Supplementary information

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

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S1: Sample Preparation

Deep Eutectic Solvent (DES) is a mixture of quaternary ammonium salt: choline chloride (ChCl; melting point 302 °C) and hydrogen bond donor (HDB): Urea (CH_4N_2O; melting point 133 °C). In a DES, the molecular complexes of halide ion and hydrogen-bond-donors (HBD) alter the free energy and lead to the depression of the freezing point (12 ° C) of the mixture. Moreover, DES is a very viscous liquid with a viscosity of 750 cP at 25 °C and density of 1.25 g/cm^3.

In the present investigation, the choline chloride (ChCl)-urea based DES samples was prepared by mixing the two components in a molar ratio of 1(ChCl):2(urea). After mixing, the samples are stirred at 80 °C until a homogenous colorless liquid is formed. Synthesis of AuNPs in DES is achieved by employing the sputter deposition technique. During sputtering, a current of 20 mA and an argon pressure of 0.05 mbar are applied. The distance between the Au target and DES surface is typically 3.5 cm. The surface area of DES exposed to the sputtering was 8 cm^2 and the volume of DES is about 5 ml. Five different samples have been prepared by selecting gold-sputtering times of 30, 60, 120, 180 and 300 seconds. Immediately after the completion of sputtering, the samples are stirred for 60 seconds.

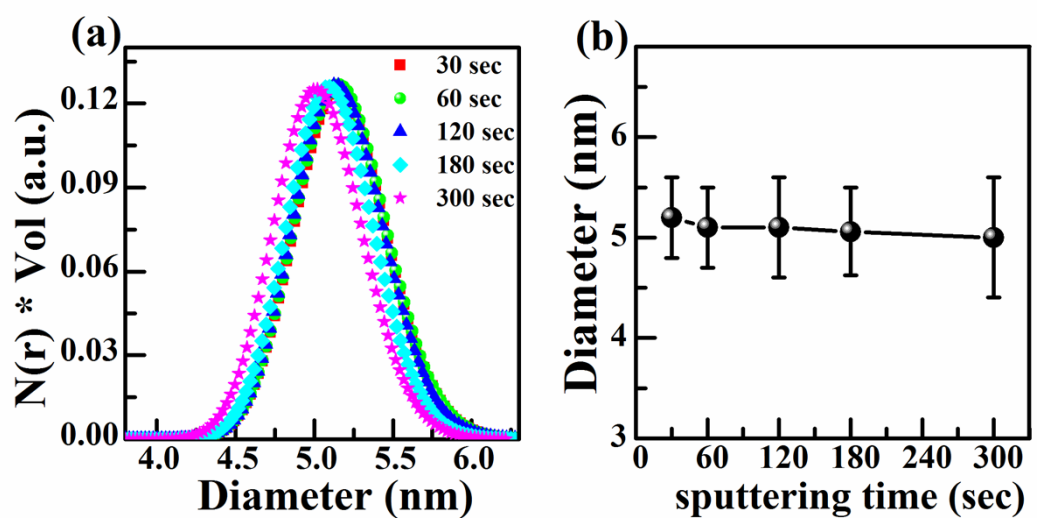
S2: SAXS data fitting

SAXS experiments were performed to reveal the distribution of AuNPs and to estimate quantitatively the structure parameters such as shape, size and polydispersity [1, 2]. The samples were sealed in 1.0 mm (in diameter) quartz glass capillaries. During measurements, the capillaries were placed in a low pressure chamber (10^{-4} mbar) to reduce the air scattering. The experiments were performed at a fixed X-ray energy of 8000 eV at the SAXS beamline at BESSY II synchrotron at Helmholtz-Zentrum Berlin (HZB) [3]. The photons scattered by the samples were collected by using a gas filled 2D multi-wire proportional counter. Raw scattering images were corrected for transmission, photon flux, dead-time of the detector electronics, solid angle distortion and sensitivity of detector pixels. After circular averaging the final scattering curves were obtained. A pre-calibrated glassy carbon standard sample was used to scale the scattering curves to differential scattering cross sections per unit volume. A silver behenate sample (peak at q=1.076 nm^{-1}) was used to calibrate the q scale. It should be noted that the time difference between the completion of gold-sputtering and the SAXS measurement was about 5 h.

The structure parameters of the AuNPs are evaluated by using a non-linear least square fitting routine. A sphere structure model combined with a lognormal size distribution of particles is

