 0.3% gold chloride solution) and a freshly prepared $NaBH_4$ solution (25 mg in 20 mL of water) were added. The resultant mixture stood for 3 h under mild stirring. And the gold-nanoparticle-modified SiNWs were obtained by centrifugation (5000 rpm, 30 min) many times until the solution became clear.

2.4. Characterization

The morphology of the products was observed using transmission electron microscopy (TEM) (JEOL-1230) in conventional transmission mode using 80 keV, high-resolution TEM (FEI Tecnai G^2 20ST) in conventional transmission mode using 200 keV, SEM (JSM-6360), and/or fluorescence microscope (Zeiss MC80DX). The distribution of the chemical composition of the nanowires was characterized by energy dispersive X-ray (EDX) spectrometer, attached to the FEI Tecnai G^2 20ST microscope. For SEM investigations, the as-synthesized product was pasted on an Al substrate by carbon conducting paste. For TEM investigations, the product was ultrasonicated in deionized water for 20 min, and then a drop of the suspension was placed on a holey copper grid with carbon film behind. The electronic absorbance spectra were measured with SHIMADZU UV-2450 spectrophotometer in 1 cm path length cuvettes. The photoluminescence (PL) spectrum was investigated with a HITACH F-2500 fluorescence spectrophotometer at room temperature.

3. Results and discussion

The shapes of products were observed by the high-resolution transmission electron microscopy (HR-TEM). Fig. 1a and b shows the TEM images of gold-particle-modified SiNWs with gold nanoparticles embedded in and/or attached on the SiNWs. The length and diameter of the nanowires were about 200–2000 nm and about 20–30 nm, respectively. The distribution of the chemical composition of the nanowires was characterized using EDX spectroscopy (Fig. 1c). In Fig. 1c, C (0.257 eV) and Cu (0.939 eV, 8.058 eV, and 8.931 eV) peaks were contributed from the copper grid that served as the sample support for transmission electron microscopy (TEM) analysis. Other peaks were Si (1.730 eV), O (0.530 eV) and Au (2.167 eV, 9.722 eV, and 11.496 eV). The response peaks of gold element were very obvious. The EDX spectroscopy indicated that the nanowires are composed of Si, O and Au.

The optical properties of the as-prepared gold-nanoparticle-modified SiNWs were investigated at room temperature by absorption and fluorescent spectroscopy. Fig. 2 illustrates the UV–vis absorption spectrum of the synthesized nanowires (solid line and dash dot line), core–shell nanoparticles (dot line) and gold nanoparticles (dash line) in water. Compared with the plain silica nanowires [27], a pronounced SPR absorption peak at 528 nm appeared in the absorption spectrum of gold-particle-modified nanowires, which indicated that the gold nanoparticles were embedded in and/or attached on SiNWs [28]. According to previous reports [29,30], this strong surface-plasmon-resonance (SPR) absorption peak of gold nanoparticles could be potentially used for biosensing applications. In the absorption spectrum of SiNW with gold nanoparticles on its surface, it had hardly induced a red-shift of absorption peak wavelength compared with the gold colloid, whereas there were SPR absorption peak red-shift (from 520 nm to 528 nm) in the spectra of the core–shell nanoparticles and the gold-particle-embedded nanowires because of the increase of the local refractive index around the gold nanoparticles [31]. Because the inter-particle separation distances of gold nanoparticles in the nanowires were within a large range, the absorption spectrum of the nanowires was broad. And the AuSiNWs displayed a new

