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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

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This paper describes the influence of the chain length and the functional group steric accessibility of thiols modifiers on the phase transfer process efficiency of water synthesized gold nanoparticles (AuNPs) to toluene. The following thiols were tested: 1-decanethiol, 1,1-dimethyldecanethiol, 1-dodecanethiol, 1-tetradecanethiol and 1-oktadecanethiol. Nanoparticles (NPs) synthesized in water were precisely characterized before the phase transfer process using Atomic Force Microscopy (AFM) and Transmission Electron Microscopy (TEM). The optical properties of AuNPs before and after the phase transfer were studied by the UV-Vis spectroscopy. Additionally, the particle size and size distribution before and after the phase transfer of nanoparticles were investigated using Dynamic Light Scattering (DLS).

It turned out that the modification of NPs surface was not effective in the case of 1,1-dimethyldecanethiol, probably because of the difficult steric accessibility of the thiol functional group to NPs surface. Consequently, the effective phase transfer of AuNPs from water to toluene did not occur. In toluene the most stable were nanoparticles modified with 1-decanethiol, 1-dodecanethiol and 1-tetradecanethiol.

Keywords: gold nanoparticles, phase transfer, thiols, 1-decanethiol, 1,1-dimethyldecanethiol, 1-dodecanethiol, 1-oktadecanethiol, 1-tetradecanethiol.

INTRODUCTION

Metal nanoparticles attract much attention especially in optics[1] and electronic[2, 3] as a consequence of their unique physical and chemical properties compared with bulk material[4]. Nowadays, the synthesis and surface modification of metal nanoparticles are significant for their utilization as building blocks in memory devices[5–7]. The usage of nanoparticles in memory elements requires non-aqueous solvents because water can cause the damage of surface structure of memory devices components.

Nanoparticles (NPs) can be prepared in both polar[8] as well as non-polar solvents[9–12]. Syntheses of nanoparticles in nonpolar solvents are generally based on the usage of several main routes: water-in-oil microemulsions[13, 14], reversed micelles process[9, 15], reduction of metal ions in the organic phase in the presence of a capping agent[11, 16, 17] or the phase transfer process from the aqueous phase with phase transfer agents[12, 18–22]. Recently, the phase transfer process has become the main way to obtain monodisperse nanoparticles in organic solvents.

The phase transfer process of nanoparticles from water to organic solvents allows the usage of water synthesized nanoparticles with various surface modifiers (e.g. alkylamines[18, 19], thiols[12, 20, 21], carboxy acids[22], dithiophosphoric acids etc.). The main advantage of this process is that during the transfer of nanoparticles from water to organic solvent it is possible to remove all unwanted synthesis reagents (by-products of the synthesis, unbounded stabilizers and water) that may have a negative impact, especially in the case of their usage in electronic applications. Moreover, the behaviour of the memory device depends on the type of nanoparticles coating which determines their dispersion as well as electronic behaviours. Therefore, the choice of a suitable nanoparticles surface modifier is a very interesting matter to study.

Among many different compounds used for nanoparticles surface modification, thiols are the most commonly used in the case of gold nanoparticles (AuNPs). These systems have attracted significant interest because of their importance in both science and technological applications such as catalysis, optics or chemical sensing.

This paper describes the phase transfer process of gold nanoparticles from water to toluene with the usage of alkyl thiols with different chain length to produce a stable organic colloid. Studies present the effects of the chain length and the steric accessibility of the functional group of thiol compounds on the phase transfer efficiency of gold nanoparticles form water to toluene.

MATERIALS AND METHODS

Materials

Gold (III) chloride hydrate (Sigma-Aldrich, ≥ 49%), tannic acid (Fluka), sodium citrate tribasic dihydrate (Sigma-Aldrich, ≥ 99.0%), 1-decanethiol (Fluka 95.0%), 1,1-dimethyldecanethiol (Sigma-Aldrich 98.0%), 1-dodecanethiol (Sigma-Aldrich 98.0%), 1-tetradecanethiol (Sigma-Aldrich 98.5%), 1-oktadecanethiol (Sigma-Aldrich 98.0%) were used as received. Toluene (Chempur 99.0%) and acetone (Chempur 99.0%) used for the phase transfer process were distilled before the use. For all aqueous preparations deionized water obtained from Deionizer Millipore Simplicity UV system (resistance 18.2 MΩ) was used. All glassware was cleaned using aqua regia, rinsed with distilled water and Millipore purified water and dried in an oven at 110°C before the use.

