

Effect of the Alkyl Chain Length of Secondary Amines on the Phase Transfer of Gold Nanoparticles from Water to Toluene

Katarzyna Soliwoda,[†] Emilia Tomaszewska,[†] Beata Tkacz-Szczesna,[†] Ewelina Mackiewicz,[†] Marcin Rosowski,[†] Adam Bald,[‡] Christian Blanck,[§] Marc Schmutz,[§] Jiří Novák,^{||} Frank Schreiber,^{||} Grzegorz Celichowski,[†] and Jaroslaw Grobelny^{*,†}

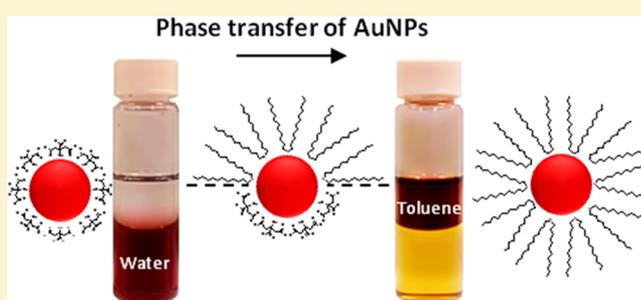
[†]Department of Materials Technology and Chemistry and [‡]Department of Physical Chemistry of Solutions, Faculty of Chemistry, University of Lodz, Pomorska 163, 90-236 Lodz, Poland

[§]Institut Charles Sadron, CNRS-Université de Strasbourg, 23 rue du loess, 67034 Strasbourg, France

^{||}Institute of Applied Physics, Eberhard Karls Universität Tübingen, Auf der Morgenstelle 10, 72076 Tübingen, Germany

S Supporting Information

ABSTRACT: In the present paper we describe a phase transfer of aqueous synthesized gold nanoparticles (AuNPs) from water to toluene using secondary amines: dioctylamine, didodecylamine, and dioctadecylamine. The effect of the hydrocarbon chain length and amount of amines on the transfer efficiency were investigated in the case of nanoparticles (NPs) with three different sizes: 5, 9, and 13 nm. Aqueous colloids were precisely characterized before the transfer process using UV–vis spectroscopy, dynamic light scattering (DLS), small-angle X-ray scattering (SAXS), and transmission electron microscopy (TEM). Nanoparticles were next transferred to toluene and characterized using UV–vis and DLS techniques. It was found that dioctadecylamine provides the most effective transfer of nanoparticles. No time-dependent changes in the NP size were observed after 12 days, showing that the dioctadecylamine-stabilized nanoparticles dispersed in toluene were stable. This indicates that long hydrocarbon chains of dioctadecylamine exhibit sufficiently hydrophobic properties of nanoparticles and consequently their good dispersibility in nonpolar solvent.



1. INTRODUCTION

Metal nanoparticles are attractive for catalysis,^{1–3} optics,^{4–6} electronics,^{7,8} and biology^{9–12} because of various unusual chemical and physical properties compared with metal atoms or bulk metal.¹³ Scientific interest is also motivated by the use of nanoparticles in the synthesis of new materials with improved resistance to wear.^{14,15}

Presently, a large body of work is concerned with using metal nanoparticles (NPs) in memory elements.^{16–18} It is already known that elements created by incorporation of metallic nanoparticles in organic or polymeric materials demonstrate a memory effect when subjected to an electrical bias.¹⁹ However, the use of nanoparticles in memory elements requires nonpolar solvents because polar solvents can cause damage of the surface structure of memory device components.

An important requirement in the case of using nanoparticles in electronic devices is to prepare stable and well-dispersed NPs in solvents commonly used in plastic electronics (e.g., dichlorobenzene,¹⁶ toluene,^{20,21} methyl benzoate,²² *n*-hexane, ethyl acetate, etc.). However, the most important issue in electronic devices is to prepare nanoparticles repeatedly isolated on the specific surface or substrate. The idea to solve this problem is to functionalize the NP surface with the

appropriate ligand that will prevent nanoparticles from agglomeration and/or aggregation in nonpolar solvent or while being deposited on the substrate. Moreover, in the case of the memory device the choice of the surface modifier is crucial as the substances present on the NP surface determine the electronic behavior of the device. Therefore, the choice of a suitable nanoparticle surface modifier is a very interesting matter to study.

There are different possible methods to obtain nanoparticles in nonpolar solvents, e.g., transfer during nanoparticle synthesis (e.g., the Brust–Schiffrin method^{23,24}) and transfer of water-synthesized nanoparticles with ligand exchange^{25,26} or via electrostatic interactions.²⁷ A phase transfer process gives the opportunity not only to obtain nanoparticles in nonpolar solvent but also represents an effective way to functionalize nanoparticles with a suitable ligand. Hence, the phase transfer involving ligand exchange is an important issue in obtaining nanoparticles with different functional groups. In a phase transfer process nanoparticles are first prepared in water under

Received: March 25, 2014

Revised: May 21, 2014

Published: June 3, 2014

optimized conditions and then subjected to ligand exchange to realize the phase transfer from an aqueous solution to organic media. Although this method involves two steps and requires additional stabilizing agents, it provides great control of the particle size and degree of polydispersity in nonpolar solvent.²⁸ Moreover, all reagents that may have a negative impact, especially in the case of electronic applications, remain in the aqueous phase (e.g., byproducts of NP synthesis). Presently, there are numerous protocols for the transfer of water-prepared nanoparticles to organic media using thiols,^{20,29–31} alkylamines,^{25,32} phosphines,³³ carboxylic acids,^{34,36} etc.

It is well-known that the thiol group provides good dispersibility and stability of the nanoparticles in organic media.^{17–20} Although amines form only a weak bond with the gold surface, the amine-modified nanoparticles are also very stable in nonpolar solvents.²⁸ Therefore, secondary amines can potentially be used as ligands in a phase transfer process and can be useful in obtaining densely packed self-organized structures on the substrate.

In this paper we describe the use of secondary amines that consist of two long alkyl chains in the AuNP phase transfer process from water to toluene. It is expected that these amines will provide AuNPs with hydrophobic properties and consequently good stability and dispersibility in toluene. Therefore, it is of interest to research whether and how secondary amines with different chain lengths act as phase transfer and stabilizer agents for gold nanoparticles (AuNPs) in nonpolar solvent. Moreover, it has been studied how the secondary amine concentration affects the stability of gold nanoparticles in toluene. To the authors' knowledge, the comparative studies connected with the transfer of gold nanoparticles to toluene using secondary amines such as dioctylamine, didodecylamine, and dioctadecylamine are presented for the first time.

2. EXPERIMENTAL SECTION

2.1. Preparation of Aqueous Colloids. The aqueous AuNP colloids [colloid 1 (5 nm, 100 ppm), colloid 2 (9 nm, 50 ppm), and colloid 3 (13 nm, 110 ppm)] were prepared according to the chemical reduction method (see the Supporting Information).

2.2. Nanoparticle Surface Modification and the Phase Transfer Process. For the surface modification of gold nanoparticles three secondary amines with different chain lengths were used: dioctylamine [(C₈H₁₇)₂NH], didodecylamine [(C₁₂H₂₅)₂NH], and dioctadecylamine [(C₁₈H₃₅)₂NH]. The alkylamines with long hydrophobic chains were selected as AuNP surface modifiers because of a good potential ability to stabilize the metal organosols for a long time. The surface structures of amines used for nanoparticle modification are shown in Figure 1 (calculations with a single molecule using HyperChem: geometrical optimization MM+, Polak–Ribiere algorithm, terminal condition RMS gradient 0.1 kcal/Å·mol in vacuo).