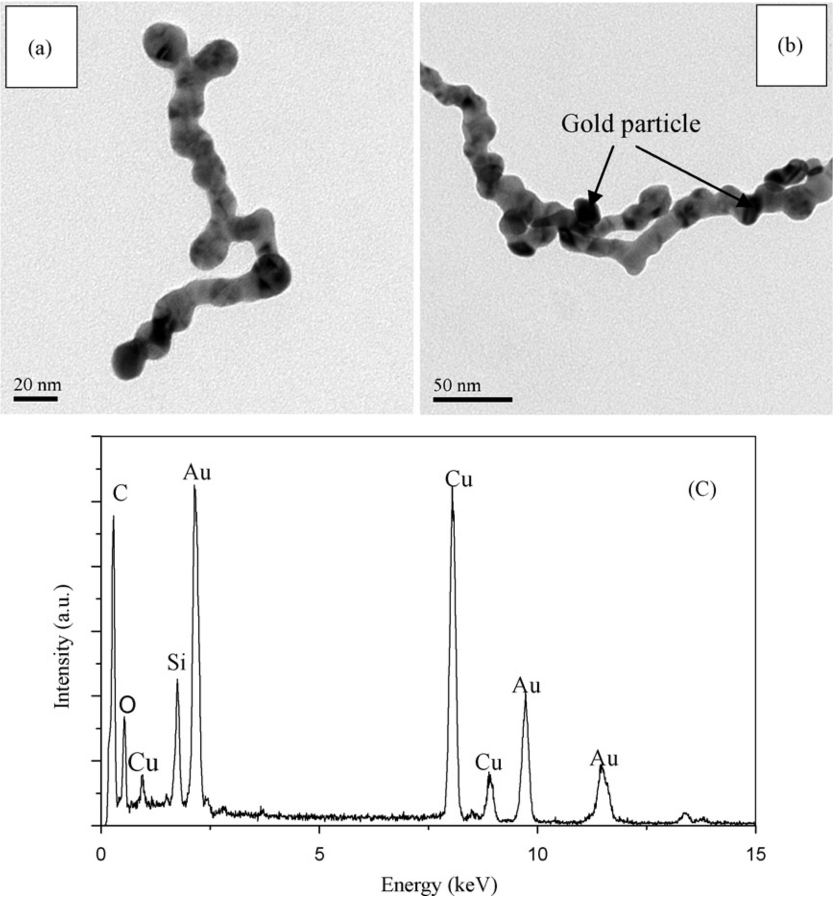

Fig. 1. TEM images and EDX spectrum. (a and b) TEM images of the as-prepared gold-nanoparticle-modified silicon oxide nanowires; (c) an EDX spectrum of a nanowire.

absorption band at longer wavelength due to coupling of surface plasmons between closely spaced particles [32].

In our experiments, AuSiNWs showed strong photoluminescence while silica nanoparticles were not photoluminescent. The emission and excitation PL spectra of AuSiNWs in solid state are shown in Fig. 3. The striking emission spectrum revealed that the synthesized AuSiNWs had a strong blue luminescence centered at 440 nm (2.83 eV) and a weak emission peak at 340 nm (3.66 eV), which was consisted with the previous report [33]. Fig. 4 is the fluorescence micrograph of AuSiNWs. According to the previous reports [34,35], the 340 nm (3.66 eV) luminescence band was ascribed to the neutral oxygen vacancies (≡Si–Si≡). The 440 nm (2.83 eV) band was caused by some intrinsic diamagnetic defect centers, such as the twofold coordinated silicon lone pair centers (O–Si–O). The attached and embedded gold nanoparticles caused the large amount of defects in AuSiNWs and greatly enhanced the absorption at 440 nm (2.83 eV). Compare with amorphous SiNWs [36], two weak peaks at 420 nm (3.0 eV) and 465 nm (2.7 eV) disap-

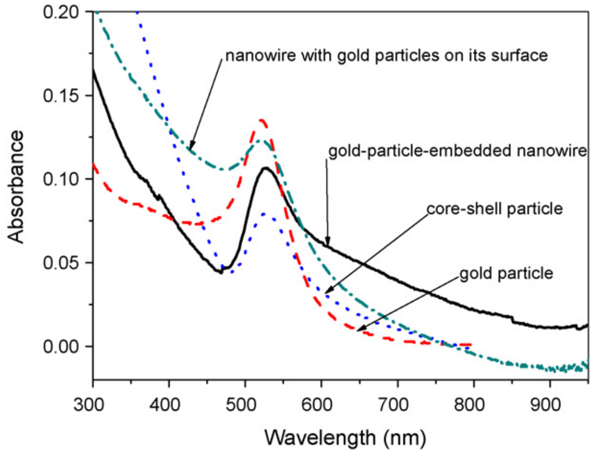

Fig. 2. The ultraviolet–visible absorption spectra of the as-synthesized gold-nanoparticle-embedded silicon oxide nanowires (solid line), gold–silica core–shell nanoparticles (dot line), gold nanoparticles (dash line), silicon oxide nanowire with gold particles on its surface (dash dot line) in water.

