Available online at www.sciencedirect.com

ScienceDirect

materialstoday: PROCEEDINGS

Materials Today: Proceedings 2 (2015) 33 – 40

5th International conference on Advanced Nano Materials

Wet-chemical passivation of anisotropic plasmonic nanoparticles for LSPR-sensing by a silica shell

Matthias Thiele*, Isabell Götz, Steffen Trautmann, Robert Müller, Andrea Csáki, Thomas Henkel and Wolfgang Fritzsche

Leibniz Institute of Photonic Technology (IPHT), Dept. Nanobiophotonics, Albert-Einstein-Straße 9, 07745 Jena, Germany

Abstract

Metal nanoparticles showing the effect of localized surface plasmon resonance (LSPR), a collective oscillation of the conduction electrons upon interaction with light, represent an interesting tool for bioanalytics. This resonance is influenced by changes in the environment, and can be therefore used for the detection of molecular layers. The sensitivity, this means the extent of wavelength resonance shift per change in refractive index in the environment, represents an important performance parameter. It is higher for silver compared to gold particles, and is also increased for anisotropic particles. So silver triangles show a high potential for highly sensitive plasmonic nanoparticles. However, the stability under ambient conditions is rather poor.
The paper demonstrates the passivation of silver triangles by silica coating using a wet-chemical approach. It compares the sensitivity for particles with and without passivation, and visualizes the passivation effect in a high resolution, single particle TEM study.

Selection and peer-review under responsibility of TEMA - Centre for Mechanical Technology and Automation.

Keywords: plasmonic nanoparticles, silver nanoparticles, silver nanotraingles, silica-shell, core/shell particles

1. Introduction

Metal nanoparticles (meNP) allow new applications in medicine, optical imaging and sensing, since their optical behavior is strongly related to the localized surface plasmon resonance (LSPR) [12, 20, 27, 26]. This effect exists only for meNP that are smaller than the wavelength of the incident light, whereby the conductive electrons behave like an oscillating dipole which is excited by the resonance frequency [12]. Influenced by the material, shape, size and surrounding medium [8], the LSPR-peak position can be tuned over the whole optical spectra and beyond, to reach a large spectral variability (Fig. 1), which makes them suitable for a wide scope of applications [4, 18].

* Corresponding author. Tel.: 0049-3641-206-360
E-mail address: matthias.thiele@ipht-jena.de

Selection and peer-review under responsibility of TEMA - Centre for Mechanical Technology and Automation.
doi:10.1016/j.matpr.2015.04.005

MeNP could have a big impact especially as optical transducers for biological sensing, since they show a high signal, no bleaching and the possibility of a label-free sensing [2, 19] combined with a high sensitivity [5, 7]. An established sensing method is the variation of the particle surrounding, by changing the refractive index (RI) [14]. For example, for a DNA-biosensor, the meNP surface can be conjugated with DNA (capture DNA) [9, 11], that is complementary to the studied analyte DNA. In the presence of analyte DNA, it will bind (hybridize), resulting in a red-shift of the LSPR-signal [16, 22]. However, the meNP acts as a transducer of LSPR-sensor and has to be well chosen. One main issue is the sensitivity of a meNP, the ratio of the shift of the plasmon peak related to the RI-unit. It is know that form-anisotropic meNP can show a higher sensitivity compared to isotropic (spherical) ones, due to the strong, geometrically determined LSPR-field [15, 23]. So there is a stronger accumulation of the field at tips (like stars), corners (like rods) and edges compared to spherical ones [15, 17, 28]. A comparison of sensitivities of different meNP-shapes in solution clearly shows a high sensitivity for core/shell and alloy meNPs [20], but the highest sensitivity is shown by silver nanotriangles, which makes them ideal candidates for LSPR-sensing [13]. With respect to the size (edge length) it is furthermore possible to tune the LSPR-peak from UV-vis-range to near infrared (Fig. 1). Unfortunately, the stability of such silver-nanotriangles is rather poor, since they have a high surface energy and will be reshaped to spherical silver nanoparticles [6, 24]. Moreover, they are chemically reactive in ambient conditions. To overcome this problem they can be stabilized by using silica, to form a protective silica layer around the nanotriangles. A usual method for coating nanoparticles is the Stöber-method [21], where the meNP are used as seeds followed by subsequently growing of silica on their surface by a catalyzed condensation of TEOS (tetraethyl-orthosilicate) using ammonia [3]. However, since silver nanoparticles in general are known for their chemical instability against ammonia, it is even harder to encapsulate silver triangles without losing their shape [25]. To overcome this problem, we took advantage of other alkaline compounds and study their influence. We investigated the aging process of nanotriangles and will present the direct protective influence of the silica layer to the triangles. Finally we will show that the silica shell will have a high influence of the sensing behavior of the nanotriangles, but also that the protected triangles will still have good sensing qualities.

