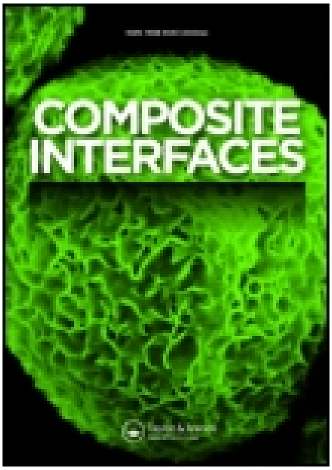


Composite Interfaces
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/tcoi20

Surface Modification of Gold Nanorods by Organosilanes

Koji Mitamura [a] , Toyoko Imae [b] , Nagahiro Saito [c] & Osamu Takai [d]

[a] Graduate School of Engineering, Nagoya University, Chikusa, Nagoya 464-8603, Japan

[b] Graduate School of Science and Technology, Keio University, Hiyoshi, Yokohama 223-8522, Japan, Graduate Institute of Engineering, Jing-Cheng Honors College, National Taiwan University of Science and Technology, 43, Section 4, Keelung Road, Taipei 10607, Taiwan;, Email: imae@mail.ntust.edu.tw

[c] Graduate School of Engineering, Nagoya University, Chikusa, Nagoya 464-8603, Japan

[d] Graduate School of Engineering, Nagoya University, Chikusa, Nagoya 464-8603, Japan, Ecotopia Science Institute, Nagoya University, Furo-cho, Chikusa, Nagoya 464-8603, Japan

To cite this article: Koji Mitamura , Toyoko Imae , Nagahiro Saito & Osamu Takai (2009) Surface Modification of Gold Nanorods by Organosilanes, Composite Interfaces, 16:4-6, 377-385, DOI: 10.1163/156855409X447138

To link to this article: http://dx.doi.org/10.1163/156855409X447138

///VSP///

Composite Interfaces 16 (2009) 377–385

COMPOSITE INTERFACES
www.brill.nl/ci

Surface Modification of Gold Nanorods by Organosilanes

Koji Mitamura [a], **Toyoko Imae** [b,*], **Nagahiro Saito** [a] **and Osamu Takai** [a,c]

[a] Graduate School of Engineering, Nagoya University, Chikusa, Nagoya 464-8603, Japan
[b] Graduate School of Science and Technology, Keio University, Hiyoshi, Yokohama 223-8522, Japan
[c] Ecotopia Science Institute, Nagoya University, Furo-cho, Chikusa, Nagoya 464-8603, Japan

Received 10 February 2008; accepted 7 July 2008

Abstract

Gold nanorods protected by hexadecyltrimethylammonium bromide were treated by an organosilane, aminopropyltriethoxysilane (APS) or vinyltrimethoxysilane (VS) in the presence of mercaptopropyltrimethoxysilane (MPS) serving as a binder. After the APS- or VS-treatment, a shell about 4 nm thick surrounding the nanorods was found by means of transmission electron microscopy. Its formation enabled the nanorods to be dispersed in polar media (ethanol, methanol, acetone and acetonitrile/water mixtures).

Keywords

Gold nanorod, hydrophilic nanorod, hexadecyltrimethylammonium bromide, organosilane, aminopropyltriethoxysilane, vinyltrimethoxysilane, mercaptopropyltrimethoxysilane, surface modification

1. Introduction

Gold nanorods, as distinct from spherical gold nanoparticles, possess ‘anisotropy’ in mechanical, optical and chemical properties [1–5]. Thus, the nanorods display two plasmon absorption bands in visible and near-infrared regions, while spherical nanoparticles exhibit only one plasmon band in the visible region [6]. Owing to such properties, the gold nanorods are attracting attention as one of highly functional materials [5, 7]. In practice, biomedical researchers focused on the property that the gold nanoparticles deformed in their shape from rod to sphere under strong irradiation of a near-IR ray and simultaneously generated thermal energy. The deformation of nanorods enables the release of the loaded drugs like DNA on the nanorods [5], and the thermal energy kills human cancer cells *in vitro* [7].