For the phase transfer process each of the modifiers was prepared as a 0.01% toluene solution. The modifier amount corresponds to 5, 10, 20, 50, and 100 modifier molecules/nm² of NP surface. To fully replace the ligand already adsorbed on the NP surface (citrate), an excess of incoming ligand (amine) should be provided. Moreover, the process of AuNP stabilization with amines in toluene is an equilibrium process in which the ligand adsorption and desorption processes constantly occur. Hence, the excess amine was primarily necessary for the effective phase transfer process of AuNPs from water to toluene and secondarily to obtain stable organic colloids. Because of the unbound excess amines, it was not possible to accurately determine the number of ligand molecules adsorbed on the surface of the NPs as was done by Rosa et al.³⁵

AuNPs were transferred from water to toluene by modifying them with dioctylamine, didodecylamine, and dioctadecylamine. To the

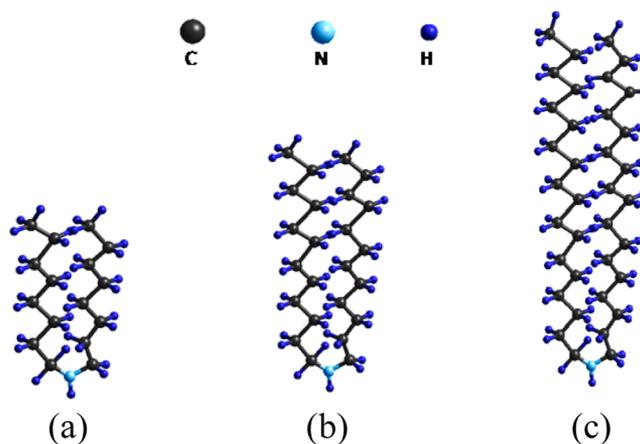


Figure 1. Structures of secondary amines used for surface modification of gold nanoparticles: dioctylamine [(C₈H₁₇)₂NH] (a), didodecylamine [(C₁₂H₂₅)₂NH] (b), and dioctadecylamine [(C₁₈H₃₅)₂NH] (c).

aqueous nanoparticle colloid 1, 2, or 3 were added acetone and toluene with one of the amines. Acetone was added to reduce the surface tension between the water and toluene phases.³⁶ The weight ratio of aqueous colloid to acetone to toluene was 2:1:1. The biphasic system was shaken for 5 min and then left for another 2 min. Subsequently, the system spontaneously separated into two layers, a toluene phase and a water phase, which were investigated using UV–vis and dynamic light scattering (DLS) techniques.

2.3. Characterization of Gold Nanoparticles. The UV–vis spectra of the original and transferred nanoparticles as well as the water phase after the transfer process were recorded to confirm the success of the phase transfer process. A UV–vis spectrophotometer (USB2000 + detector (miniature fiber optic spectrometer), Ocean Optics, HL-2000 (tungsten halogen light sources), with 1 cm quartz cuvette) was used. Moreover, aqueous colloids 1–3 and toluene phases after the transfer process were analyzed for NP size and size distribution using the DLS technique. The DLS measurements were carried out with a DLS Nano ZS Zetasizer system (Malvern Instruments). A He–Ne laser with the wavelength at 633 nm was used as the light source, and the measurements were performed with a scattering angle of 173° (a measurement temperature of 25 °C; aqueous colloids, medium viscosity 0.887 mPa·s, material refractive index 1.330; toluene colloids, medium viscosity 0.556 mPa·s, dispersant refractive index 1.496, material refractive index 1.330). Aqueous nanoparticle colloids were filtered out through a 0.1 μm poly(vinylidene fluoride) (PVDF) membrane before the measurements. Transmission electron microscopy was performed on a TECNAI G2 Sphera. The images were acquired with an Eagle2K slow-scan charge-coupled device (ssCCD) camera (FEI). Samples for transmission electron microscopy (TEM) were prepared as follows: A 5 μL volume of the aqueous colloids was deposited onto a freshly glow discharged carbon-covered copper grid (400 mesh). The suspension was left for adsorption of nanoparticles on the carbon support for 2 min, and the remaining solution was removed using filter paper. The analysis software was used for measurements of the NP size, and the size distribution histogram was obtained from a selection of 2000, 1000, and 400 nanoparticles for samples 1–3, respectively. The small-angle X-ray scattering (SAXS) measurements were performed at the ID02 beamline at the European Synchrotron Radiation Facility (ESRF; Grenoble, France). Colloids 1–3 were added to 2 mm capillaries for the scattering experiments. The beamline was set to an X-ray wavelength of 0.1 nm, and the scattered intensity was collected using a Frelon Kodak CCD camera at a distance of 2 m from the sample. The recorded 2D patterns were azimuthally integrated to one-dimensional scattering functions, $I(q)$. The SAXS signals from solutions of the reaction products without the gold nanoparticles, corresponding to the respective colloids, were used for the background scattering correction.

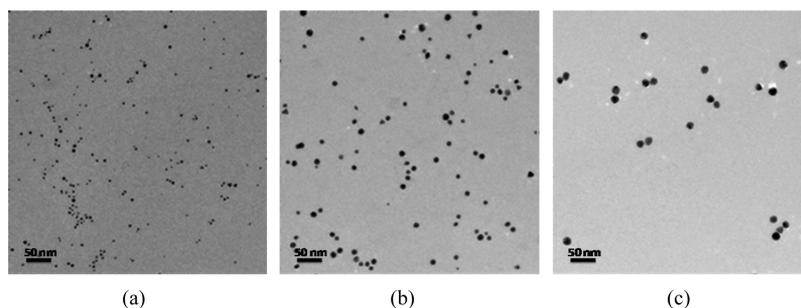


Figure 2. TEM micrographs of the citrate-stabilized AuNPs of colloid 1 (a), colloid 2 (b), and colloid 3 (c). The scale bar in all three micrographs is 50 nm.

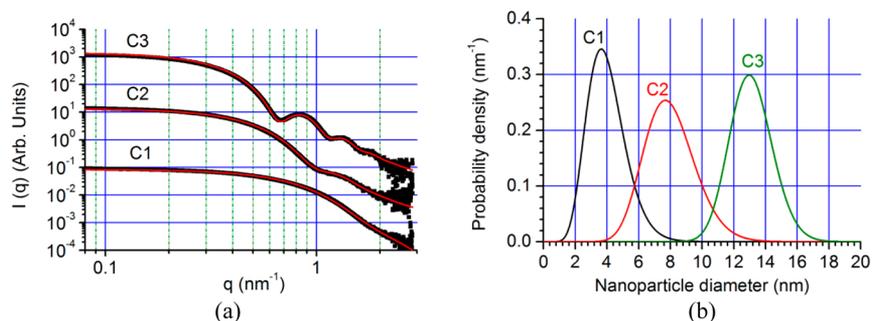


Figure 3. (a) Small-angle X-ray scattering profiles measured on colloids 1–3 (black points) and best simulations of the measured data using the SAXS model described in the text (full red lines). (b) Size distributions of NPs in colloids 1–3 (curves C1–C3), which correspond to the best fits of SAXS data in (a).