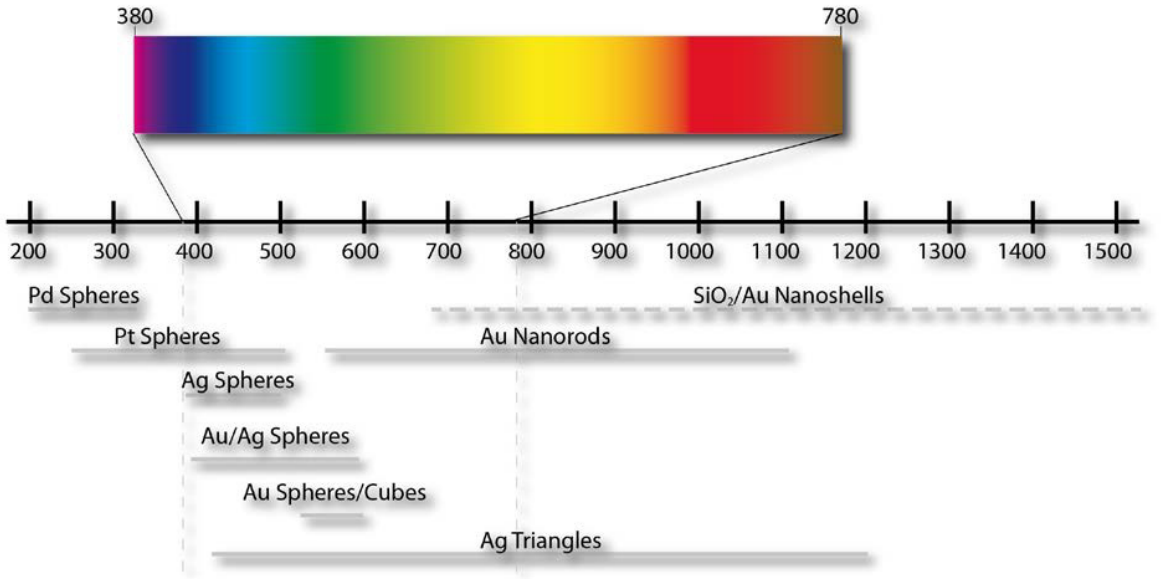

Fig. 1. Overview about the spectral ranges of plasmonic nanoparticles made by different materials and forms

2. Methods and Materials

2.1. Synthesis of silver nanotriangles

The production of silver nanotriangles is a modified method based on the work of Aherne et al [1]. This two-step synthesis is split in a synthesis part; in which silver seed particles with dimensions of about 14-150 nm are prepared. The second, the growing part uses the prepared seeds to start a two dimensional growth that results in silver triangles. For the seed synthesis, 5 ml sodium citrate (2.5 mM, Carl Roth GmbH + CO. KG, Karlsruhe, Germany) is used in a 15 ml PMMA centrifuge tube on a vortex mixer (Vortex-Genie 2; USA Scientific, Ocala FL). Under permanent shaking 250 µl Poly(sodium 4-styrenesulfonate) (0.5 g/l; 70 kDa, Sigma-Aldrich Chemie GmbH Munich, Germany) and 300 µl of a fresh, in ice water prepared $NaBH_4$ solution (10 mM, Carl Roth GmbH + CO. KG, Karlsruhe, Germany) are added. In the next step, 5 ml of $AgNO_3$ (0,5 mM; Merck KGaA Darmstadt, Germany) at a constant rate of 1 ml/min are added. After a few minutes of adding silver ions, the colorless solution turns from bright green/yellow to yellow (Figure 3 left tube).