Aqueous gold nanoparticles synthesis

Gold nanoparticles aqueous colloid was prepared as follows: aqueous chloroauric acid solution (93.8 g, 1.84 · 10^{-6}%) was boiled and vigorously stirred under reflux. A mixture of sodium citrate (4.5 g, 0.877%) and tannic acid (1.7 g, 1%) was next added into a solution and the colour immediately changed from yellow to dark red. The whole mixture was stirred for additional 15 minutes and cooled down. The final concentration of AuNPs in colloid was 100 ppm.

Gold nanoparticles surface modifiers

The phase transfer of aqueous synthesized nanoparticles into non-polar solvent requires hydrophobization of nanoparticles surface. For surface modification of gold nanoparticles, thiols with different chain length were used. The structures of compounds used for gold nanoparticles modification are shown in Figure 1 (calculations with a single molecule using HyperChem: geometrical optimalization MM+; Polak-Ribiere algorithm; terminal condition RMS gradient 0.1 kcal/Å · mol in vaccuo).

For the phase transfer process modifiers were prepared as 0.01% toluene solutions. The modifier amount corresponds to the 10 molecules per 1 nm^2 of nanoparticles surface.

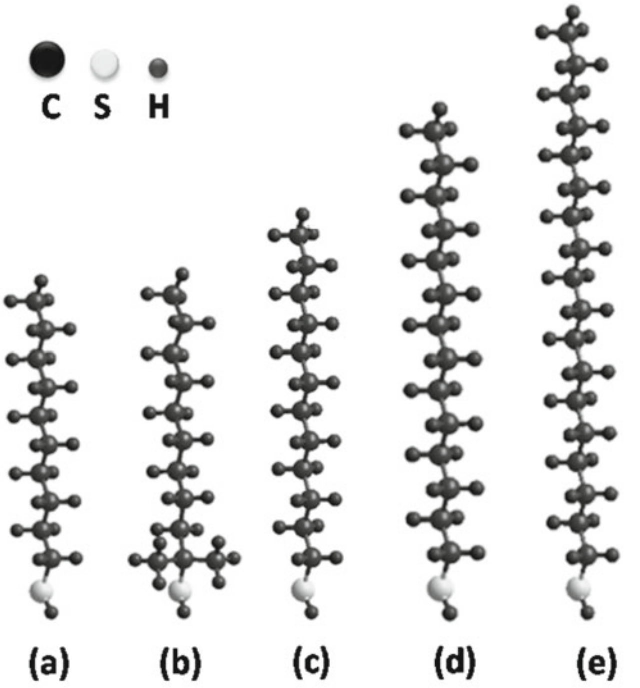


Figure 1. Structure of thiols used for surface modification of gold nanoparticles: 1-decanethiol (a), 1,1-dimethyldecanethiol (b), 1-dodecanethiol (c), 1-tetradecanethiol (d), 1-octadecanethiol (e)

Gold nanoparticles phase transfer process

Gold nanoparticles were transferred from aqueous solutions to toluene by modifying them with each of the five modifiers (see Fig. 1). To the aqueous nanoparticles colloid an acetone and toluene with each of the five modifiers was added. The modifiers were prepared as a 0.01% toluene solutions. The weight ratio of aqueous nanoparticles colloid/acetone/toluene was 2:1:1, respectively. An acetone was added to reduce the surface tension between the phases[23]. The biphasic system was vortex for 60 s and then left for another 60 s. Subsequently, the mixture spontaneously separated into two layers: a toluene phase now containing the modified AuNPs and the aqueous phase. The transfer process was observed by the dark red colouration of the organic phase and a corresponding loss of colour from the aqueous phase. The presence of nanoparticles in a toluene was confirmed with UV–Vis spectrophotometer. Moreover, the toluene phase was analyzed for NPs size and size distribution using DLS technique.

Methods

The formation of gold nanoparticles in the aqueous solvent and the presence of nanoparticles in toluene after the phase transfer process were determined using a UV-Vis spectroscopy. The spectrophotometer USB2000 + detector (miniature fiber optic spectrometer) from Ocean Optics with tungsten halogen light sources (HL-2000) was used. The absorption measurements were carried out at room temperature using 1 cm quartz cuvette.