3. RESULTS AND DISCUSSION

3.1. Nanoparticle Characterization. Before the phase transfer process aqueous colloids 1–3 were precisely characterized using UV–vis, DLS, and TEM techniques. The maximum of the absorption band was recorded at $\lambda_{\text{max}} = 521$ nm, $\lambda_{\text{max}} = 529$ nm, and $\lambda_{\text{max}} = 518$ nm for colloids 1–3, respectively (Figure S1, Supporting Information). The mean size of the gold nanoparticles determined from DLS measurement was 9 ± 2 , 15 ± 3 , and 18 ± 3 nm for colloids 1–3, respectively (Figure S1). Moreover, the DLS measurements also revealed that the colloids are highly monodisperse without any agglomerates or aggregates.

The size and monodispersity of the nanoparticles in all three colloids were also investigated using TEM and the SAXS technique.

Figure 2 shows representative TEM images of colloids 1–3. It is clear from the pictures that the nanoparticles are highly monodisperse with a mean size of about: 5 ± 1 , 9 ± 2 , and 13 ± 1 nm for colloids 1–3, respectively. The shape of the nanoparticles is spherical in all cases.

Additionally, SAXS was used for the determination of the size and polydispersity of the NPs. The measured SAXS profiles of colloids 1–3 are shown in Figure 3a. The information on the NP size was retrieved by modeling measured SAXS curves using calculations of scattering on spherical nanoparticles, $I(q) = A \langle |F(q,R)|^2 \rangle_R$. Here, A is a proportionality constant, $F(q,R) = 4\pi R^3 \frac{(\sin qR - qR \cos qR)}{(qR)^3}$ is the form factor of a sphere of radius R , and $\langle |F(q,R)|^2 \rangle_R$ stands for averaging over scattering potentials of nanoparticles of different radii. The polydispersity of the nanoparticle size was taken into account by considering the Schultz statistical distribution of the nanoparticle core radii.³⁷ Optimal model parameters, including the average diameter of the NPs and their polydispersity, were

obtained via minimization of the sum of squares of differences between the experimental and model data using the Levenberg–Marquardt algorithm.³⁸ The best fits of the experimental SAXS data are shown in Figure 3a by continuous red lines. The corresponding average diameters of the NPs in colloids 1–3 amount to 4.0 ± 1.0 , 8.0 ± 0.5 , and 13.1 ± 0.1 nm, respectively, and the relative polydispersities (i.e., relative size variance) were $30 \pm 10\%$, $20 \pm 3\%$, and $10.2 \pm 0.5\%$, respectively. The size distributions of the respective colloids derived from the size parameters are shown in Figure 3b.

The sizes of the nanoparticles measured using the DLS and TEM/SAXS techniques are different. As expected the size of the nanoparticles from DLS measurements is bigger than that from the TEM and SAXS techniques. This is because in DLS the hydrodynamic size is measured whereas in TEM/SAXS the geometric size of NPs deposited on the surface is measured.³⁹ Therefore, the size of the nanoparticles from DLS measurements was not taken into account for the calculation of the average size of the gold nanoparticles in colloids. The average size of nanoparticles from TEM and SAXS measurements is 5 ± 1 , 9 ± 2 , and 13 ± 1 nm for colloids 1–3, respectively. It was crucial to precisely determine the size and shape of the NPs to define the nanoparticle surface area available for modification as the amount of amines used for modification corresponds to the number of modifier molecules per square nanometer of NP surface and is equal to 5, 10, 20, 50, and 100.

3.2. Surface Modification and the Phase Transfer Process. The effect of the surface modification of nanoparticles with secondary amines was easily visible as water phase discoloration and corresponding organic phase coloration or formation of a precipitate at the interface (Table S1, Supporting Information). For each of the amines used the surface of the nanoparticles was modified by exchanging the original ligand with dioctylamine, didodecylamine, and dioctadecylamine. The

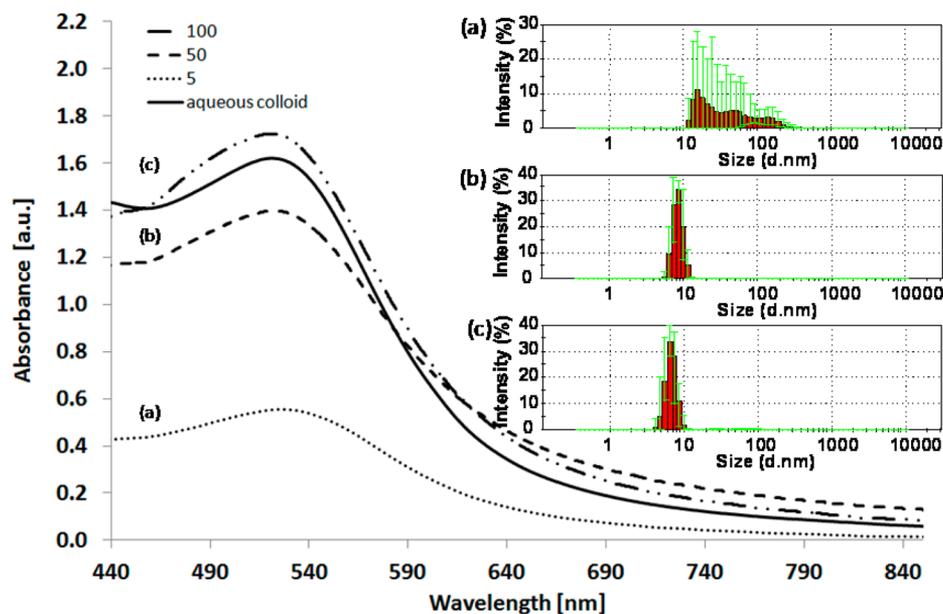


Figure 4. UV–vis spectra of colloid 1 before and after the phase transfer process with the use of different amounts of didodecylamine $[(C_{12})_2NH]$: 5, 50, and 100 modifier molecules/nm² of NP surface with the corresponding size distribution histograms obtained from DLS measurement.

research indicates that the surface modification of gold nanoparticles with amines through the phase transfer process occurs via a ligand exchange mechanism. Yang et al.⁴⁰ suggested that the modification of citrate-stabilized AuNPs with alkylamines through the phase transfer process from water to organic solvents occurs via a ligand exchange mechanism. Leff et al.⁴¹ investigated organically soluble gold nanocrystals functionalized with primary amines using IR, NMR, UV–vis, MS, X-ray photoelectron spectroscopy (XPS), TEM, X-ray diffraction (XRD), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and elemental analysis. They showed that the amine/gold surface interaction is charge-neutral and is best described by a weak covalent bond. Moreover, TGA measurements confirmed that gold nanocrystals are indeed almost exclusively covered by neutral amine ligands. The secondary amines are very similar to alkylamines in regard to headgroup reactivity, which determines the type of interactions with the AuNP surface. Therefore, there are no contraindications to the ligand exchange as a mechanism of phase transfer of NPs from water to toluene in the case of secondary amines. It is obvious that the degree of citrate ion displacement by the amines may not be equal to 100% and both citrate and amines may be adsorbed on the surface of the NPs. However, the high phase transfer process efficiency and the high stability of NPs in nonpolar solvent (toluene) indicate a sufficient surface modification of NPs with a hydrophobic compound (secondary amine).