After the synthesis is completed, the prepared seed particles are used to grow them to nanotriangles. For this purpose 5 ml ultrapure water in a 15 ml centrifuge tube is again used on a vortex mixer. Under strict shaking, 75 µl of a freshly prepared ascorbic acid solution (10 mM; Carl Roth GmbH + CO. KG, Karlsruhe, Germany) is added, followed by various amounts of the as-prepared seeds. The amount of seeds varies between 10 µl and 650 µl, the amount determining the edge length of the later triangles, that also correlates with the color of the solution and the LSPR-peak position as one can see in Fig 3. A high amount of seeds in the solution yields smaller triangles, whereby a low amount of seeds results in larger ones. After adding the seeds, 3 ml of $AgNO_3$ (0.5 mM) are added at a rate of 1 ml/min. Within a few seconds a color change is observed, starting from yellow to the appropriate color for the used amount of seeds. After the reaction is completed, it is necessary to add 500 µl of sodium citrate (25 mM) to achieve a charge stabilization of the triangles.

2.2. Silica-shell around the silver nanotriangles

The prepared triangles will be stabilized by adding a silica shell. For the preparation, 1 ml of the nano triangle solution was added to 7.51 ml ethanol containing the described concentration (1 mM, 2 mM and 4 mM) of TEOS (Sigma-Aldrich Chemie GmbH Munich, Germany) in a glass flask under rigorous stirring. To initialize the hydrolysis, 1.01 ml of an 8.8 M dimethylamine solution (DMA, Merck KGaA Darmstadt, Germany) was added and stirred for 2 days in the dark at 8°C. After the reaction is completed, the solution was washed two times by centrifugation, redispersed first in ethanol and finally in water.

2.3. Characterization

The prepared particles were stored in the dark at 8°C until they were characterized using transmission electron microscopy (TEM, Zeiss DSM 960, Jena, Germany), high resolution TEM (Jeol JEM_3010, Japan) and scanning force microscopy (Nanoscope III, Bruker Corporation Billerica, MA, USA). For the sensitivity measurements, refractive index series were prepared from different concentrations of D-glucose (Sigma-Aldrich Chemie GmbH Munich, Germany) in water from 0 to 60 m/V%. After mixing with the nanoparticles, the resulting plasmon peaks were measured using Jasco V-630 (JASCO Germany GmbH, Gross-Umstadt, Germany)

3. Results and Discussions

Silver triangles in various sizes were prepared as described. A wide range of colors of the various solutions is observed (Fig. 2a). Apparently it is the result of the different sizes, which lead to variations in the localized surface plasmon resonance (LSPR) bands. When comparing the color and the size of each particle preparation, the correlation between size and color of its resonance band become apparent (Fig. 2a). As already stated, the sensitivity

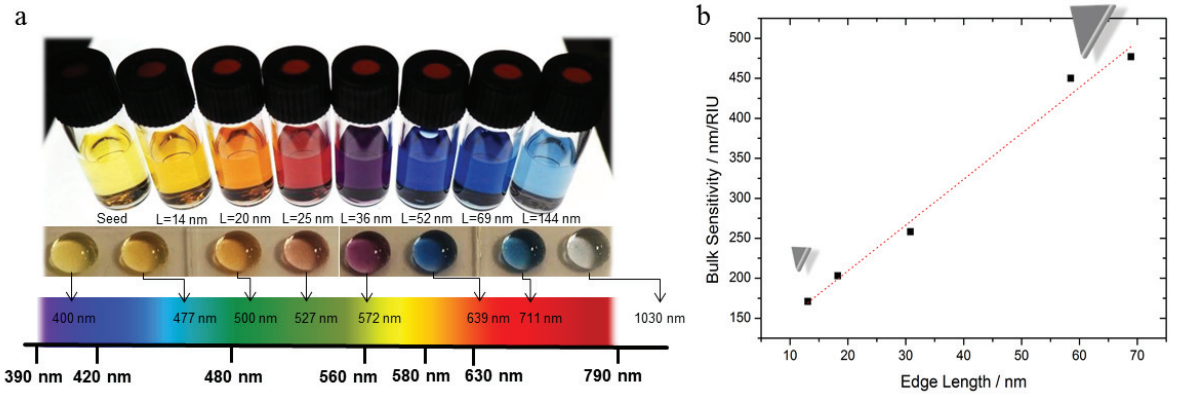

Fig. 2. (a) Solution of silver nanotriangles tuned from VIS to NIR with corresponding edge length (L) and LSPR-peak position.(b) Corresponding sensitivity in dependency on their dimension. In both cases are edge lengths calculated by setting the thickness to 8 nm (mean thickness from AFM) [1].