DLS studies were performed with a Nano ZS Zetasizer system (Malvern Instruments) equipped with a (He-Ne) laser (633 nm) in a quartz cell at scattering angle 173° (measurement temperature 25°C; aqueous colloids: medium viscosity 0.8872 mPa · s, material refractive index 1.330; toluene colloids: medium viscosity 0.5564 mPa · s, dispersant refractive index 1.496, material refractive index 1.330). Before DLS measurement aqueous colloids were filtered (0.2 μm polyvinylidene fluoride (PVDF) membrane). In the case of colloids in toluene no filtration or other preliminary treatment of reaction solutions was applied.

AFM imaging was carried out in a tapping mode using a commercially available microscope Solver P47 (NT-MDT, Russia). The AFM measurements were carried out at room temperature using a rectangular silicon nitride cantilever (NSC 35/Si_3N_4/AlBS, MikroMasch). For AFM measurements gold nanoparticles were deposited on silicon wafer substrate according to the procedure described in[24].

The size and shape of AuNPs in aqueous solvent was determined using a transmission electron microscope (JEM-1200EX; accelerating voltage 120 kV). Samples for TEM measurements were prepared by depositing a nanoparticles colloid onto the copper grid coated with a thin amorphous carbon film. Gold nanoparticles sizes were measured from the TEM micrographs using Motic Plus 2.0 software. The size distribution histogram was prepared after measuring at least 100 particles in the case of both AFM and TEM characterization.

RESULTS AND DISCUSSION

Aqueous gold nanoparticles colloid

Gold nanoparticles synthesized in water using chemical reduction method were characterized using UV-Vis spectroscopy and DLS technique. The absorption band is typical for gold nanoparticles with a maximum in λ = 521 nm and the mean size of nanoparticles measured using DLS technique is about 9 ± 2 nm (Fig. 2).

The size of gold nanoparticles was also investigated using microscopic techniques (AFM and TEM) in order to determine the size and shape of nanoparticles. It was crucial to define the nanoparticles surface area available for modification because the amount of thiols used for modification corresponds to 10 modifier molecule per 1 nm^2 of nanoparticle surface.

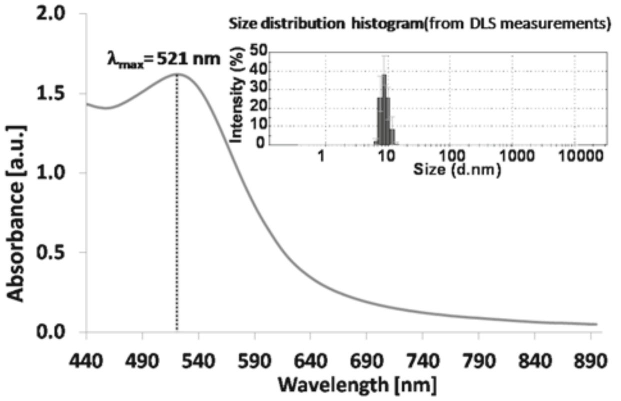
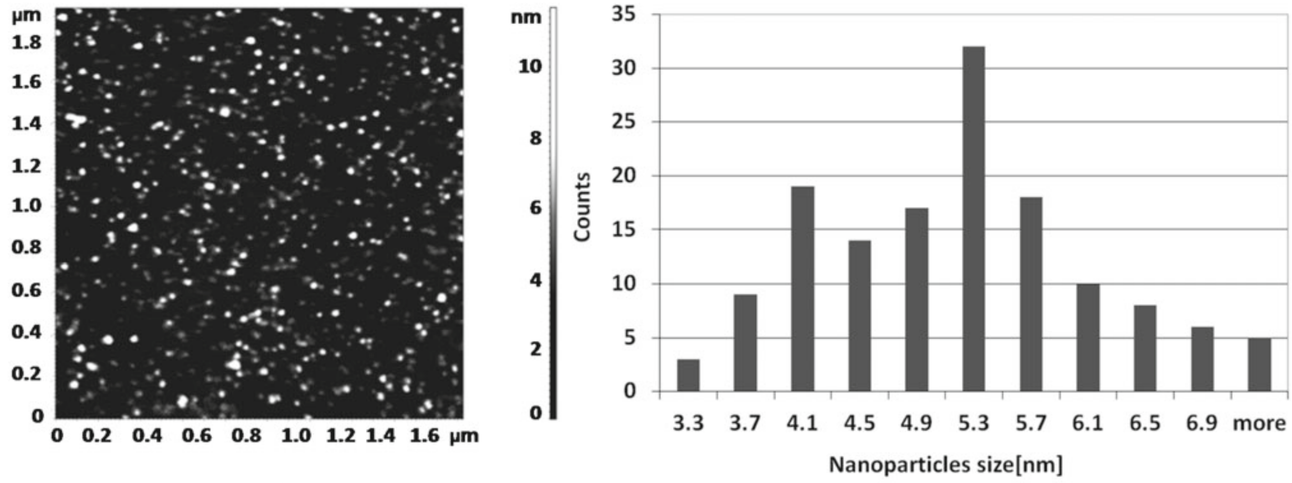