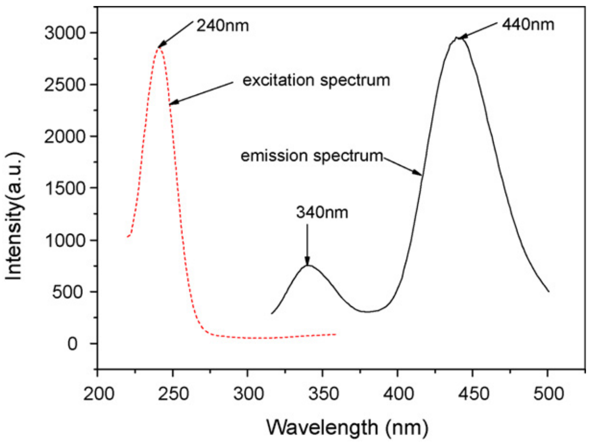

Fig. 3. The PL spectrum at room temperature under excitation at 240 nm (solid line) and the excitation spectrum (dotted line) of the as-synthesized gold-nanoparticle-modified silicon oxide nanowires.

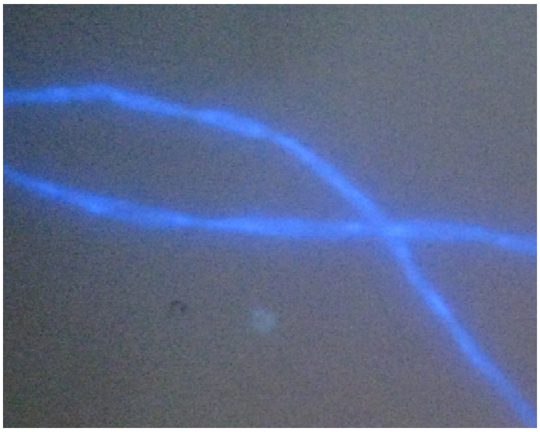

Fig. 4. The fluorescence micrograph of as-prepared gold-particle-modified silica nanowires.

peared in the emission spectrum of AuSiNWs due to overlapping of the strong absorption band centered at 440 nm (2.83 eV).

To further understand the formation mechanism, we used plain silica nanoparticles instead of Au@SiO$_2$ core–shell nanoparticles to prepare silica nanowires in the same procedure. The plain silica nanoparticles with a diameter of about 400 nm were prepared according to StÖber's procedure [37]. Silica nanowires with many gold nanoparticles attachments were formed (shown in Fig. 5c and d) and did not show any absorption in near-infrared range (dash dot line in Fig. 2), which indicated there was no core–shell structural nanoparticles [38]. Through the microscopy investigation in each step, we found nanowires were forming in the MPTMOS modification process. The formation of disulfide bonds might provide bridges between the silica particles and mediate the reorganization of the silica particles to form elongated clusters (shown in Fig. 5b). Fig. 5b clearly shows that the interconnected colloidal particles were deforming into wires while the lone colloidal particle did not change, which implied that the high surface strain energy of colloidal particles could be minimized by deformation of the interconnected colloidal particles into wires. The free SH groups on the surface of resulting wires conjugated with the added gold colloid. The subsequent reduction of chloroauric acid caused more gold atoms to deposit on these colloid nucleation sites and made the gold particles bigger on the surface of wires. The observed nanowires (shown in Fig. 5c and d) were ultimately formed in solution. Fig. 6 is the schematic representation of our proposed formation process of SiNWs with gold nanoparticles attachments on its surface, and the formation of AuSiNWs followed the same mechanism. Because gold particle had ably been encapsulated in silica particle before deformation of interconnected silica particles into wire, there were many gold particles embedded in silica wire. During the preparation of Au@SiO$_2$ core–shell nanoparticles, gold-free silica particles were also formed at the same time and could participate in the formation of AuSiNWs. Therefore, the separation distance between nearest-neighbor Au particles would have a large variability, as shown in Fig. 1, which resulted in the broad absorption spectrum of AuSiNWs. If pure Au@SiO$_2$ core–shell nanoparticles could be prepared, we believed that the embedded Au nanoparticles would be consistently well spaced and the absorption spectrum of AuSiNWs would be narrow.

