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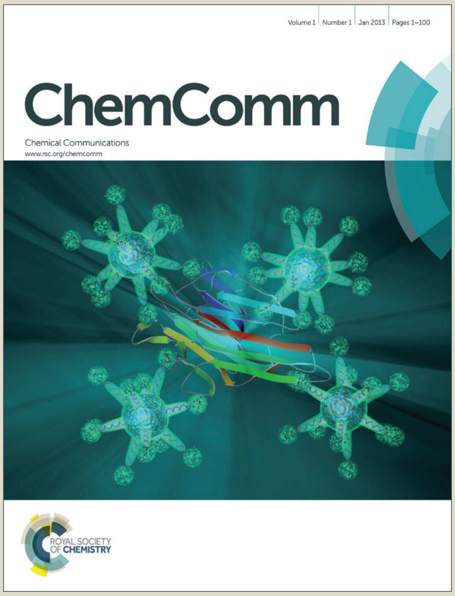

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Self-assembly of gold nanoparticles on deep eutectic solvent (DES) surfaces

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Self-assembly of gold nanoparticles was obtained by sputter deposition on DES. SAXS and TEM investigations reveal the formation of spherical nanoparticles with a mean diameter of 5±0.5 nm. For extended sputtering times, the number density of AuNPs increases linearly and a very pronounced 1st and 2nd shell ordering is observed.

During the last two decades, it was manifested that metallic nanoparticles (NPs) with different sizes and morphologies exhibit new properties with promising optical, plasmonic heating, bio-analytical, theranostics and chemical applications[1]. For catalytic studies, the size, composition and the stability of the NPs is crucial[1c, 1d]. Therefore, it is mandatory to fully understand the basic formation, growth, stabilization and coarsening mechanisms of NPs, which have been studied in different matrices (colloidal solutions[1c-d], glass[2] and modern ionic liquids[3,5a-c] including Deep Eutectic Solvents (DES))[3]. Current interest in self-assembly (SA) of AuNPs motivates us to investigate their collective properties for fundamental studies, technological and catalytic applications[1-4]. DES have genuine applications as "Green Solvents" in various fields of science and technology[3d,5d-e] due to their unique properties such as ionic character, bio-degradability, non-toxicity, high ionic conductivities and the ability to dissolve many metal oxides and chlorides. DES can act as a stabilizer and therefore can be a novel matrix for fundamental studies on nucleation, growth and SA of metal NPs.

As for gold, there are several effective synthesis methods such as chemical synthesis, microwave assisted synthesis and physical vapor deposition (PVD)[3e,3f]. It must be emphasized that physical sputtering deposition has been shown to offer a clean strategy for forming NPs on surfaces with low vapor pressure such as ionic liquids and DES[6]. Still, the growth and stabilizing mechanisms of AuNPs in ionic liquids and DES are not fully understood and therefore vividly debated [7].

In this communication we describe the SA of AuNPs synthesized by sputter deposition onto DES surfaces. In our pilot study we focused on novel choline chloride (ChCl)-urea based DES samples, which were discovered only a decade ago by Abbott *et al* [5e]. Details of the AuNPs-DES sample preparation are given in S1. The main goal of this work is to estimate the effect of sputtering time on the structure parameters and to evaluate the growth mechanisms of the AuNPs. We have performed SAXS measurements to obtain the average size, size distributions and shape of the AuNPs for specific deposition times. Details of the SAXS measurements and fitting procedures are given in S2. Our results lead us to understand the time dependent growth and the stability of AuNPs with respect to the effect of ionic liquids as surrounding environments.

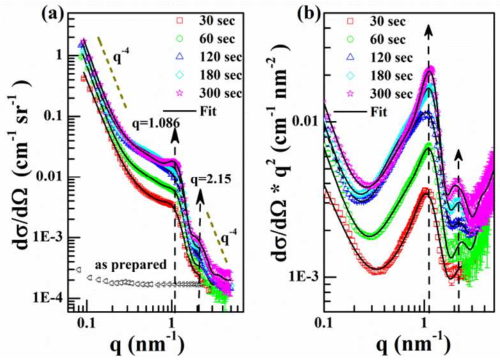

Figure 1 (a) SAXS curves for the as-prepared DES reference sample and Au sputtered samples. The sputtering time was 30, 60, 120, 180 and 300 sec. (b) Kratky plot of the SAXS curves (shown in Figure 1a). The two arrows show the first and second order peak.

Figure 1(a) shows the SAXS curves of the as-prepared DES reference sample and the gold-sputtered samples at room temperature. The scattering curves are scaled to differential scattering cross section per unit volume and plotted as a function of the momentum transfer vector *q*. It is obvious that the intensity of the scattering curves for gold-sputtered samples are significantly higher than that of the as-prepared, gold free DES sample. The SAXS curve for 30 sec gold-sputtering time shows two small broad peaks ($q=1.086$ nm^{-1} and $q=2.15$ nm^{-1}), while for prolonged sputtering times these peaks are more pronounced and their sharpness increases at the same constant *q* values. This indicates that the size of the individual NPs is not varying significantly (see figure S3 (b)). The pronounced sharpness of the peaks reveals the presence of ordering of the AuNPs for extended sputtering times.