Figure 2. UV-Vis absorption spectrum and the size distribution histogram from DLS measurements (by intensity) of the aqueous AuNPs stabilized with mixture of citrate and tannic acid

The AFM image with the corresponding size distribution histogram of the aqueous AuNPs stabilized with mixture of citrate and tannic acid is presented in Figure 3.

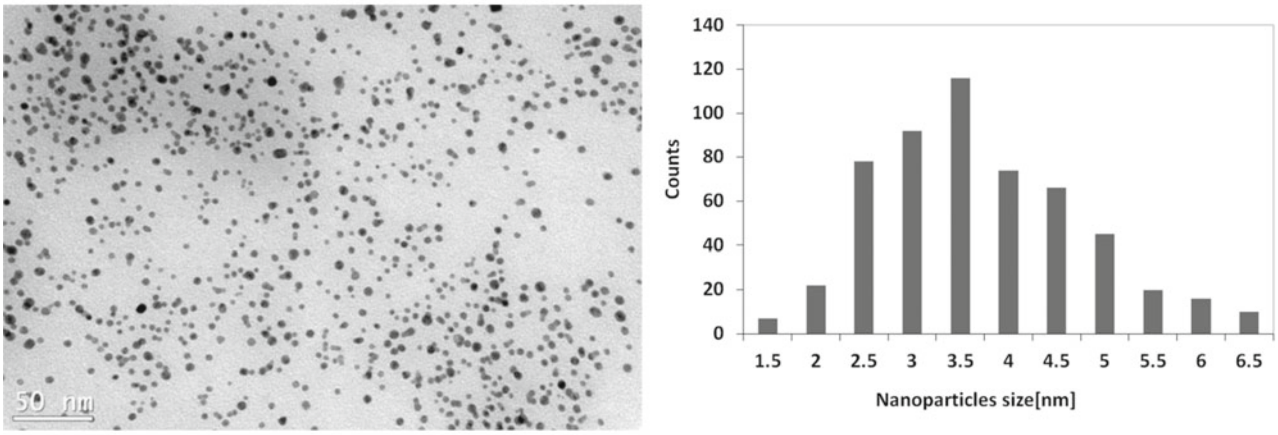
The mean size of gold nanoparticles from AFM measurements is 5.4 ± 1.0 nm (measured in a perpendicular direction to the surface). As gold nanoparticles deposited on silicon wafer surface are spherical, the apparent widths would be different than the real, because of the extended effect of the AFM tip. Hence, the size and shape of AuNPs were also investigated using TEM. Figure 4 presents the TEM micrograph of gold nanoparticles with the size distribution histogram.