To prove the hypothesis about the formation of SiNWs, we did important experiments under N$_2$ protection to prevent the

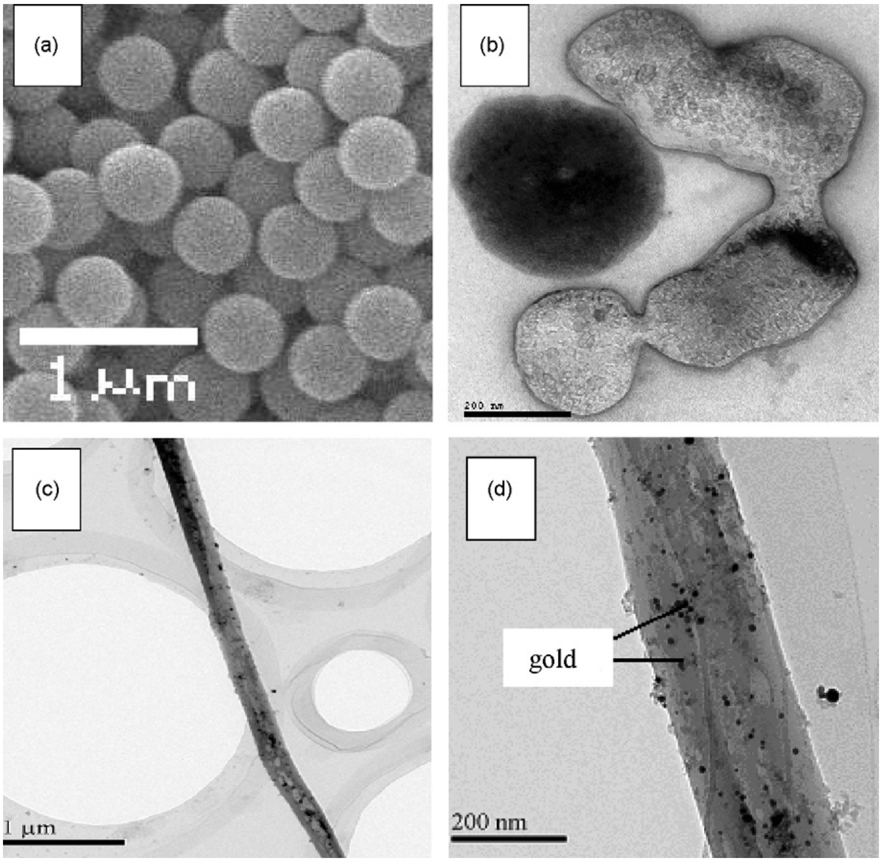

Fig. 5. (a) SEM image of the silica nanoparticles made using TMS according to the StÖber procedure; (b) TEM image showing the deformation of interconnecting colloidal particles into wires; (c) and (d) TEM images of the as-synthesized nanowires made using silica colloidal particles.