However, there are still some problems with the medical applications of the gold nanorods, including surface modification, biocompatibility, etc. which remain

---

[*] To whom correspondence should be addressed. Present address: Graduate Institute of Engineering, Jing-Cheng Honors College, National Taiwan University of Science and Technology, 43, Section 4, Keelung Road, Taipei 10607, Taiwan. E-mail: imae@mail.ntust.edu.tw

DOI:10.1163/156855409X447138

to be solved. On the preparation of gold nanorods, it is required to protect them with a large amount of cationic surfactant, hexadecyltrimethylammonium bromide (CTAB), which is not biocompatible and prevents the reaction on the surface of the gold nanorod. Consequently, the surface modification of CTAB-coated gold nanorods is one of the most important subjects for their medical and industrial applications.

This work deals with the surface treatment of the gold nanorods by two types of organosilanes. They are aminopropyltrimethoxysilane (APS) and vinyltrimethoxysilane (VS). The APS- or VS-modification enables the gold nanorods to hybridize with polypeptides or plastics, respectively, by using the functional groups of organosilanes. However, it should be considered that CTAB on gold nanorods hardly interacts with a hydrolysate of Si–OR (usually, R is a short alkyl group), that is, silanol (Si–OH). Consequently, linkers between gold nanorods and organosilanes are required. Then mercaptopropyltrimethoxysilane (MPS) was employed as a linker. In comparison with the previous investigations for the surface modification of gold nanorods [2, 3, 5, 7–17], the present procedure is advantageous for self-assembling or ordering of nanorods [18].

2. Materials and Methods

2.1. Preparation of Gold Nanorods

Preparation of gold nanorods was performed by a seeded method [8]. A freshly prepared aqueous solution (0.016 cm^3) of 0.01 M $NaBH_4$ was added dropwise into a yellow aqueous solution (0.3 cm^3) of 0.25 mM $HAuCl_4$ and 0.095 M CTAB with a mild stirring. This seed solution colored brown. Separately, an aqueous solution (0.16 cm^3) of 0.01 M $AgNO_3$ and an aqueous solution (0.15 cm^3) of 0.1 M ascorbic acid were added into a yellow aqueous solution (20.0 cm^3) of 0.5 mM $HAuCl_4$ and 0.095 M CTAB under a mild stirring. The resultant growth solution was transparent. The seed solution (0.30 cm^3) was mixed with the growth solution (20.0 cm^3), and the mixture was kept for at least 12 h. Finally, the color of the solution became brownish red. The preparation of the gold nanorods was carried out at 30°C.

2.2. Surface-Modification of Gold Nanorod

Excess CTAB in an as-prepared gold nanorod dispersion (1.0 cm^3) was removed by centrifugation (47 000 rpm for 20 min). Then the supernatant was taken out by decantation and the residue was redispersed in water. After the centrifugation procedure was repeated, an ethanol solution (0.010 cm^3) of 10 mM MPS was added to the resultant dispersion (1.0 cm^3), and the mixture was vigorously stirred for 30 min. After that, an ethanol solution (0.030 cm^3) of 10 mM APS or VS and an aqueous solution (0.005 cm^3) of 1 N NaOH were added to this mixture, and the aging was carried out at 30°C for 24 h. The aged mixture (water/ethanol mixture (25 : 1 (v/v)) was diluted by ethanol to be water : ethanol = 1 : 4 (v/v).

2.3. Measurements

TEM observation was carried out on a JEM-2500TS and H-7000. The specimens for TEM observations were prepared by evaporating solvent (0.005 cm^3) from a nanorod dispersion on a carbon-deposited copper grid. UV-vis absorption spectra were recorded on a Shimazu UV-vis spectrometer (UV-1650PC). A quartz cell (1 cm path length) was used.

3. Results and Discussion

The synthesis of gold nanorods at high yield has been performed by a seed-mediated method [8], a UV irradiation method [9] or an electrochemical method [10]. In the present report, the seed-mediated method was adopted, since it is relatively simple and requires only standard laboratory glassware without any specific apparatus. However, even if any other preparation methods described above are applied, a large amount of CTAB (about 0.1 M) is used as a protector of the gold nanorods, which makes the subsequent surface modification difficult. Several literature references have reported that the surface modifications were accompanied by at least double centrifugations (or extractions) in order to remove the excess CTAB [2, 3, 5, 7–12]. Thus, in the present study, the same procedure was carried out (see Experimental section). The resultant gold nanorods of an average aspect ratio 3.8 ± 0.3 were confirmed by transmission electron microscopic (TEM) images (see Fig. 1) and displayed two bands (at 520 and 808 nm) in a UV-vis absorption spectrum as shown in Fig. 2(a).