3.3. Effect of the Modifier Type and Modifier Concentration. **3.3.1. Dioctylamine $[(C_8H_{17})_2NH]$.** In the case of two of the three colloids (1 and 2), the surface of AuNPs is modified with dioctylamine but the phase transfer does not occur and nanoparticles are agglomerated at the interface. Even an increase of the modifier amount does not allow the efficient phase transfer of nanoparticles from water to toluene. In the case of colloid 3 an increase of the modifier amount allows the nanoparticles to transfer from the aqueous phase to the organic solvent. However, the hydrocarbon chain length of the modifier is too short to ensure stabilization of the nanoparticles in toluene. It may be surprising that in the case of

dioctylamine it was not possible to transfer smaller nanoparticles—colloids 1 and 2 (NP sizes about 5 and 9 nm, respectively)—but it was possible to transfer nanoparticles from colloid 3 (13 nm). However, these colloids were synthesized using different procedures (see the Experimental Section). It is obvious that the synthesis reagents affect the nanoparticle surface conditions and consequently the surface availability for further modification. In the case of colloids 1 and 2 the citrate ions and products of tannic acid oxidation as well as their complexes may be adsorbed on the nanoparticle surface. Thus, in the case of colloids 1 and 2 the nanoparticle surface availability for further modification may be substantially low in comparison with that of colloid 3 synthesized without sodium citrate. The toluene phase has a gray color in the case of AuNPs (colloid 3) modified with dioctylamine. This indicates that dioctylamine allows transfer of gold nanoparticles to toluene, but the chain length of this modifier is too short to fully stabilize nanoparticles in the organic phase.

3.3.2. Didodecylamine $[(C_{12}H_{25})_2NH]$. In the case of colloid 1 the use of didodecylamine as a surface modifier allows the transfer of nanoparticles from the aqueous phase to toluene. The maximum of the absorption band was observed in the characteristic region at about 520–530 nm (Figure 4). The use of a small amount of didodecylamine (5 molecules/nm² of NP surface) causes the nanoparticles to be present in both phases as well as at the interface. Agglomerates are also present in the organic phase, which can be easily seen in the size distribution histograms from DLS measurements (Figure 4 a).

The increase of the modifier amount not only increases the phase transfer efficiency but simultaneously provides nanoparticles with better stability (Figure 4b,c). The size of the nanoparticles after the phase transfer to toluene with didodecylamine is approximately 8 nm without any agglomerates in the case of 50 or 100 molecules/nm² of NP surface. The nanoparticle size (colloid 1) after the phase transfer (8 ± 1 nm) differs slightly from the size of nanoparticles in water (9 ± 2 nm), and these changes are within the measurement error.

In the case of colloid 2 (9 nm) the use of didodecylamine allows the surface modification of AuNPs but does not allow

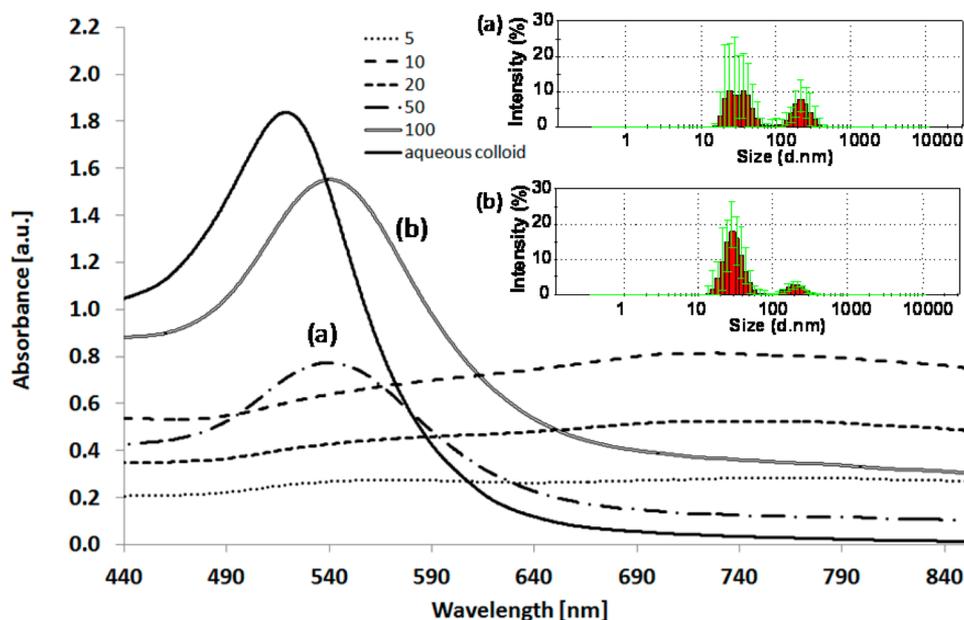


Figure 5. UV-vis spectra of aqueous colloid 3 (13 nm) before and after the phase transfer process with the use of different amounts of didodecylamine $[(C_{12})_2NH]$: 5, 10, 20, 50, and 100 modifier molecules/ nm^2 of NP surface with the corresponding size distribution histograms obtained from DLS measurement.

the phase transfer of nanoparticles from the aqueous phase to toluene. Modified nanoparticles were present as a precipitate at the interface. It is well-known that the transfer efficiency is influenced by the type and amount of the modifier as well as the type of solvent. Other factors affecting the phase transfer process are the size of the nanoparticles and the NP surface conditions—the type of molecules adsorbed on the NP surface. In the case of colloid 2 the size of the nanoparticles (9 nm) is too “big” and the modifier chains are too short to ensure NP dispersibility in nonpolar solvent. The hydrophobic interactions provided by the exchanging ligands on these nanoparticles can be too weak to pull nanoparticles to the toluene. As a consequence, NPs are at the interface in the form of a precipitate.

In the case of colloid 3 (13 nm) the use of didodecylamine allows the surface modification of AuNPs independent of the modifier amount used, but a stable colloid in toluene was obtained when at least 50 modifier molecules/ nm^2 of nanoparticle surface were used (Figure 5).

For these samples the characteristic maximum of the absorption band was observed on UV-vis spectra at $\lambda_{\text{max}} = 541$ nm and $\lambda_{\text{max}} = 545$ nm for 50 and 100 modifier molecules/ nm^2 of NP surface, respectively. The most effective was a phase transfer with the use of 100 modifier molecules/ nm^2 of NP surface as in this case the absorption band is the most intense. However, the nanoparticle bands after the transfer process are broader and shifted toward longer wavelengths compared with those of the aqueous colloid (518 nm). The band shape and maximum position as well as DLS results clearly indicate the aggregation and/or agglomeration of nanoparticles in organic solvent.

3.3.3. Dioctadecylamine $[(C_{18}H_{35})_2NH]$. An effective phase transfer process from water to toluene was observed in the case of colloid 1 modified with dioctadecylamine. This process was independent of the modifier amount used, i.e., 10, 20, or 50 molecules/ nm^2 of NP surface. All of the dioctadecylamine-modified nanoparticles (colloid 1) displayed a characteristic

AuNP single plasmon resonance in the visible region with λ_{max} at about 525 nm (Figure 6).