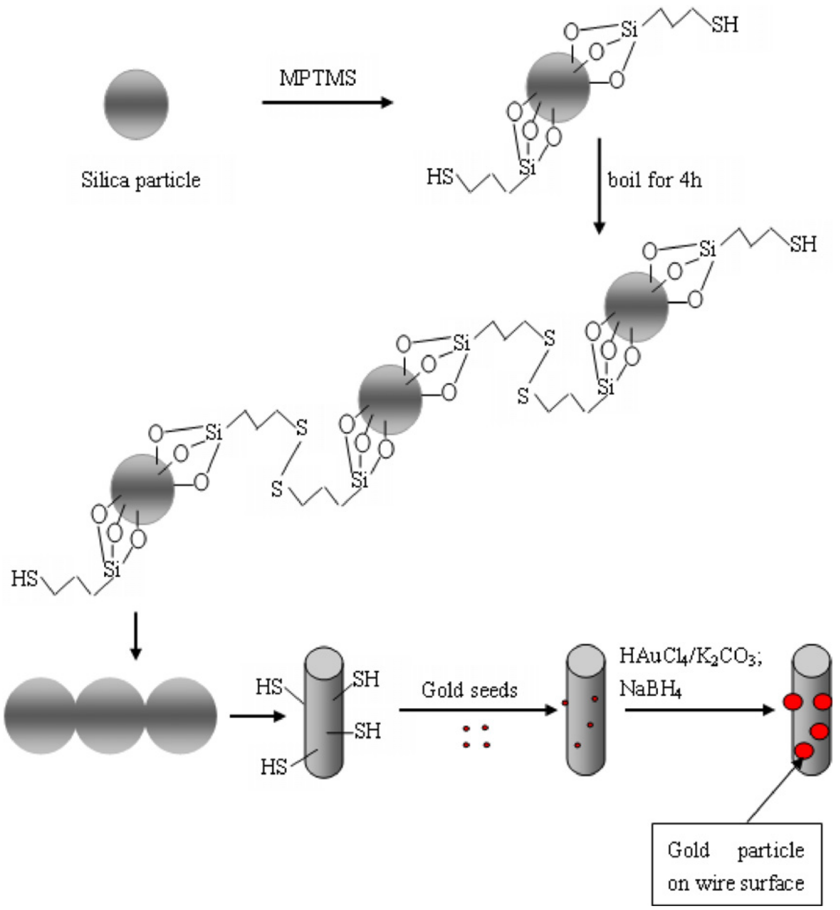

Fig. 6. The schematic representation of the formation process of silica nanowires with gold nanoparticles attachment by sol–gel self-assembly method.

–SH group from being oxidized to form disulfide bonds. Therefore, MPTMOS would be in a reduced form and could not perform as a linker to reorganize the nanoparticles. The result was what we expected and no SiNW was formed under the N_2 condition, which clearly indicated the formation of disulfide bonds played a key role on the formation of SiNWs and strongly supported our proposed mechanism.

The exact reason for the preferential formation of the 1-D structure was not entirely clear. But we believed that the steric encumbrance played an important role. It is possible that more than one disulfide bonds is required to adjoin two colloidal particles and the pearl necklace-like structure facilitates the formation of a greater number of intermolecular disulfide bonds between two adjacent colloidal particles. Because only one free sulfhydryl group is present in each MPTMOS molecule, the number of disulfide bonds between colloidal particles would be reduced by the congested particle arrangement associated with the 2- or 3-D structure. Therefore, the 1-D structure comprising interconnected particles is more stable than that of the 2- or 3-D structure, and formation of 1-D nanowire is favorable.

It is interesting that the diameters of the nanowires were smaller than that of the corresponding nanoparticles. But our experiments showed that the bigger the particles the thicker the formed nanowires. Therefore, it is expected to prepare different sizes of SiNWs by controlling the experimental conditions in our new method.

Future work is needed to improve this new method for the large-scale synthesis of Au-nanoparticle-modified SiNWs such as developing the efficient process to fabricate Au@SiO_2 core–shell nanoparticles in a high yield and eliminating some steps or shortening the reaction time. For example, air or some appropriate oxidants can be used to expedite the oxidation of the MPTMOS-modified nanoparticles and form disulfide bonds faster and efficiently. Also, ultrasonic irradiance may be applied to promote the deformation of the interconnected colloidal particles into wires and improve the yield.

4. Conclusions

In summary, we had successfully developed a novel method to prepare SiNWs. In this new approach, the MPTMOS played an important role in the formation of the nanowires. The high surface strain energy of colloidal particles could be minimized by deformation of the interconnected colloidal particles into wires. All experiment procedures were practical and safe, and special apparatus was avoided. This method allows for SiNW synthesis in solution without high temperatures or vacuum, which is helpful for making large quantities of SiNWs at low cost. Furthermore, the synthesized SiNWs have gold nanoparticle attachments on their surface, where they are potentially accessible to molecules for sensing applications.

Acknowledgments

This work was supported by research grants from the National 863 Key Special Project of China (Project No. 2007 AA021810). We thank Huai Hua Medical College for the support of Key Talent.

References

[1] W.L. Barnes, A. Dereux, T.W. Ebbesen, Surface plasmon subwavelength optics, Nature 424 (2003) 824–830.