The mean size of AuNPs from TEM measurements is about 3.5 ± 1.2 nm and the shape of nanoparticles is mostly spherical. Differences in the size of gold nanoparticles determined by different techniques (DLS, AFM and TEM) are caused by the specificity of each technique not by the measurements error. In the case of TEM and AFM the geometric size of NPs deposited on the surface is measured. In DLS technique, the hydrodynamic size is measured. This size corresponds to the ball model, which has the same diffusion coefficient as a measured nanoparticle. In consequence, the size of the measured nanoparticle can differ from that determined by the microscopic techniques.



a) b)

Figure 3. AFM image (a) with the corresponding size distribution histogram (b) of the aqueous AuNPs stabilized with mixture of citrate and tannic acid



a) b)

Figure 4. TEM micrograph (a) with the corresponding size distribution

Gold nanoparticles modified with thiols

The presence of nanoparticles in toluene after the phase transfer process was confirmed with UV–Vis spectroscopy. UV-Vis spectra of gold nanoparticles in toluene modified with different thiols: 1-decanethiol, 1,1-dimethyldecanethiol, 1-dodecanethiol, 1-tetradecanethiol, 1-octadecanethiol are shown in Figure 5.

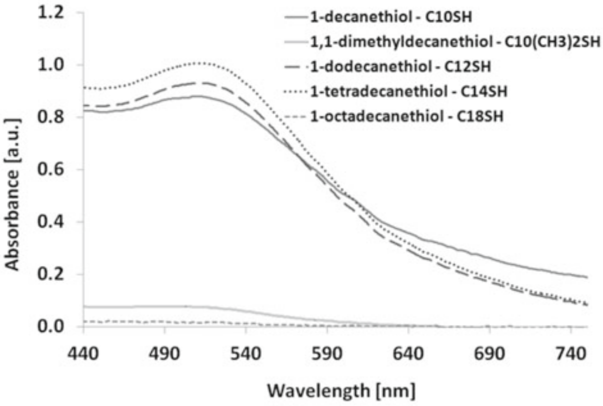


Figure 5. UV-Vis absorption spectra of gold nanoparticles in toluene modified with different thiols: 1-decanethiol, 1,1-dimethyldecanethiol, 1-dodecanethiol, 1-tetradecanethiol, 1-octadecanethiol

The UV-Vis spectra confirm the phase transfer of nanoparticles from aqueous phase to toluene in the case of three out of five modifiers: 1-decanethiol, 1-dodecanethiol and 1-tetradecanethiol. In the case of 1,1-dimethyldecanethiol and 1-octadecanethiol in the UV-Vis spectra absorption peak characteristic for the gold nanoparticles is not observed. This clearly indicates that no phase transfer of gold nanoparticles from the aqueous phase to the organic phase occurred in the case of these modifiers. It is possible that in the case of 1-octadecanethiol the alkyl chain is too long (18 carbon atoms) to form a self-assembled monolayer on the nanoparticles surface. It is already known that in the case of 1-octadecanethiol more than one projection of tilt domains on Au (111) surface was observed[25, 26]. Moreover, the arrangement of modifier chains on nanoparticles surface can also be disordered (random or chaotic) or some alkyl chains may be bent. Some of alkyl chains may be adsorbed on nanoparticles surface but the number of these chains is insufficient to provide nanoparticles stabilization in toluene. As a consequence it is not possible to receive gold nanoparticles in toluene using 1-octadecanethiol.

To investigate the effect of the functional group steric accessibility on the phase transfer efficiency of nanoparticles to toluene, two thiol modificators were used: 1-dodecanethiol and 1,1-dimethyldecanethiol. These two thiols have the same length of the hydrocarbon chain, but differ in case of groups next to the sulfur atom. In consequence the sulfur group steric accessibility is various for these modifiers. In 1-dodecanethiol the sulfur atom is next to two hydrogen atoms, whereas in 1,1-dimethyldecanethiol next to methyl groups. A methyl group is bigger compared with a small hydrogen atom and the steric accessibility of sulfur atom in modification process can be more difficult in the case of 1,1-dimethyldecanethiol than in 1-dodecanethiol. It was observed that modification of gold nanoparticles occurred in both cases, but nanoparticles were transferred to toluene only in case of 1-dodecanethiol. In case of 1,1-dimethyldecanethiol nanoparticles were agglomerated in the interphase. This was confirmed using UV-Vis spectroscopy (Fig. 5). A characteristic maximum band was observed only for gold nanoparticles in toluene modified with 1-dodecanetiol at 509 nm. No characteristic band was observed in the case of 1,1-dimethyldecanethiol. These results indicate that functional group steric accessibility has a great impact on the phase transfer efficiency of AuNPs to toluene in the case of thiol compounds.