The absorption band is the most intense in the case of 50 modifier molecules/ nm^2 of NP surface, which indicates that in this case the phase transfer process was the most effective (Figure 6c). Further increasing the modifier amount to 100 molecules/ nm^2 of NP surface does not increase the efficiency of the phase transfer process (results not shown). This indicates that for the effective transfer of colloid 1 to toluene with dioctadecylamine there is no need to use more than 50 modifier molecules/ nm^2 of NP surface. It should also be noted that in none of the water phases after the phase transfer process were nanoparticles observed (Figure 6). Thus, in the case of 10 modifier molecules/ nm^2 of NP surface, some of the nanoparticles must be present at the interface because the absorption band is less intense than in the other cases (20 or 50). The NP size after transfer to toluene with dioctadecylamine does not change in any case compared to that of aqueous nanoparticles and is about 9 nm. This indicates that the use of even a small amount of dioctadecylamine provides a good stabilization of nanoparticles in toluene. Moreover, gold nanoparticles in toluene are stable over time. The maximum of the absorption band in the UV-vis spectrum recorded after 12 days does not change in any case. The DLS results also indicate that the size of the nanoparticles is stable with time.

For colloid 2 (9 nm) the surface modification occurs in all cases. This was observed by discoloration of the aqueous phase after the phase transfer process. The maximum of the absorption band for toluene colloids was observed at a wavelength of 527 nm (Figure 7).

No peak related to gold nanoparticles was observed in the case of aqueous phases after the transfer process. The almost complete loss in intensity of the surface plasmon vibration band indicates that close to 100% phase transfer of the modified nanoparticles from water to toluene had occurred. The band maximum for toluene colloids does not shift in time, which indicates system stability. The AuNP mean size in toluene

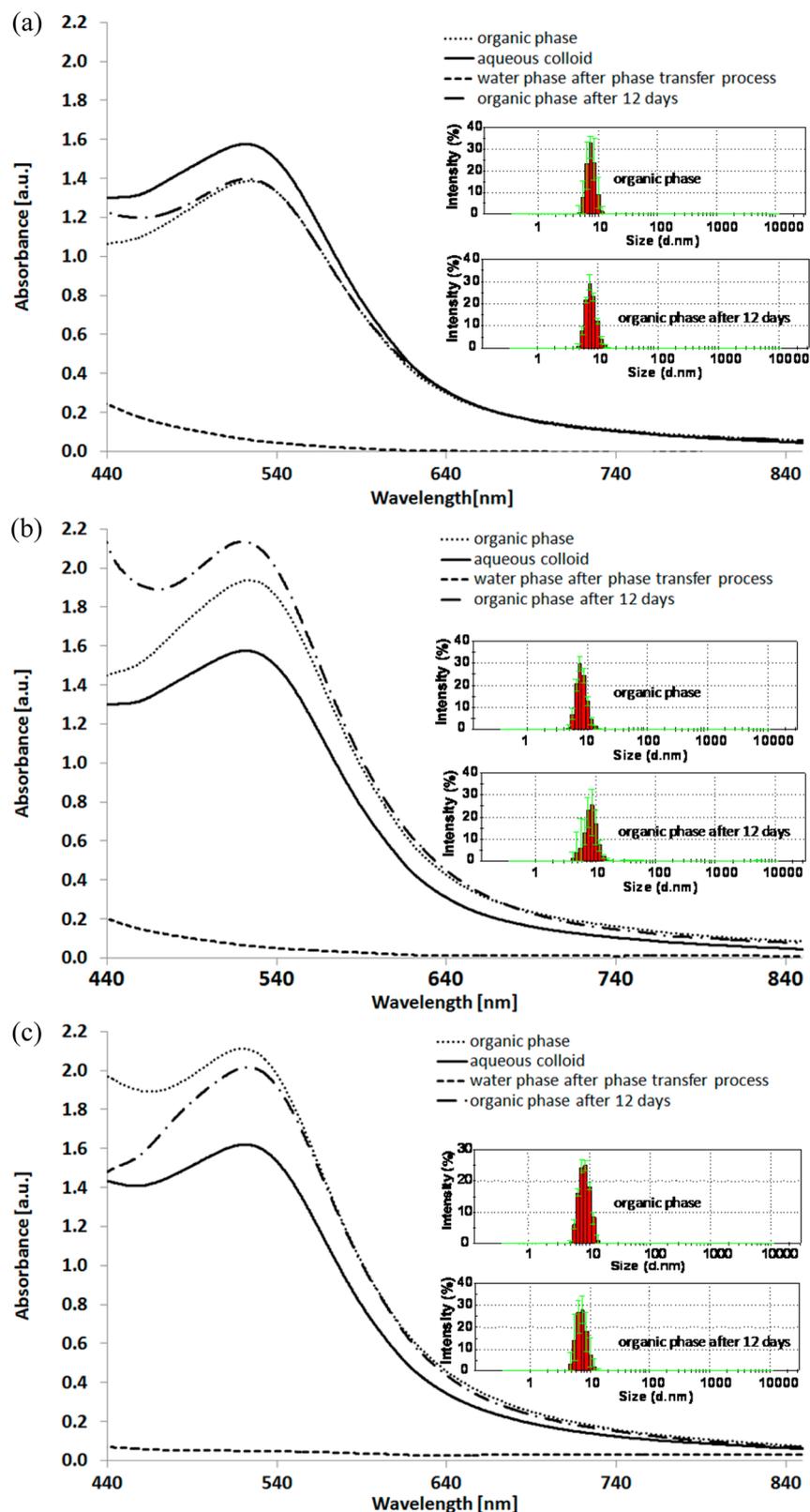


Figure 6. UV–vis spectra of colloid 1 (5 nm) after the phase transfer process with different amounts of dioctadecylamine $[(C_{18})_2NH]$: 10 (a), 20 (b), and 50 (c) modifier molecules/nm² of NP surface with corresponding size distribution histograms after the phase transfer and after 12 days measured using the DLS technique.

measured by DLS is about 12 ± 2 nm. The slight changes observed in the size of AuNPs modified with amine in toluene compared to that of aqueous colloids (15 ± 3 nm) are caused by the changes in the NP surface modifier. In the case of

aqueous colloids the hydrodynamic diameter measured in DLS depends on the substances adsorbed on the NP surface and the thickness of the electrical double layer that moves with the nanoparticle (citrate ions in aqueous colloids), which depends