[2] Y. Fedutik, V. Temnov, U. Woggon, E. Ustinovich, M. Artemyev, Exciton–plasmon interaction in a composite metal–insulator–semiconductor nanowire system, J. Am. Chem. Soc. 129 (2007) 14939–14945.

[3] D. Voss, Condensed-matter physics: switch-hitter materials tantalize theorists, Science 292 (2001) 1987.

[4] H.F. Zhang, C.M. Wang, E.C. Buck, L.S. Wang, Synthesis, characterization, and manipulation of helical SiO_2 nanosprings, Nano Lett. 3 (2003) 577–580.

[5] X Zhang, Z. Liu, C. Wong, S. Hark, N. Ke, S. Wong, Fabrication and optical properties of erbium-doped silicon-rich silicon oxide nanofibers, J. Phys. Chem. C 111 (2007) 4083–4086.

[6] Y. Huang, X. Duan, Y. Cui, L.J. Lauhon, K.H. Kim, C.M. Lieber, Logic gates and computation from assembled nanowire building blocks, Science 294 (2001) 1313–1317.

[7] Y. Cui, Z. Zhong, D. Wang, W.U. Wang, C.M. Lieber, High performance silicon nanowire field effect transistors, Nano Lett. 3 (2003) 149–152.

[8] Z. Tang, N.A. Kotov, M. Giersig, Spontaneous organization of single CdTe nanoparticles into luminescent nanowires, Science 297 (2002) 237–240.

[9] X.T. Zhou, J.Q. Hu, C.P. Li, D.D.D. Ma, C.S. Lee, S.T. Lee, Silicon nanowires as chemical sensors, Chem. Phys. Lett. 369 (2003) 220–224.

[10] Y. Cui, Q. Wei, H. Park, C.M. Lieber, Nanowire nanosensors for highly sensitive and selective detection of biological and chemical species, Science 293 (2001) 1289–1292.

[11] A.K. Salem, P.C. Searson, K.W. Leong, Multifunctional nanorods for gene delivery, Nat. Mater. 2 (2003) 668–671.

[12] E. Bekyarova, Y. Ni, E.B. Malarkey, V. Montana, J.L. McWilliams, R.C. Haddon, V. Parpura, Applications of carbon nanotubes in biotechnology and biomedicine, J. Biomed. Nanotechnol. 1 (2005) 3–17.

[13] K. Peng, M. Zhang, A. Lu, N.B. Wong, R. Zhang, S.T. Lee, Ordered silicon nanowire arrays via nanosphere lithography and metalinduced etching, Appl. Phys. Lett. 90 (2007) 163123.

[14] H. Nakamura, Y. Matsui, Silica gel nanotubes obtained by the sol–gel method, J. Am. Chem. Soc. 117 (1995) 2651–2652.

[15] L. Wang, D. Major, P. Paga, D. Zhang, M.G. Norton, D.N. McIlroy, High yield synthesis and lithography of silica-based nanospring mats, Nanotechnology 17 (2006) 298–303.

[16] Y. Wu, T. Livneh, Y.X. Zhang, G. Cheng, J. Wang, J. Tang, M. Moskovits, G.D. Stucky, Templated synthesis of highly ordered mesostructured nanowires and nanowire arrays, Nano Lett. 4 (2004) 2337–2342.

[17] J. Hahm, C.M. Lieber, Direct ultrasensitive electrical detection of DNA and DNA sequence variations using nanowire nanosensors, Nano Lett. 4 (2004) 51–54.

[18] J.H. He, Y.Y. Zhang, J. Liu, D. Moore, G. Bao, Z.L. Wang, ZnS/silica nanocable field effect transistors as biological and chemical nanosensors, J. Phys. Chem. C 111 (2007) 12152–12156.

[19] P.K. Sekhar, S.N. Sambandam, D.K. Sood, S. Bhansali, Selective growth of silica nanowires in silicon catalysed by Pt thin film, Nanotechnology 17 (2006) 4606–4613.

[20] R.S. Wagner, W.C. Ellis, Vapor–liquid–solid mechanism of single crystal growth, Appl. Phys. Lett. 4 (1964) 89–90.