For nanoparticles modified with 1-decanethiol, 1-dodecanethiol and 1-tetradecanethiol the maximum absorption band was observed in the region characteristic for gold nanoparticles: 509 nm, 511 and 513, respectively. The maximum absorption for nanoparticles modified with 1-decanethiol, 1-dodecanethiol and 1-tetradecanethiol in toluene was observed at lower wavelengths compared with the citrate/tannic acid-modified nanoparticles in water (521 nm). These changes in maximum band gap are attributed to changes in the refractive index of the surrounding medium (water and toluene) as well as nanoparticles shell (citrate/tannic acid mixture and thiols) which have an impact on the local surface plasmon resonance (LSPR) of nanoparticles. Moreover, the increase of the modifier alkyl chain length causes the shift of the maximum absorption of nanoparticles to longer wavelengths for 1-decanethiol, 1-dodecanethiol and 1-tetradecanethiol which may be caused by the increased nanoparticles shell thickness.

Colloids in toluene modified with 1-decanethiol, 1-dodecanethiol and 1-tetradecanethiol were also investigated using DLS technique in order to assess the agglomeration state and to measure the nanoparticles size (Fig. 6 a, c, e).

From DLS measurements of AuNPs before and after the phase transfer it was estimated that their diameters are: 4 ± 1 and 5 ± 1 nm for 1-decanethiol and 6 ± 1 and 6 ± 1 nm, for both 1-dodecanethiol and 1-tetradecanetiol. Toluene colloids were stable even after storage for several months. This is graphically illustrated in DLS size distribution histograms recorded from the toluene gold nanoparticles after two months (Fig. 6 b, d, f). A comparison of DLS histograms shows that negligible size changes of gold nanoparticles have occurred after two months of storage.

The maximum absorption bands and hydrodynamic diameters of nanoparticles modified with mixture of citrate and tannic acid, 1-decanethiol, 1-dodecanethiol and 1-tetradecanethiol are collected in Table 1.

The slight changes of the nanoparticles sizes (measured by DLS technique) may be attributed to changes in the interactions of compounds attached to the AuNPs surface. As it was already mentioned in case of DLS the NPs size that is measured is the hydrodynamic diameter of the theoretical sphere which diffuses with the same speed as the measured nanoparticle. This hydrodynamic size is related to the metallic core of nanoparticles and all substances adsorbed on the surface of nanoparticles (e.g., stabilizers) as well as the thickness of the electrical double layer (salvation shell), moving along with the particle. The thickness of the electrical double layer

Table 1. The maximum absorption bands (λ_{max}) and hydrodynamic diameters of nanoparticles modified with mixture of citrate and tannic acid, 1-decanethiol, 1-dodecanethiol and 1-tetradecanethiol

	λ_{max} (nm) (UV-Vis)	hydrodynamic diameter (nm) (DLS)	
Ligand		after phase transfer	after 2 months
Mixture of citrate and tannic acid	521	9 ± 2	9 ± 2
1-decanethiol	509	4 ± 1	5 ± 1
1-dodecanethiol	511	6 ± 1	6 ± 1
1-tetradecanethiol	513	6 ± 1	6 ± 1