Size distributions (see figure S3 (a)) reveal the formation of particles of about 5 nm in diameter and the distributions do not differ significantly with the gold-sputtering time. This observation is in line with Torimoto's work [6]. Evaluated average diameters of the

AuNPs (see figure S3 (b)) obtained after fitting the SAXS curves also not vary significantly with the gold-sputtering time.

Figure 2(a) shows the calculated structure factor for the sample deposited for 300 sec. The strong peak at q=1.3 nm^{-1} gives a scattering correlation length of 4.8 ± 0.2 nm. The correlation length is comparable to the diameter of the AuNPs. Moreover, the radial distance distribution function *G(r)* shown in figure 2(b) also has a strong peak at 5.5±0.3 nm and two weak peaks at 9 and 11.8 nm. All these values provide information about neighboring nanoparticles in the 1st and 2nd shell. In figure 2(c), the evaluated potential mean force (PMF) shows that the minimum of the energy is obtained at 5.5 nm, which is the nearest distance between two selected individual particles.

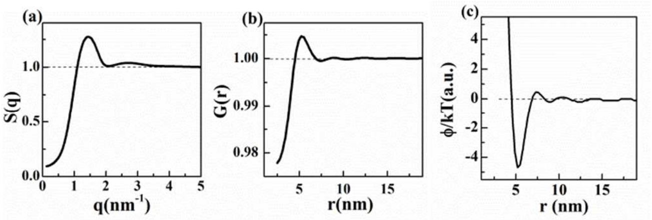

Figure 2 (a) The structure factor *S(q)* evaluated by SAXS curve fitting. (b)The pair distance distribution function *G(r)* evaluated by using the *S(q)*. (c) The potential mean force calculated by using *G(r)* for the sample deposited for 300 sec.

The physical mechanism of self-assembly of AuNPs in DES can be understood as follows: It is proposed that during sputtering the Au atoms are highly mobile on the DES surface. These atoms start to aggregate into individual AuNPs. After 30 sec gold-sputtering time we observed 5 nm diameter nanoparticles. For prolonged sputtering times up to 300 sec we would expect a further growth of these particles with a final average size of $10^{1/3}$*5 nm (approx. 10.77 nm) in diameter. However, this is not observed experimentally. Prolongation of sputtering time does not cause any significant change of the size of NPs (see figure S3 (b)). This is also in agreement with standard UV-VIS investigations (see figure S5). Further direct evidence stems from Cryo-TEM micrographs, which convincingly reveal that the size of the gold nanoparticles do not grow beyond 5 nm in diameter as shown in Figure 3.

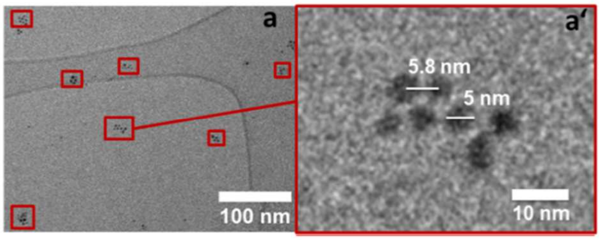

Figure 3 Cryo-TEM micrographs of gold nanoparticles in DES synthesized by sputter deposition at 20 mA and 0.05mbar (argon pressure). (a and a') 300 sec without stabilizer.

Moreover, figure 3a' shows the 1st and 2nd shell ordering of AuNPs while no ordering is observed for the sample stabilized by bis-((2-Mercaptoethyl)-trimethyl-ammonium) disulfide dichloride (S4 and S5).

For prolonged sputtering times only a higher concentration of AuNPs is observed. The concentration of Au is around 1.6 mM and the particle number density approximately of the order of 10^{14} NPs/cm^3. As expected, the dependence of the number density over sputtering time is almost linear. Earlier, Torimoto et al. also reported the same phenomenon of self-terminating growth for the sputter deposition of Au on different kinds of ionic liquids. But they did not report any evidence about the self-assembly and ordering of the metal NPs in ionic liquids [6]. This is surprising in few of the fact that there are 10^{18} ternary ionic liquids and eutectic mixtures [8]. Our results on self-assembled AuNPs in DES could be an excellent model for novel fundamental studies of nanoscale SA in ionic liquids. The combination of (i) specific attractive and repulsive interactions between the NPs and (ii) the outstanding physiochemical templating characteristics of ionic liquids and eutectic mixtures will form a firm basis for explaining in detail the self-assembly and ordering of nanoparticles *(vide infra)* [8,5c,9]. The origin of the attractive forces between the 5 nm AuNPs is due to the size and inter-particle's distance dependent long-range van der Waals interaction[10]. These strong interaction forces always tend to yield SA domains, aggregates or tend to form irreversibly precipitates. Our study shows that the attraction can be counter-balanced by electrostatic repulsion provided by the ionic template of DES with a minimum allowable distance of about 0.8 nm. Since the DES has an ionic behavior that means the DES surface has positive and negative ions, which can significantly affect the growth and self-assembly of nanoparticles. It is observed that after deposition there is a formation of floating rafts with a large excess of negative surface charges on the AuNPs[11]. The ionic and templating behavior of DES could probably also provide the magnitude of entropic freedom for ordering to occur in the DES matrix. Moreover, the evaluated PMF indicates that the central particle interacts with the 1st and 2nd shell neighboring particles. The inter-particle distance is about 5.5±0.3 nm.