The surface modification of the excess CTAB-removed nanorods was performed, according to Scheme 1. That is, (1) binding of MPS molecules on the nanorod surface, (2) hydrolysis of Si–OR (R = C_2H_5 or CH_3) groups of organosilanes (MPS

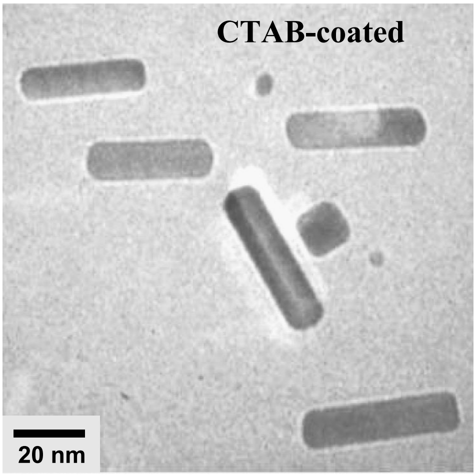


Figure 1. A TEM image of CTAB-coated gold nanorods (in water, after 24 h of preparation).

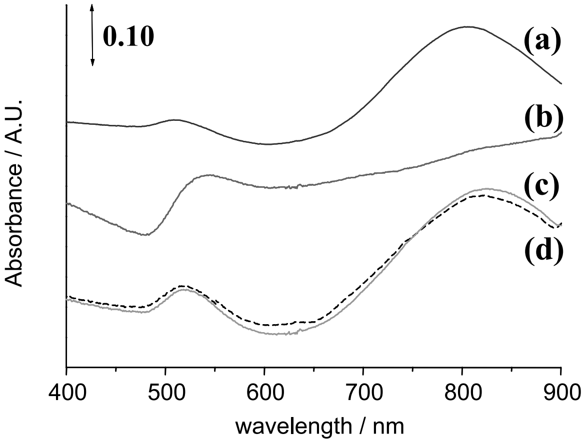
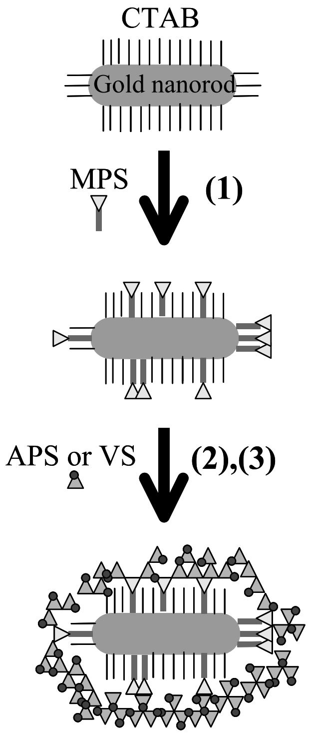


Figure 2. UV-vis absorption spectra of gold nanorods. (a) CTAB-coated (in water, after 24 h of preparation), (b) CTAB-coated (in water/ethanol mixture, immediately after preparation). (c) VS-modified (in water/ethanol mixture, after 24 h from addition of VS), (d) VS-modified (in water/ethanol mixture, after 1 week from addition of VS).



Hydrophilic gold nanorod

Scheme 1. Schematic illustration of surface modification process of gold nanorod. (1) Replacement of CTAB with MPS, (2) hydrolysis of organosilanes, (3) dehydration condensation of organosilanes.

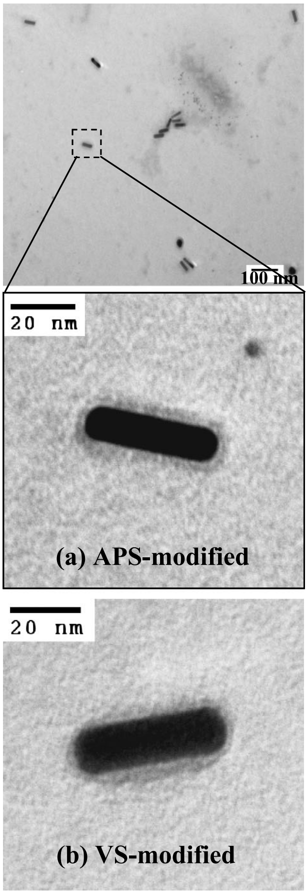


Figure 3. TEM images of hydrophilic gold nanorods (in water, after 24 h of preparation). (a) APS-modified, (b) VS-modified.