is of highest concern for possible sensing applications. Therefore, silver triangles of different sizes (edge lengths, L) were tested for their sensing properties using refractive index standards in solution (bulk sensitivity). A range of bulk-sensitivities between 200 and 600 nm/RIU were determined (Fig. 2b). A linear correlation between the size and the sensitivity was observed, whereas the bulk sensitivity can be calculated by equation one.

$$Bulk\ Sensitivity = 5.73 \cdot L + 94.40 \quad [nm/RIU] \tag{1}$$

In general, larger particles exhibit better sensitivity. However, at the same time, increasing size shifts the position of the LSPR band towards the infrared, moving out of the visible range. In conclusion, the particles show a convincing sensitivity in a suitable spectral range. When working with silver nanoparticles, a rather fast aging is observed [6, 28]. Thereby the surface seems to react with components of the atmosphere, resulting in an irreversible change. This process was studied on the ultramicroscopic scale at a single particle. While the particle scanned directly after synthesis shows the expected triangular shape (Fig. 3a), AFM imaging of the same particle after 12 hours in air shows significant structural changes: At all three corners, a significant growth of material is observed. This clearly results in a changed LSPR band, so that these particles have no defined and fixed LSPR band. This effect hinders a simple bioassay (measuring the same particle before and after analyte binding), but also the design of particles of a certain fixed LSPR band.

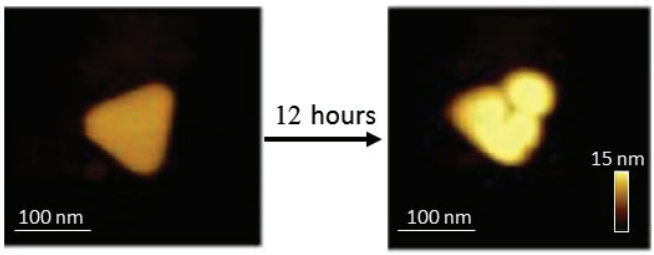

Fig. 3. AFM images of the same single triangle without a stabilizing silica layer/shell before (left) and after (right) aging for 12 hours in air.

A passivating layer as protection of the silver particle against the environment represents one approach to solve this problem. A silica coating of spherical silver particles was demonstrated using dimethylamine (DMA) [10] as source for the ammonia needed in the silica synthesis. In order to protect the more sensible silver nanotriangles, an additional protection layer of mercaptohexadecanoic acid (MHA) was introduced. We studied the stability of silver

nanotriangles in DMA and found that the particles only slowly decay (less than 10% loss in LSPR band amplitude in 10 min), so that for a fast and immediate starting reaction, the effect should be negligible. Therefore, the silica shells for the silver nanotriangles were synthesized using DMA.

Table 1. Used concentration of TEOS and corresponding LSPR-peak maxima, thickness of the generated silica shell and the radius of the tip as a marker for etching by using DMA as a basic catalyzer for the modified Stöber-method.

	Amount of precursor			
	no TEOS	1 mM TEOS	2 mM TEOS	4 mM TEOS
λ_{max}	666 nm	692 nm	689 nm	696 nm
Shell thickness	-	1.5 ± 0.8 nm	60 ± 5 nm	83 ± 6 nm
Tip radius	6.2 ± 1.8 nm	8.5 ± 0.8 nm	7.1 ± 1.4 nm	7.7 ± 1 nm

Varying the starting concentration of the silica-source TEOS, the thickness of the silica shell around the silver nanotriangles can be tuned between a very few and hundred nanometers (Tab. 1 and Fig. 4). Using this parameter, both thin layers (preserving the original nano triangle geometry) as well as large spherical shells are possible.