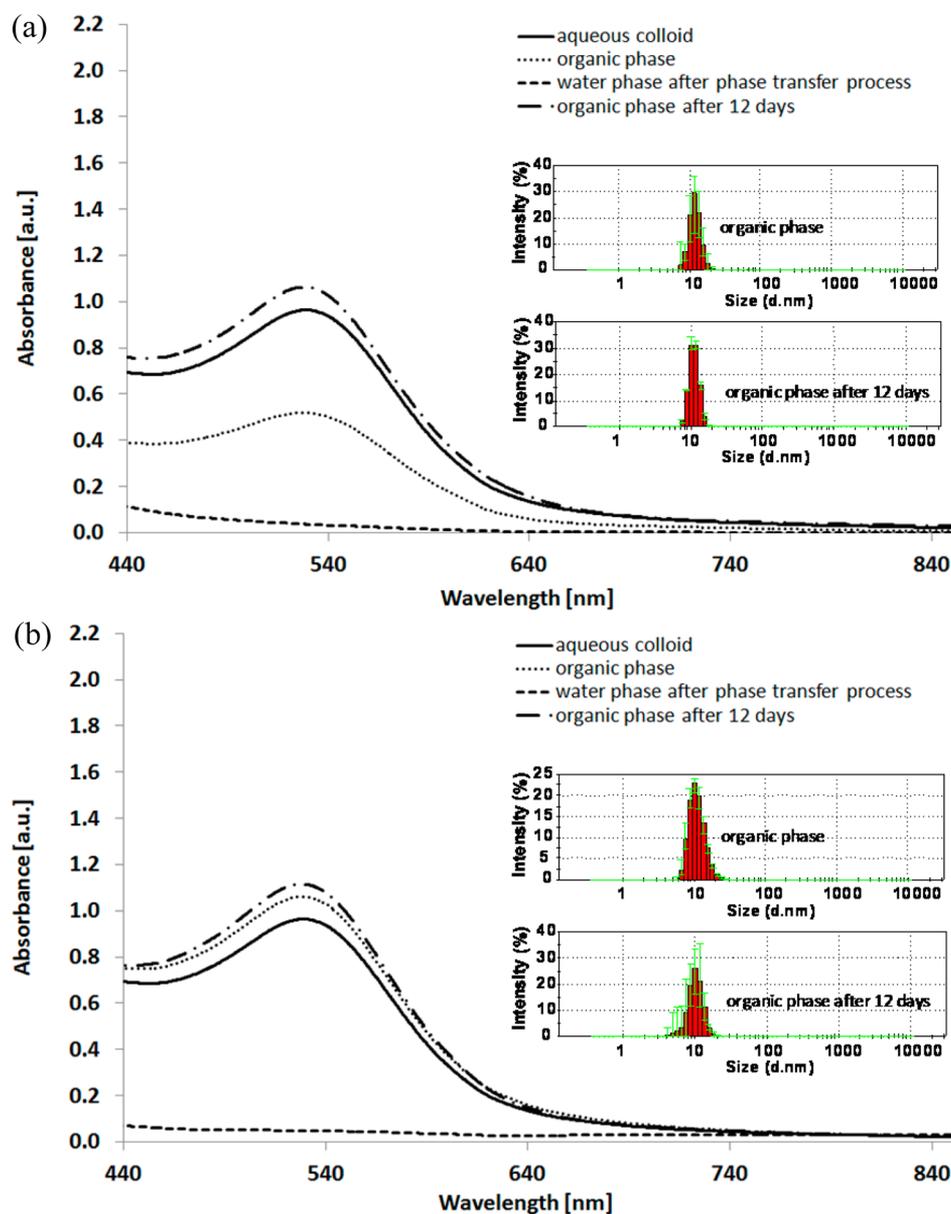


Figure 7. UV-vis spectra of colloid 2 (9 nm) after the phase transfer process with different amounts of dioctadecylamine $[(C_{18})_2NH]$: 20 (a) and 50 (b) modifier molecules/ nm^2 of NP surface with corresponding size distribution histograms after the phase transfer and after 12 days measured using DLS.

on the substances both present in the colloid and adsorbed on the NPs. In contrast, in the case of AuNPs modified with amines in toluene, no double layer is present and the NP size is connected to its hydrodynamic size, which is enlarged by the ligand layer adsorbed on its surface. Thus, the NP sizes in water and toluene may differ slightly.

The most effective phase transfer of AuNPs modified with dioctadecylamine to toluene was observed in the case of colloid 3 (13 nm) (Figure 8). Even the use of a small amount of dioctadecylamine (10 molecules/ nm^2 of NP surface) causes the transfer of gold nanoparticles to toluene (Figure 8a). This was observed by discoloration of the aqueous phase and simultaneously the dark red coloration of the toluene phase after the phase transfer process. The maximum of the absorption bands for toluene systems was observed at about 526 nm in each case. These bands are slightly shifted compared to that of the aqueous colloid ($\lambda_{\text{max}} = 518 \text{ nm}$). This is due to

the changes in the refractive index of the medium from water ($n = 1.330$) to toluene ($n = 1.494$). No characteristic band at 520–530 nm was observed for water phases after the transfer process.

The size of the dioctadecylamine-modified nanoparticles in toluene measured using the DLS technique is about $17 \pm 2 \text{ nm}$ (Figure 8) and is negligibly different from the NP size in aqueous colloid 3 (18 nm). No changes in the position of the absorption band or the size of the nanoparticles were observed over time. This clearly indicates the stability of modified nanoparticles in toluene.

4. CONCLUSIONS

Aqueous synthesized gold nanoparticles were successfully transferred from water to toluene with the use of a secondary amine. The transfer process took place via the ligand exchange mechanism (citrate to amine). Three different ligands,

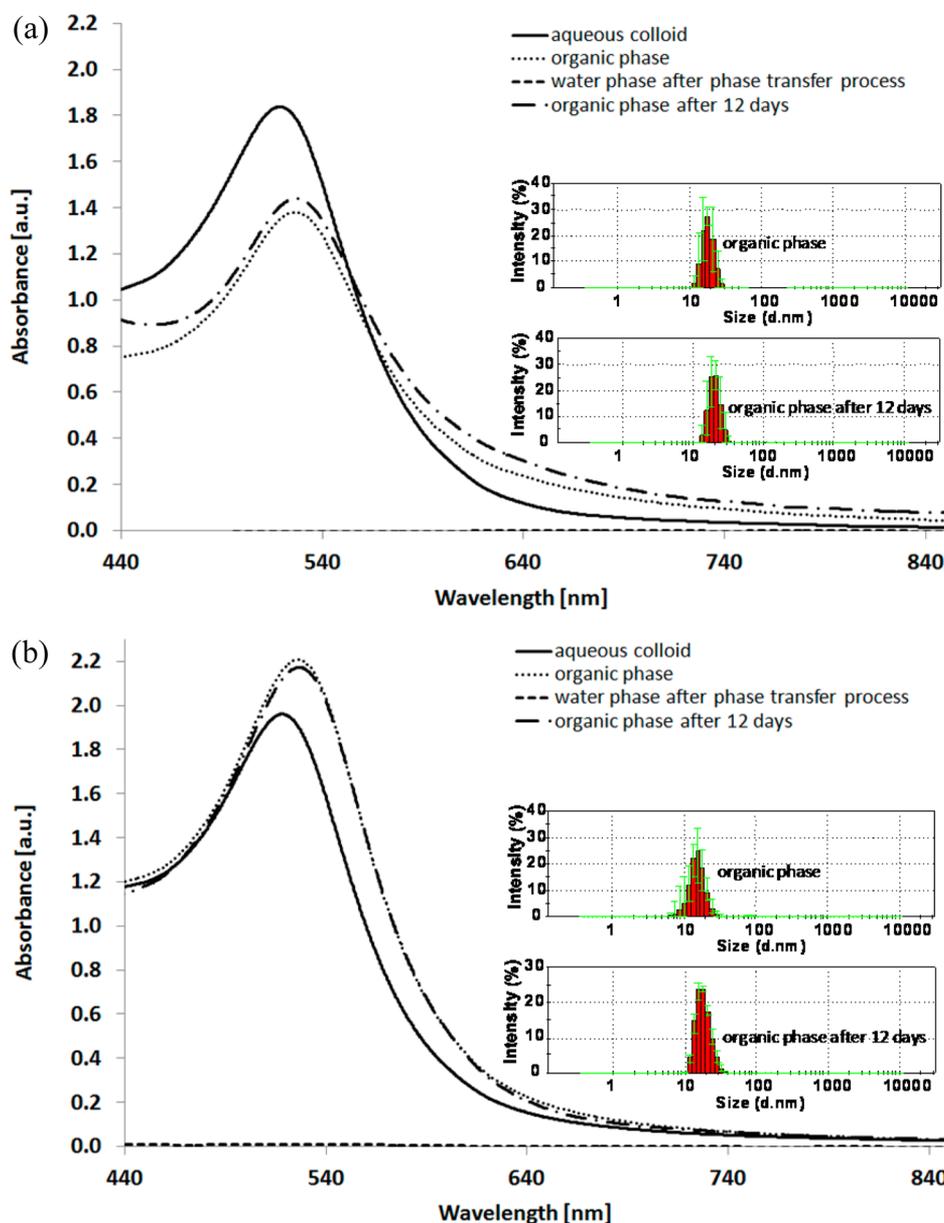


Figure 8. UV-vis spectra of colloid 3 (13 nm) after the phase transfer process with different amounts of dioctadecylamine $[(C_{18})_2NH]$: 20 (a) and 50 (b) modifier/nm² of NP surface with corresponding size distribution histograms after the phase transfer and after 12 days measured using the DLS technique.

dioctylamine, didodecylamine, and dioctadecylamine, and NPs with three different sizes, 5, 9, and 13 nm, were investigated.