and APS or VS) and (3) dehydration condensation (polymerization), namely, formation of a siloxane bond (Si–O–Si) among MPS and APS or VS. As the result of such reactions, the nanorods are covered by polymerized APS or VS, as illustrated in Scheme 1. The nanorods after the treatments adopted the core-shell structure in both cases of APS and VS reactions, as shown in Fig. 3. The shell was visualized at the lower contrast than the gold nanorod. The shell thickness was not necessarily uniform but averaged about 4 nm in both cases (APS and VS). Even after the triple dilution with ethanol, the shells remained, indicating that the shells were strongly fixed on the nanorods. It is obvious that the shells were constructed by a siloxane bond of APS or VS with MPS on the nanorods. However, no shell was formed when only MPS (without any APS or VS) was taken, and most nanorods precipitated or adhered on the glassware within 24 h. The former phenomenon results from the addition of ethanol but the latter was induced by a condensation reaction between MPS groups on nanorods or between MPS group on a nanorod and the glass wall

(SiO_2), although such phenomena never occurred after the reaction with APS or VS.

On the modification of gold nanorods by organosilanes, although hydrolysis of Si–OR groups and polymerization of Si–OH groups are essential, their reaction rates and the efficiency of shell formation are affected by concentrations of organosilanes, alkalinity and CTAB as described below. With increase in the concentration of APS or VS (from 300 to 700 μM), large aggregates of nanorods were formed, though small amounts of aggregates existed even at a low concentration of APS or VS. This is attributable to the subsequent side reaction in dehydration condensation, that is, the reaction between free Si–OH groups of APS (or VS) (homogeneous reaction). The rapid growth of APS or VS polymers brings on the fusion of the nanorods as well as the thickening of the shells.

In general, acid or alkali is used as a catalyst for a sol–gel reaction. In the present work, when a small amount of an aqueous 1 N NaOH solution was added to the nanorod dispersion ($pH = 8–9$), the shells were visualized on TEM images (see Fig. 3). However, a precipitate was produced in alkaline media ($pH = 11–12$) and never redispersed in water or ethanol, since the polymerization reaction and cross-linking of nanorods was accelerated.

Free CTAB in a nanorod dispersion also influenced the formation of the shell. Without any centrifugation treatment ($[\text{CTAB}] = 95$ mM, $[\text{Au}] = 0.5$ mM), the dispersion was turbid but the shell on the gold nanorod was not observed by TEM, although the nanorods after double centrifugation treatments ($[\text{CTAB}] \sim 0.16$ mM, $[\text{Au}] = 0.5$ mM) were wrapped by the shells (see Fig. 3). At the condition without centrifugation, CTAB strongly protected the nanorods, and MPS scarcely attached on the nanorods, corresponding to the absence of the reaction (1) in Scheme 1. Thus the homogeneous polymerization between free APS or VS caused the lack of the nanorod shell and the turbidity of the dispersion. On the other hand, after the triple centrifugations were carried out, CTAB concentration was so lowered that the unprotected nanorods formed an insoluble product without redispersion, indicating the impossibility of reaction with organosilanes.

The modified gold nanorods, which were obtained at the optimum conditions of the concentrations of the organosilanes, alkali and CTAB, displayed different features from those of the CTAB-coated gold nanorods. Although a dispersion of the CTAB-coated nanorods turned blue and precipitated within an hour in a polar organic solvent-rich environment (e.g. water : ethanol $= 1:4$ (v/v)), the modified nanorods were stable at the same environment for more than one week. After addition of ethanol to the aqueous dispersion of CTAB-coated nanorods, the UV-vis absorption band around 800 nm changed to a shoulder on a long-wavelength band and a band around 500 nm was red-shifted (see Fig. 2(a) and 2(b)), indicating the formation of the large aggregates. The red shift in a UV-vis absorption band of CTAB-coated nanorods associated with coagulation was also reported in a solvent (methanol) of lower polarity than water [10]. CTAB on the nanorods could be released in relatively low polar solvents such as ethanol, methanol, acetone and acetonitrile/water mixtures.