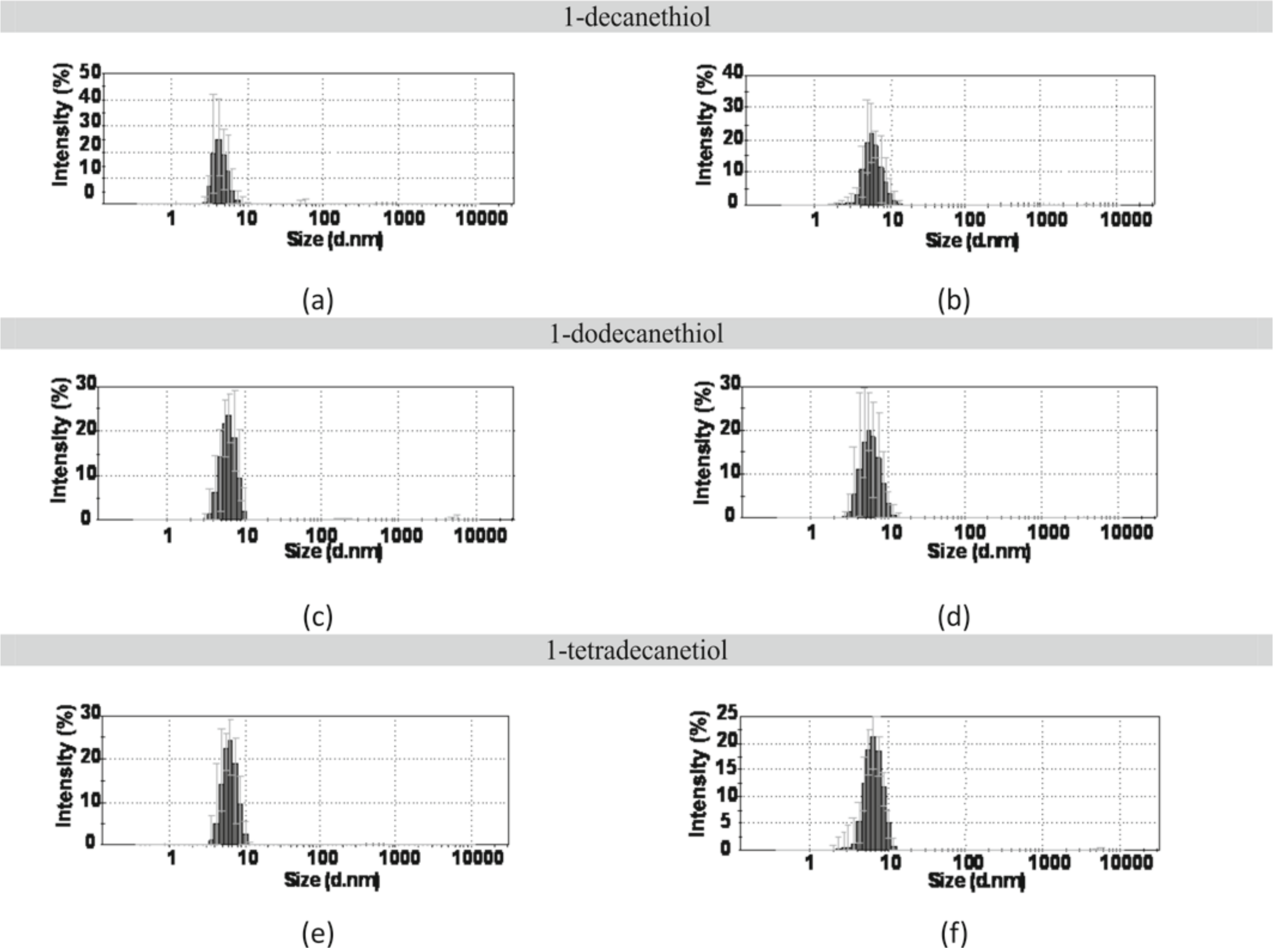


Figure 6. The size distribution histograms of the gold nanoparticles in toluene modified with 1-decanethiol, 1-dodecanethiol and 1-tetradecanethiol after the phase transfer process (a), (c), (e) and after 2 months (b), (d), (f)

and its influence on the measured size of nanoparticles depends on the substances present in the colloid as well as adsorbed on the nanoparticles surface. In aqueous colloid the negative citrate ions are adsorbed on nanoparticles surface, whereas in toluene colloid thiols are covalently bonded to nanoparticles surface. Thus, in each case, the interactions in the electrical double layer are different. Consequently, the size of the nanoparticles modified with mixture of citrate and tannic acid in the aqueous phase may be bigger compared with the size of thiol-nanoparticles in toluene.

CONCLUSIONS

It was found that the phase transfer of gold nanoparticles from water to toluene is not possible in case of thiols with long alkyl chain length e.g. 1-octadecanethiol, where chains may be disordered or bent on nanoparticles surface. In a consequence, hydrophobicity of nanoparticles is insufficient to stabilize AuNPs in non-polar solvent (toluene). Studies also revealed that functional group steric accessibility have a great impact on the phase transfer efficiency of AuNPs to toluene in case of thiol compounds. Moreover, it was found that thiol compounds act not only as an effective phase transfer agents but also provide an effective stabilization for gold nanoparticles in toluene for several months. This makes nanoparticle-thiol system very useful in optoelectronic application for example as a component of ink for printing electronic.

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