It was found that the modifier amount and the chain length are critical factors affecting the transfer efficiency. The most effective phase transfer process of gold nanoparticles to toluene was observed in the case of dioctadecylamine compared with dioctylamine and didodecylamine.

The experiments revealed that with the use of an amine with two C₈ hydrocarbon chains it was not possible to obtain a stable gold organosol in toluene. In the case of an amine with two C₁₂ hydrocarbon chains, it was possible to transfer and stabilize only the smallest tested gold nanoparticles with a size of 5 nm (colloid 1). The thickness of the organic layer adsorbed on the nanoparticle surface was sufficient to separate nanoparticles with a size of 5 nm and prevent their agglomeration. Secondary amines with two C₈ or C₁₂ hydrocarbon chains are too short to provide bigger nano-

particles (colloids 2 and 3 of AuNPs with sizes of about 9 and 13 nm, respectively) with stabilization and dispersibility in toluene. Most probably, the C₈ and C₁₂ hydrocarbon chains from amines adsorbed on adjoining nanoparticles can penetrate each other to a specific distance. This in turn may reduce the distance between nanoparticles, increase the interaction of the metallic cores, and lead to loss of nanoparticle stability. As a consequence, the aggregation process may occur. It results in stabilization of large objects which is not possible in toluene with the use of dioctylamine and didodecylamine. It is also possible that the protective layer (organic shell) may not be thick enough to separate two metallic cores at a specific distance that would prevent metallic contact. The attraction forces between the metallic nanoparticle cores (van der Waals interactions) are stronger than the van der Waals interactions between the hydrocarbon chains of the amine adsorbed on the

nanoparticle surface. This leads to metallic contacts and consequently nanoparticle agglomeration.

Only with the use of dioctadecylamine was it possible to obtain stable organosols for each of the investigated colloids 1–3 with three different sizes, 5, 9, and 13 nm, respectively. This is due to the fact that long hydrocarbon chains (C_{18}) in the dioctadecylamine structure provide nanoparticle stability and dispersibility in toluene caused by the hydrophobic shell. In the case of dioctadecylamine with two long alkyl chains, the efficiency to create lasting van der Waals interactions between chains is higher than in the case of dioctylamine or didodecylamine. The amine layer adsorbed on the nanoparticle surface is therefore highly packed and impenetrable in the case of dioctadecylamine. Thus, the penetration process (solvent and other alkyl chains from amines adsorbed on different nanoparticle surfaces) occurs inside the protective organic layer only to such a distance that does not cause the loss of nanoparticle stability.

The stability tests revealed that no particle growth and no changes in the positions of the surface plasmon resonant peaks were observed in the case of these dioctadecylamine-modified nanoparticles even after 12 days. These results confirm that the aggregation and/or agglomeration processes were avoided by using dioctadecylamine as a nanoparticle-protecting agent and the resulting organosol shows a high degree of stability.

■ ASSOCIATED CONTENT

■ Supporting Information

Additional experimental details, UV–vis spectra and size distribution histograms (DLS technique) of colloids 1–3, and photographs of nanoparticles after the phase transfer process with the use of different types and amounts of surface modifier (dioctylamine, didodecylamine, and dioctadecylamine) for colloids 1–3. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

■ Corresponding Author

*E-mail: jgobel@uni.lodz.pl. Fax: +48 42 6355832. Phone: +48 42 6355837.

■ Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the FP7-NMP-2010-SMALL-4 program (Hybrid Organic/Inorganic Memory Elements for Integration of Electronic and Photonic Circuitry, HYMEC), Project 263073. It was also supported by the Polish Ministry of Science and Higher Education via funds for science in 2011–2014 allocated for the cofounded international project. We acknowledge M. Sztucki (European Synchrotron Radiation Facility (ESRF), Grenoble, France) and F. Zhang (University of Tübingen) for help with the SAXS experiments.

■ REFERENCES

(1) Jia, Ch.-J.; Schüth, F. Colloidal metal nanoparticles as a component of designed catalyst. *Phys. Chem. Chem. Phys.* **2011**, *13*, 2457.
(2) Banerjee, A.; Theron, R.; Scott, R.W. J. Redispersion of transition metal nanoparticle catalysts in tetraalkylphosphonium ionic liquids. *Chem. Commun.* **2013**, *49*, 3227.

(3) Cuenya, B. R. Synthesis and catalytic properties of metal nanoparticles: Size, shape, support, composition, and oxidation state effects. *Thin Solid Films* **2010**, *518*, 3127.

(4) Murphy, C. J.; Sau, T. K.; Gole, A. M.; Orendorff, C. J.; Gao, J.; Gou, L.; Li, T. Anisotropic metal nanoparticles: synthesis, assembly, and optical applications. *J. Phys. Chem. B* **2005**, *109* (29), 13857.

(5) Shipway, A. N.; Katz, E.; Willner, I. Nanoparticles affays on surfaces for electronic, optical and sensor applications. *ChemPhysChem* **2000**, *1*, 18.

(6) Zhang, Y. J.; Huang, R.; Zhu, X. F.; Wang, L. Z.; Wu, Ch. X. Synthesis, properties, and optical applications of noble metal nanoparticle-biomolecule conjugates. *Chin. Sci. Bull.* **2012**, *57*, 238.

(7) Ko, S. H.; Park, I.; Pan, H.; Grigoropoulos, C. P.; Pisano, A. P.; Luscombe, C. K.; Fréchet, J. M. J. Direct nanoimprinting of metal nanoparticles for nanoscale electronics fabrication. *Nano Lett.* **2007**, *7*, 1869.

(8) Fendler, J. H. Chemical self-assembly for electronic applications. *Chem. Mater.* **2001**, *13*, 3196.

(9) Conde, J.; Doria, G.; Baptista, P. Noble metal nanoparticles applications in cancer. *J. Drug Delivery* **2012**, No. 751075.

(10) Liao, H.; Nehl, C. L.; Hafner, J. H. Biomedical applications of plasmon resonant metal nanoparticles. *Nanomedicine* **2006**, *1*, 201.

(11) Duncan, B.; Kim, Ch.; Rotello, V. M. Gold nanoparticle platforms as drug and biomacromolecule delivery systems. *J. Controlled Release* **2010**, *148*, 122–127.

(12) Doria, G.; Conde, J.; Veigas, B.; Giestas, L.; Almeida, C.; Assuncao, M.; Rosa, J.; Baptista, P. V. Noble metal nanoparticles for biosensing applications. *Sensors* **2012**, *12*, 1657.