On the other hand, for the VS-modified nanorods in a water/ethanol mixture, two plasmonic bands were seen at 519 and 824 nm after 24 h and were slightly shifted to 520 and 819 nm, respectively, after one week (see Fig. 2(c) and 2(d)). It is clear that the optimum modification by means of organosilanes produces the stability and the affinity of the gold nanorods in solvents of lower polarity such as ethanol. The similar tendency was observed in methanol, acetone and acetonitrile/water mixtures, different from as-prepared nanorods with CTAB shells, as described above. This difference of dispersity in mediums indicates that the affinity of gold nanorods with solvents can be varied by the modification with the organosilanes.

There have been many efforts made to modify the surface of gold nanorods. The gold nanorods were electrostatically coated by polyelectrolytes, where the polymers tend to cross-link among nanorods and produce large aggregates [13]. On surface reaction with thiol compounds, they preferentially reacted at the facet of short axis on the nanorod but not at the whole surface [3, 5, 14]. Additionally, SiO_2-coated gold nanorods were synthesized through polyelectrolyte coating [15] or thiol coupling [11, 12]. In the former, there are many steps to obtain the coated nanorods, and in the latter, CTAB on the nanorod surface was replaced with phosphatidylcholine to reduce the toxicity for living cells [16].

Industrial requirements in the surface modification of the gold nanorods are strong binding, whole covering, multi-functionalization, dispersibility in target solvents and simplicity of the procedure. From this viewpoint, we paid attention to the ‘silane-coupling reaction’. In that case, organosilanes as the coupling reagents are very easy to load with various functional groups, depending on the type of organosilanes used. On a target scaffold possessing OH groups, organosilanes covalent-bond and grow through polymerization. The reaction is completed by only a process of immersing the scaffold into the reaction medium for an appropriate period in the presence of a small quantity of water. Furthermore, depending on the function of the organosilanes, the solubility and stability of nanorods in an intended solvent are varied. Thus, the silane-coupling reaction with organosilanes is an available and advantageous way to load selected functional groups onto the gold nanorods, where the OH groups are provided.

The modification of gold nanorods using the formation of a siloxane bond (Si–O–Si) of inorganic silica was performed by some groups [10, 11, 15, 17]. Pérez-Juste *et al.* [11] have used MPS as a linker and sodium silicate as a shell precursor on the gold nanorod with a similar aspect ratio as in the present work. They mentioned that the CTAB caused the homogeneous reaction between silicates but contributed slightly to the heterogeneous reaction (shell formation). Both reactions were also observed in the present work, as described above. The shell thickness (5–7 nm) of the sodium silicate-modified nanorod in the literature [11] was slightly thicker than that (4 nm) of the organosilane-modified nanorod in the present work. The difference is due to the distinct experimental conditions, such as the type of precursors, concentration of the chemicals (Si, OH–) and growth period.

There is a report that three kinds of polyelectrolytes and a tetraethoxysilane (TEOS) were used as a linker and a shell maker, respectively, and finally thick silica shells (controllable between 12–52 nm) were formed surrounding gold nanorods [15]. In this case, the thick silica shells are not necessarily predominant in the optical or plasmonic coupling between adjacent nanorods (the plasmonic coupling can be dominantly observed, when the closest distance between adjacent gold nanorods with a cross-sectional radius of 5 nm is less than 20 nm in side-by-side arrangement [19]). Furthermore, the procedure of TEOS-modification consisted of three cycles of polymer deposition and centrifugation, involving the shell formation. Thus, the number of preparation steps is larger than that in the present organosilane-modification. The present work is the first report on the surface modification of gold nanorods with only organosilanes *via* a silane-coupling reaction. It is the advantage of the present procedure that, by using the only organosilanes (APS or VS), the thin shell structures were created efficiently through a fewer number of preparation steps.

Despite the wide availability of the gold nanorods that originate from their anisotropy, the on-demand surface modification has not been sufficiently often suggested. The difficulty of the surface modification mainly coming from the strong adsorption of CTAB on the gold nanorods was overcome by the modification which is triggered by the attachment of MPS on the nanorods, since CTAB molecules on the nanorods are substituted with MPS in some degree. After the treatment by the organosilanes (APS or VS), hydrophilic thin shells ($\sim$4 nm) were formed on the whole surface of the nanorods. Then these modifications enabled the gold nanorods to be protected by the organosilanes on their whole surfaces and provided the solubility and stability to the nanorods in less polar solvents than water. Thus it is concluded that the surface modifications of gold nanorods developed in the present work can achieve the stability in the intended solvents and change their affinities to chemicals. Then the modifications can relax the limitation in utility of gold nanorods and open up the possibility for the medical and industrial applications of gold nanorods.