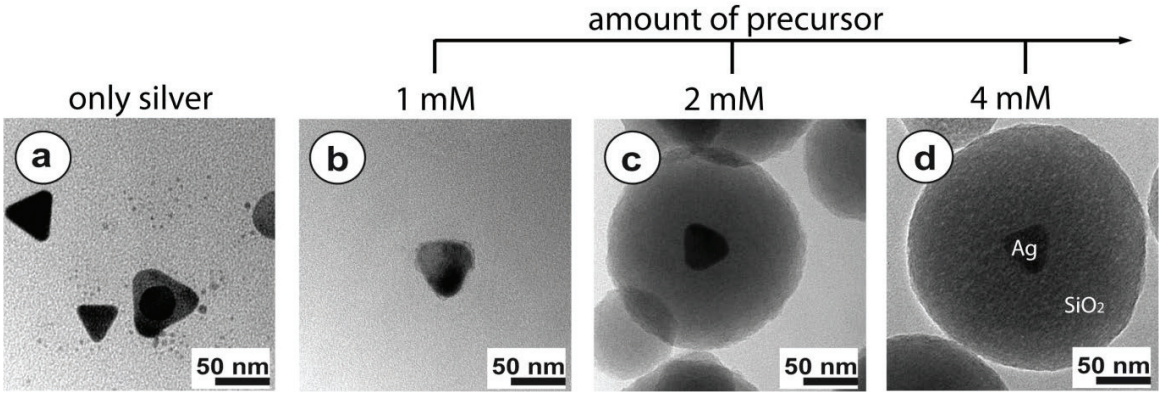

Fig. 4: Corresponding TEM-images to Table 1 of core-shell triangles with different silica shell thicknesses prepared with various concentrations of TEOS, starting from (a) 0 mM, (b) 1 mM to (c) 2 mM and finally (d) 4 mM.

For bioanalytical applications, the response of the LSPR signal of the particles to refractive index changes of the surrounding represents the key parameter. When the particles are covered by a passivating layer, is this response still observed? And to what extent? In order to clarify this issue, the sensitivity of particles of 56 nm side lengths was studied with and without a silica layer of 83 nm thickness. Therefore, the refractive index of the surrounding was changed, and the resulting wavelength shift in resonance measured and plotted as nm shift per refractive index unit (RIU). Nanotriangles without layer exhibited a sensitivity of about 555 nm/RIU (Fig. 5), which is in agreement with the plot shown in Fig. 2b. When a silica layer of about 83 nm was applied, a sensitivity of 283 nm/RIU was found. Compared to typical sensitivity values below 100 nm/RIU (Au spheres), 170 nm/RIU (Ag spheres) or 180 nm/RIU (Au nanorods), this value represents still a significant gain in sensitivity, now in combination with a stabilized nanoparticle and a surface which allows for standard attachment chemistry as utilized in the case of glass or silicon for DNA or protein microarray technologies.

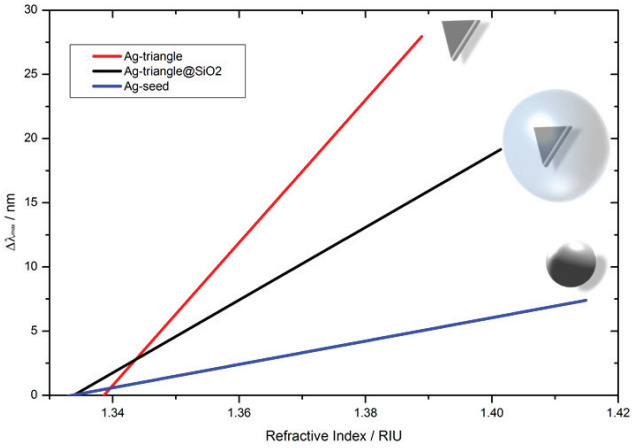

Fig. 5.Sensitivity of silver triangles with an edge length of around 56 nm with silica shell of 83 nm thickness (black line, 283nm/RIU) and without (black line, 555 nm/RIU). For comparison (the thickness of the triangles is 8 nm), the blue line represents a silver sphere of 8 nm diameter (91 nm/RIU).

For this quite thin protecting layer, a characterization of the protecting ability is quite challenging. Best visualization is achieved in a TEM, when the e-beam is absorbed accordingly by the various materials, with metals having a much higher contrast compared to silica as shown in Fig. 4. So single-particle studies were conducted in high-resolution TEM studying the behavior of the coated particles under the influence of the electron beam (Fig. 6), which is known to have damaging effect. In order to demonstrate the effect of the electron beam on protected as well as unprotected particles, a particle with an incomplete silica shell was chosen. Here, the silica cover showed two defects, which are marked by the red arrows in Fig. 6a. Following the effect of the electron beam over time, one can clearly see that the destructive processes starts on these sites of the pinholes. This observation demonstrates that the silica layer passivates the underlying silver against damaging effects, even on these small dimensions of just a few nanometers.