(13) Maillard, M.; Giorgio, S.; Pileni, M. P. Silver nanodisks. *Adv. Mater.* **2002**, *14*, 1084.

(14) Piwonski, I.; Soliwoda, K. The effect of ceramic nanoparticles on tribological properties of alumina sol–gel thin coatings. *Ceram. Int.* **2010**, *36*, 47.

(15) Piwoński, I.; Soliwoda, K.; Kisiełowska, A.; Stanecka-Badura, R.; Kadziola, K. The effect of the surface nanostructure and composition on the antiwear properties of zirconia–titania coatings. *Ceram. Int.* **2013**, *39*, 1111.

(16) Yang, Y.; Ouyang, J.; Ma, L.; Jia-Hung Tseng, R.; Chu, C.-W. Electrical switching and bistability in organic/polymeric thin films and memory devices. *Adv. Funct. Mater.* **2006**, *16*, 1001.

(17) Tsoukalas, D. From silicon to organic nanoparticles memory devices. *Philos. Trans. R. Soc., A* **2009**, *367*, 4169.

(18) Kim, T. W.; Yang, Y.; Li, F.; Kwan, W. L. Electrical memory devices based on inorganic/organic nanocomposites. *NPG Asia Mater.* **2012**, *4*, e18.

(19) Prakash, A.; Ouyang, J.; Lin, J. L.; Yang, Y. Polymer memory device based on conjugated polymer and gold nanoparticles. *J. Appl. Phys.* **2006**, *100*, 054309 1.

(20) Soliwoda, K.; Tomaszewska, E.; Tkacz-Szczesna, B.; Rosowski, M.; Celichowski, G.; Grobelny, J. The influence of the chain length and the functional group steric accessibility of thiols on the phase transfer efficiency of gold nanoparticles from water to toluene. *Polym. J. Chem. Technol.* **2014**, *16*, 86.

(21) Ha, H. J.; Jeong, S. W.; Oh, T.-Y.; Kim, Y. S.; Choi, K.; Lee, Y. D.; Baek, J.; Ju, B. K. The effect of Au nanoparticle on metal organic semiconductor field effect transistor on plastic substrate by transfer method. *2012 IEEE International Conference on Electron Devices and Solid State Circuit (EDSSC)*, Bangkok, Dec 3–5, 2012; Institute of Electrical and Electronics Engineers (IEEE): Piscataway, NJ, 2012; pp 1–4.

(22) Tekin, E.; Gans, B.-J.; Schubert, U. S. Ink-jet printing of polymers—from single dots to thin film libraries. *J. Mater. Chem.* **2004**, *14*, 2627.

(23) Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whyman, R. Synthesis of thiol derivatised gold nanoparticles in a two phase liquid/liquid system. *J. Chem. Soc., Chem. Commun.* **1994**, 801.

(24) Perala, S. R. K.; Kumar, S. On the mechanism of metal nanoparticle synthesis in the Brust–Schiffrin method. *Langmuir* **2013**, *29*, 9863.

- (25) Wang, X.; Xu, S.; Zhou, J.; Xu, W. A rapid phase transfer method for nanoparticles using alkylamine stabilizers. *J. Colloid Interface Sci.* **2010**, *348*, 24.
- (26) Li, X. Y.; Tang, Y.; Ge, G. L. Preparation and potential characterization of highly dispersible phosphate-functionalized magnetite nanoparticles. *Sci. China: Phys., Mech. Astron.* **2011**, *54*, 1766.
- (27) Wei, Y.; Yang, J.; Ying, J. Y. Reversible phase transfer of quantum dots and metal nanoparticles. *Chem. Commun.* **2010**, *46*, 3179.
- (28) Karg, M.; Schelero, N.; Oppel, C.; Gradzielski, M.; Hellweg, T.; Klitzing, R. Versatile phase transfer of gold nanoparticles from aqueous media to different organic media. *Chem.—Eur. J.* **2011**, *17*, 4648.
- (29) Goulet, P. J. G.; Bourret, G. R.; Lennox, R. B. Facile phase transfer of large, water-soluble metal nanoparticles to nonpolar solvents. *Langmuir* **2012**, *28*, 2909.
- (30) Gaponik, N.; Talapin, D. V.; Rogach, A. L.; Eychmuller, A.; Weller, H. Efficient phase transfer of luminescent thiol-capped nanocrystals: from water to nonpolar organic solvents. *Nano Lett.* **2002**, *2*, 803.
- (31) Lala, N.; Lalbegi, S. P.; Adyanthaya, S. D.; Sastry, M. Phase transfer of aqueous gold colloidal particles capped with inclusion complexes of cyclodextrin and alkanethiol molecules into chloroform. *Langmuir* **2001**, *17*, 3766.
- (32) Kumar, A.; Mukherjee, P.; Guha, A.; Adyantaya, S. D.; Mandale, A. B.; Kumar, R.; Sastry, M. Amphoterization of colloidal gold particles by capping with valine molecules and their phase transfer from water to toluene by electrostatic coordination with fatty amine molecules. *Langmuir* **2000**, *16*, 9775.
- (33) Woehrle, G. H.; Brown, L. O.; Hutchison, J. E. Thiol-functionalized, 1.5-nm gold nanoparticles through ligand exchange reactions: scope and mechanism of ligand exchange. *J. Am. Chem. Soc.* **2005**, *127*, 2172.
- (34) Machunsky, S.; Peuker, U. A. Liquid-liquid interfacial transport of nanoparticles. *Phys. Sep. Sci. Eng.* **2007**, No. 34832.
- (35) Rosa, J. P.; Lima, J. C.; Baptista, P. V. Experimental photophysical characterization of fluorophores in the vicinity of gold nanoparticles. *Nanotechnology* **2011**, *22*, 415202.
- (36) Qian, H.; Zhu, M.; Andersen, U. N.; Jin, R. Facile, large-scale synthesis of dodecanethiol-stabilized Au₃₈ clusters. *J. Phys. Chem. A* **2009**, *113*, 4281.
- (37) Kotlarchyk, M.; Chen, H. S. Analysis of small angle neutron scattering spectra from polydisperse interacting colloids. *J. Chem. Phys.* **1983**, *79*, 2461.
- (38) Press, W. H.; Teukolsky, S. A.; Vetterling, W. T.; Flannery, B. P. *Numerical Recipes in C—The Art of Scientific Computing*, 2nd ed.; Cambridge University Press: Cambridge, U.K., 1992.
- (39) Tomaszewska, E.; Soliwoda, K.; Kadziola, K.; Tkacz-Szczesna, B.; Celichowski, G.; Cichomski, M.; Szmaja, W.; Grobelny, J. Detection limits of DLS and UV-Vis spectroscopy in characterization of polydisperse nanoparticles colloids. *J. Nanomater.* **2013**, No. 313081.
- (40) Yang, J.; Lee, J. Y.; Deivaraj, T. C.; Too, H.-P. A highly efficient phase transfer method for preparing alkylamine-stabilized Ru, Pt, and Au nanoparticles. *J. Colloid Interface Sci.* **2004**, *277*, 95–99.
- (41) Leff, D. V.; Brandt, L.; Heath, J. R. Synthesis and characterization of hydrophobic, organically-soluble gold nanocrystals functionalized with primary amines. *Langmuir* **1996**, *12*, 4723–4730.