Acknowledgements

KM appreciates the 21st COE programs (Program number 14COEB01-00 and 14COEB01-00) in Nagoya University for financial support.

References

1. K. Esumi, K. Matsuhisa and K. Torigoe, Preparation of rodlike gold particles by UV irradiation using cationic micelles as a template, *Langmuir* **11**, 3285–3287 (1995).
2. M. A. El-Sayed, Some interesting properties of metals confined in time and nanometer space of different shapes, *Acc. Chem. Res.* **34**, 257–264 (2001).

3. K. G. Thomas, S. Barazzouk, B. I. Ipe, S. T. S. Joseph and P. V. Kamat, Uniaxial plasmon coupling through longitudinal self-assembly of gold nanorods, *J. Phys. Chem. B* **108**, 13066–13068 (2004).
4. J. Pérez-Juste, I. Pastoriza-Santos, L. M. Liz-Marzán and P. Mulvaney, Gold nanorods: synthesis, characterization and applications, *Coordin. Chem. Rev.* **249**, 1870–1901 (2005).
5. P. K. Sudeep, S. T. S. Joseph and K. G. Thomas, Selective detection of cysteine and glutathione using gold nanorods, *J. Amer. Chem. Soc.* **127**, 6516–6517 (2005).
6. S. Link and M. A. El-Sayed, Size and temperature dependence of the plasmon absorption of colloidal gold nanoparticles, *J. Phys. Chem. B* **103**, 4212–4217 (1999).
7. X. Huang, I. H. El-Sayed, W. Qian and M. A. El-Sayed, Cancer cell imaging and photothermal therapy in the near-infrared region by using gold nanorods, *J. Amer. Chem. Soc.* **128**, 2115–2120 (2006).
8. T. K. Sau and C. J. Murphy, Seeded high yield synthesis of short Au nanorods in aqueous solution, *Langmuir* **20**, 6414–6120 (2004).
9. F. Kim, J. H. Song and P. Yang, Photochemical synthesis of gold nanorods, *J. Amer. Chem. Soc.* **124**, 14316–14317 (2002).
10. S. Chang, C. Shih, C. Chen, W. Lai and C. R. C. Wang, The shape transition of gold nanorods, *Langmuir* **15**, 701–709 (1999).
11. J. Pérez-Juste, M. A. Correa-Duarte and L. M. Liz-Marzán, Silica gels with tailored, gold nanorod-driven optical functionalities, *Appl. Surf. Sci.* **226**, 137–143 (2004).
12. C. Chen, Y. Lin, C. Wang, H. Tzeng, C. Wu, Y. Chen, C. Chen, L. Chen and Y. Wu, DNA-gold nanorod conjugates for remote control of localized gene expression by near infrared irradiation, *J. Amer. Chem. Soc.* **128**, 3709–3715 (2006).
13. A. Gole and C. J. Murphy, Polyelectrolyte-coated gold nanorods: synthesis, characterization and immobilization, *Chem. Mater.* **17**, 1325–1330 (2005).
14. H. Liao and J. H. Hafner, Gold nanorod bioconjugates, *Chem. Mater.* **17**, 4636–4641 (2005).
15. I. Pastoriza-Santos, J. Pérez-Juste and L. M. Liz-Marzán, Silica-coating and hydrophobation of CTAB-stabilized gold nanorods, *Chem. Mater.* **18**, 2465–2647 (2006).
16. H. Takahashi, Y. Niidome, T. Niidome, K. Kaneko, H. Kawasaki and S. Yamada, Modification of gold nanorods using phosphatidylcholine to reduce cytotoxicity, *Langmuir* **22**, 2–5 (2006).
17. S. O. Obare, N. R. Jana and C. J. Murphy, Preparation of polystyrene- and silica-coated gold nanorods and their use as templates for the synthesis of hollow nanotubes, *Nano Lett.* **1**, 601–603 (2001).
18. K. Mitamura, T. Imae, N. Saito and O. Takai, Fabrication and self-assembly of hydrophobic gold nanorods, *J. Phys. Chem. B* **111**, 8891–8898 (2007).
19. M. Gluodenis and C. A. Foss, Jr., The effect of mutual orientation on the spectra of metal nanoparticle rod–rod and rod–sphere pairs, *J. Phys. Chem. B* **106**, 9484–9489 (2002).