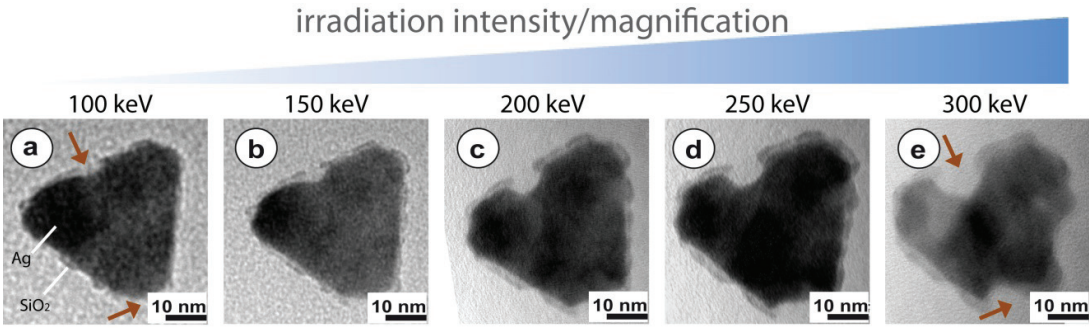

Fig. 6.Time series of a single, silica covered silver triangle in TEM, showing the structural disintegration under the influence of the electron beam. Silica thickness is less than 2 nm. This process clearly starts at the points where the silica cover is not complete (red arrows in a).

4. Conclusion

Passivation of silver nanotriangles allows an efficient protection of these otherwise often instable particles in combination with a preserved sensitivity. The utilization of a wet chemical approach for silica coating allows to control the thickness by variations of the synthesis parameters. The beneficial high sensitivity of the particles

towards refractive index change sensing is sufficiently preserved by this step, in combination with a strong protection. A high-resolution TEM study allowed to demonstrate this protection with a sub-particle resolution.

Acknowledgements

The authors acknowledge funding by DFG FR 1348/19-1 and DAAD PPP ID 57036145. We acknowledge the Leibniz Institute of Age Research – Fritz Lipmann Institute providing access to TEM and Katrin Buder for help with TEM measurements, and Andreas Undisz (FSU Jena) for assistance with high resolution TEM measurements.

References

[1] Aherne D, Ledwith D M, Gara M and Kelly J M 2008 Optical Properties and Growth Aspects of Silver Nanoprisms Produced by a Highly Reproducible and Rapid Synthesis at Room Temperature *Advanced Functional Materials* **18** 2005-16

[2] Dondapati S K, Sau T K, Hrelescu C, Klar T A, Stefani F D and Feldmann J 2010 Label-free Biosensing Based on Single Gold Nanostars as Plasmonic Transducers *ACS Nano* **4** 6318-22

[3] Guerrero-Martinez A, Perez-Juste J and Liz-Marzan L M 2010 Recent progress on silica coating of nanoparticles and related nanomaterials *Adv Mater* **22** 1182-95

[4] Huang T and Nancy Xu X H 2010 Synthesis and Characterization of Tunable Rainbow Colored Colloidal Silver Nanoparticles Using Single-Nanoparticle Plasmonic Microscopy and Spectroscopy *Journal of materials chemistry* **20** 9867-76

[5] Jakab A, Rosman C, Khalavka Y, Becker J, Trügler A, Hohenester U and Sönnichsen C 2011 Highly Sensitive Plasmonic Silver Nanorods *ACS Nano* **5** 6880-5

[6] Jiang, Zeng and Yu 2007 Thiol-Frozen Shape Evolution of Triangular Silver Nanoplates *Langmuir* **23** 2218-23

[7] Joshi G K, McClory P J, Dolai S and Sardar R 2012 Improved localized surface plasmon resonance biosensing sensitivity based on chemically-synthesized gold nanoprisms as plasmonic transducers *Journal of Materials Chemistry* **22** 923

[8] Kelly K L, Coronado E, Zhao L L and Schatz G C 2002 The Optical Properties of Metal Nanoparticles: The Influence of Size, Shape, and Dielectric Environment *The Journal of Physical Chemistry B* **107** 668-77

[9] Kim J-Y and Lee J-S 2010 Synthesis and Thermodynamically Controlled Anisotropic Assembly of DNA−Silver Nanoprism Conjugates for Diagnostic Applications *Chemistry of Materials* **22** 6684-91