[21] D.P. Yu, Q.L. Hang, Y. Ding, H.Z. Zhang, Z.G. Bai, J.J. Wang, Y.H. Zou, W. Qian, G.C. Xiong, S.Q. Feng, Amorphous silica nanowires: intensive blue light emitters, Appl. Phys. Lett. 73 (1998) 3076–3078.

[22] H. Jagannathan, Y. Nishi, M. Reuter, M. Copel, E. Tutuc, S. Guha, R.P. Pezzi, Effect of oxide overlayer formation on the growth of gold catalyzed epitaxial silicon nanowires, Appl. Phys. Lett. 88 (2006) 103113.

[23] C. Loo, A. Lowery, N. Halas, J. West, R. Drezek, Immunotargeted nanoshells for integrated cancer imaging and therapy, Nano Lett. 5 (2005) 709–711.

[24] S.J. Oldenburg, S.L. Westcott, R.D. Averitt, N.J. Halas, Surface enhanced Raman scattering in the near infrared using metal nanoshell substrates, J. Chem. Phys. 111 (1999) 4729–4735.

[25] B.V. Enüstün, J. Turkevich, Coagulation of colloidal gold, J. Am. Chem. Soc. 85 (1963) 3317–3328.

[26] N.R. Jana, L. Gearheart, C.J. Murphy, Seeding growth for size control of 5–40 nm diameter gold nanoparticles, Langmuir 17 (2001) 6782–6786.

[27] M.S. Hu, H.L. Chen, C.H. Shen, L.S. Hong, B.R. Huang, K.H. Chen, L.C. Chen, Photosensitive gold-nanoparticle-embedded dielectric nanowires, Nat. Mater. 5 (2006) 102–106.

[28] H.B. Lee, Y.M. Yoo, Y.H. Han, Characteristic optical properties and synthesis of gold–silica core–shell colloids, Scripta Mater. 55 (2006) 1127–1129.

[29] T.A. Taton, R.C. Mucic, C.A. Mirkin, R.L. Letsinger, The DNA-mediated formation of supramolecular mono-and multilayered nanoparticle structures, J. Am. Chem. Soc. 122 (2000) 6305–6306.

[30] T. Endo, K. Kerman, N. Nagatani, Y. Takamura, E. Tamiya, Label-free detection of peptide nucleic acid–DNA hybridization using localized surface plasmon resonance based optical biosensor, Anal. Chem. 77 (2005) 6976–6984.

[31] L.M. Liz-Marzán, A.P. Philipse, Synthesis and optical properties of gold-labelled silica particles, J. Colloid Interface Sci. 176 (1995) 459–466.

[32] K.C. Grabar, R.G. Freeman, M.B. Hommer, M.J. Natan, Preparation, Characterization of Au colloid monolayers, Anal. Chem. 67 (1995) 735–743.

[33] C.H. Liang, G.W. Meng, L.D. Zhang, Y.C. Wu, Z. Cui, Large-scale synthesis of –SiC nanowires by using mesoporous silica embedded with Fe nanoparticles, Chem. Phys. Lett. 329 (2000) 323–328.

[34] H. Nishikawa, T. Shiroyama, R. Nakamura, Y. Ohki, Photoluminescence from defect centers in high-purity silica glasses observed under 7.9-eV excitation, Phys. Rev. B 45 (1992) 586–591.

[35] H. Nishikawa, E. Watanabe, D. Ito, Decay kinetics of the 4.4-eV photoluminescence associated with the two states of oxygen-deficient-type defect in amorphous SiO_2, Phys. Rev. Lett. 72 (1994) 2101–2104.

[36] X.C. Wu, W.H. Song, K.Y. Wang, T. Hu, B. Zhao, Y.P. Sun, J.J. Du, Preparation and photoluminescence properties of amorphous silica nanowires, Chem. Phys. Lett. 336 (2001) 53–56.

[37] W. Stöber, A. Fink, E. Bohn, Controlled growth of monodisperse silicaspheres in the micron size range, J. Colloid Interface Sci. 26 (1968) 62–69.

[38] L.R. Hirsch, J.B. Jackson, A. Lee, N.J. Halas, J.L. West, A whole blood immunoassay using gold nanoshells, Anal. Chem. 75 (2003) 2377–2381.