In order to fully suppress the self-assembly phenomenon a strong stabilizer is required. We have shown that bis-((2-Mercaptoethyl)-trimethyl-ammonium) disulfide dichloride can be employed for this purpose (S5). Such stabilized AuNPs never tend to form a SA domain. Even when a SA domain has formed in DES, it can be converted back to stable, individual 5 nm AuNPs. Therefore, we can exclude irreversible precipitation of gold nanoparticles in DES.

In Figure 1(a), the SAXS curves reveal no change of the peak position (q=1.086 nm^{-1}) for different gold-sputtering times between 30 and 300 sec. However, the scattering intensity of the SAXS curves increases for the sample sputtered for 300 sec with respect to the curve obtained for 30 sec. This can most clearly be seen in the Kratky plot in Figure 1 (b): The *q* value (q=1.086 nm^{-1}) corresponds to the surface to surface inter-particle distance of about 0.8 nm. At extended gold-sputtering times also the second order peak at q= 2.15 nm^{-1} is clearly observed. The sharpness of the peaks in SAXS curves shows the ordering of the NPs for prolonged gold-sputtering times

The growth of the maxima in the evaluated structure factor *S(q)* and in the distance distribution function *G(r)* at higher concentrations of AuNPs is caused by the interference effects. Moreover, it indicates that the particles are not arranged in random but have a self-assembly in short-range order[12]. Prolonged gold-sputtering times lead to an increase in the ordering of the AuNPs with strong interactions. The radial distance distribution function curve indicates that the particles are arranged via 1st and 2nd shell ordering, as is evidenced by the considerable peak in *G(r)* in the range from few nanometers to 15-20 nm and long-range disorder tending to unit at values *r* larger than 20 nm. This means, the average domain size is between 10-20 nm.

High mobility of gold atoms on the DES surface means that the interaction between the Au atoms and the DES surface is small. Moreover, due to the van der Waals attraction and Brownian motion, the Au atoms or nanoparticles can move, collide and aggregate onto the DES surface as well as into the bulk. Similar kind of observation on formation of NPs in ionic liquids was reported earlier by Mudring et al (Mechanistic Scheme 2 in ref: 1e)

For shorter gold-sputtering times of 30 sec the gold atoms start to aggregate on the surface. It is possible that some of these aggregates already form NPs of stable size (5 nm in diameter). Prolongation of gold-sputtering time leads to an increase in concentration of gold atoms on the DES surface. After dispersion into the bulk they self-organize into closed-packed ordered domains (clusters of AuNPs). It is shown that the SAXS scattering occurs by few Bragg planes of the SA ordered structures in a particular domain as shown in Figure 4.

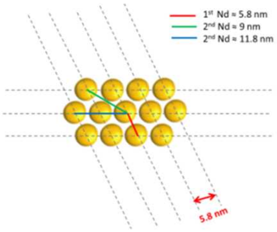

Figure 4 Schematic of a domain shows 1st and 2nd shell ordering

This phenomenon of self-assembly in ordered structure can be explained by the minimization of free energy of van der Waals attraction and electrostatic interactions. The van der Waals attractive force between particles induce the self-assembly, while the Coulomb interaction due to the ionic structure of DES provides the balancing force to create 1st and 2nd shell ordered stable structures [13].

The use of ionic liquids and eutectic mixtures as solvent and template opens up many new possibilities in the design of self-assembled ordered metallic NPs. It must also be mentioned that by way of contrast AuNPs do not form SA domains in Castor oil, which is a non-ionic, non-templating liquid [14].

Conclusions

In summary, we have observed the formation of AuNPs with an average diameter of 5 nm on DES surfaces as evaluated by SAXS and Cryo-TEM. At constant temperature, time is the most important parameter. Prolongation of the sputtering time from 30 up to 300 sec results in a higher number density of Au nanoparticles on DES surface, but did not cause a significant change of the size. However, the higher particle number density leads to a pronounced SA of the AuNPs in a regular cluster system as observed for the first time in ionic liquids. SA of mono and multimetallic nanoparticles in eco-friendly DES has a great potential in the area of fundamental catalytic studies.

Notes and references

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Electronic Supplementary Information (ESI) available: [Details of sample preparation, SAXS measurements and fitting, TEM, UV-Vis].See DOI: 10.1039/c000000x/

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