[10] Kobayashi Y, Katakami H, Mine E, Nagao D, Konno M and Liz-Marzan L M 2005 Silica coating of silver nanoparticles using a modified Stober method *J Colloid Interface Sci* **283** 392-6

[11] Liu M, Wang Z, Zong S, Zhang R, Zhu D, Xu S, Wang C and Cui Y 2013 SERS-based DNA detection in aqueous solutions using oligonucleotide-modified Ag nanoprisms and gold nanoparticles *Anal Bioanal Chem* **405** 6131-6

[12] Mayer K M and Hafner J H 2011 Localized surface plasmon resonance sensors *Chem Rev* **111** 3828-57

[13] Millstone J E, Hurst S J, Metraux G S, Cutler J I and Mirkin C A 2009 Colloidal gold and silver triangular nanoprisms *Small* **5** 646-64

[14] Mock J J, Smith D R and Schultz S 2003 Local Refractive Index Dependence of Plasmon Resonance Spectra from Individual Nanoparticles *Nano Letters* **3** 485-91

[15] Nelayah J, Kociak M, Stephan O, Geuquet N, Henrard L, Garcia de Abajo F J, Pastoriza-Santos I, Liz-Marzan L M and Colliex C 2010 Two-dimensional quasistatic stationary short range surface plasmons in flat nanoprisms *Nano Letters* **10** 902-7

[16] Schneider T, Jahr N, Jatschka J, Csaki A, Stranik O and Fritzsche W 2013 Localized surface plasmon resonance (LSPR) study of DNA hybridization at single nanoparticle transducers *J Nanopart Res* **15** 1-10

[17] Senthil Kumar P, Pastoriza-Santos I, Rodriguez-Gonzalez B, Javier Garcia de Abajo F and Liz-Marzan L M 2008 High-yield synthesis and optical response of gold nanostars *Nanotechnology* **19** 015606

[18] Si G, Ma Z, Li K and Shi W 2011 Triangular Au–Ag Nanoframes with Tunable Surface Plasmon Resonance Signal from Visible to Near-Infrared Region *Plasmonics* **6** 241-4
[19] Sönnichsen C and Alivisatos A P 2004 Gold Nanorods as Novel Nonbleaching Plasmon-Based Orientation Sensors for Polarized Single-Particle Microscopy *Nano Letters* **5** 301-4
[20] Steinbruck A, Stranik O, Csaki A and Fritzsche W 2011 Sensoric potential of gold-silver core-shell nanoparticles *Anal Bioanal Chem* **401** 1241-9
[21] Stöber W, Fink A and Bohn E 1968 Controlled growth of monodisperse silica spheres in the micron size range *J Colloid Interface Sci* **26** 62-9
[22] Stranik O, Jatschka J, Csáki A and Fritzsche W 2014 Development of new classes of plasmon active nano-structures and their application in bio-sensing and energy guiding *Front. Phys.* 1-13
[23] Xia Y, Xiong Y, Lim B and Skrabalak S E 2009 Shape-controlled synthesis of metal nanocrystals: simple chemistry meets complex physics? *Angew Chem Int Ed Engl* **48** 60-103
[24] Xiong Y 2011 Morphological changes in Ag nanocrystals triggered by citrate photoreduction and governed by oxidative etching *Chem Commun (Camb)* **47** 1580-2
[25] Xue C, Chen X, Hurst S J and Mirkin C A 2007 Self-Assembled Monolayer Mediated Silica Coating of Silver Triangular Nanoprisms *Adv Mater* **19** 4071-4
[26] Yguerabide J and Yguerabide E E 1998 Light-Scattering Submicroscopic Particles as Highly Fluorescent Analogs and Their Use as Tracer Labels in Clinical and Biological Applications: I. Theory *Analytical Biochemistry* **262** 137-56
[27] Yguerabide J and Yguerabide E E 1998 Light-Scattering Submicroscopic Particles as Highly Fluorescent Analogs and Their Use as Tracer Labels in Clinical and Biological Applications: II. Experimental Characterization *Analytical Biochemistry* **262** 157-76
[28] Zijlstra P, Paulo P M, Yu K, Xu Q H and Orrit M 2012 Chemical interface damping in single gold nanorods and its near elimination by tip-specific functionalization *Angew Chem Int Ed Engl* **51** 8352-5