found to be most appropriate. The scattering curves are fitted by the equation $I(q)=\int_0^\infty N(r)\left|V_p(r)F(q,r,\Delta\eta)\right|^2 S(q)dr + cq^{-4} + Bg$ and by using the software SASfit [4] where $F(q,r,\Delta\eta)$ is the scattering amplitude $F_{sphere}(q,r,\Delta\eta)=\Delta\eta\, 3\frac{\sin(qr)-(qr)\cos(qr)}{(qr)^3}$ of a homogenous sphere of radius r and $\Delta\eta$ is the electron density difference between the Au particle and the DES matrix. q is the magnitude of the scattering vector, which is related to the wavelength (λ) of the X-rays and scattering angle (2θ) as $|\vec{q}|=\frac{4\pi\sin\theta}{\lambda}$. The term B_g describes the scattering angle independent fluctuation scattering and the fluorescence radiation. A structure factor $S(q)$ for hard spheres with local monodisperse was appropriate [5]. This means, a particle of particular size is surrounded by similarly sized particles. The term cq^{-4} indicates the smoothness of the particles surface. We assume that there is no formation of physical fractals [6]. The volume of the spherical particle is given by $V_p(r)$. SASfit requires a pre-defined shape of the size distribution $N(r)$. While fitting, the particle size distribution and the number density of particles serve as fit variables. The uncertainties are obtained by multiple model fits. The structure factor term $S(q)$ can be used to evaluate the radial distance distribution function $G(r)$ as: $G(r)-1\propto\frac{1}{r}\int_0^\infty q[S(q)-1]\sin(qr)dq$. It gives the probability that the centers of a pair of particles will be separated by a distance r. Moreover, the potential of mean force (PMF), which defines the average work needed to bring the two particles from infinite separation to a distance r, can be evaluated by using $G(r)$ as $G(r)=\exp[-\Phi/kT]$.

S3: <u>Size distribution and size parameter</u>



(a) Lognormal distributions of the nanoparticles evaluated by fitting the respective SAXS curves (b) Resulting size (diameter) parameters of AuNPs evaluated after fitting the SAXS curves for the samples deposited for 30 up to 300 seconds.

S4: <u>TEM measurements</u>

TEM measurements performed on a JEOL JEM 2100 Cryo-TEM with a bottom-mounted TVIPS F416 CMOS camera. AuNPs were obtained after gold-sputtering on DES for 300 seconds (without any stabilizer) and 120 seconds (with stabilizer). The samples were transferred on to the lacey carbon grid. Excess liquid was removed by blotting 5 times before vitrification of the sample in liquid ethane. The grid was put in a Gatan 914 Cryo transfer sample holder and kept at around -170 °C during the observation.

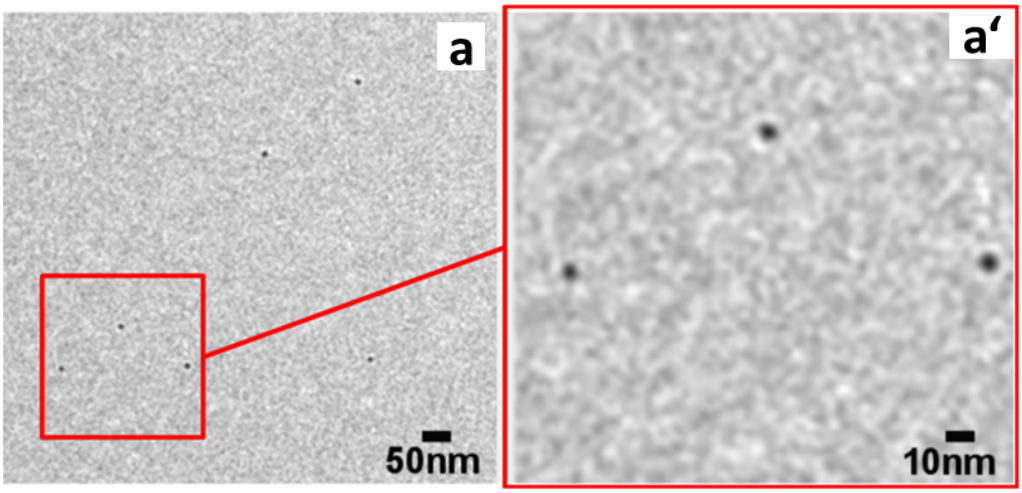
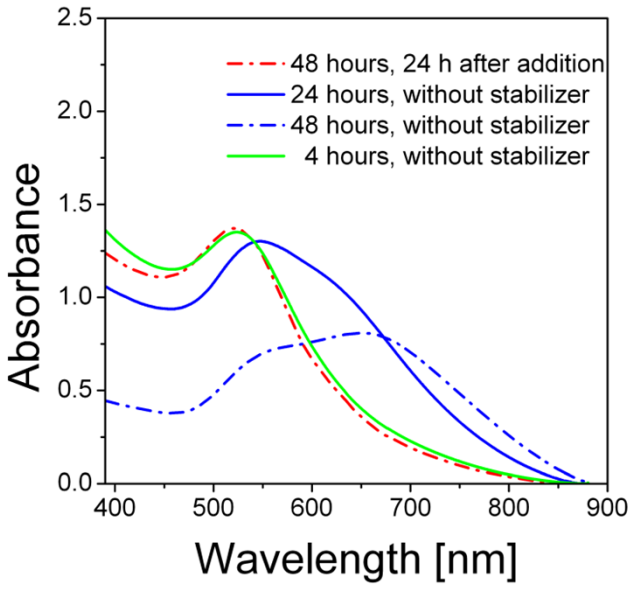


Figure: (a) Cryo-TEM micrographs of gold nanoparticles in DES synthesized by sputter deposition at 20 mA and 0.05mbar (argon pressure) for 120 sec and stabilized by stabilizer bis-((2-Mercaptoethyl)-trimethyl-ammonium) disulfide dichloride. (a') Enlarge image of a particular part (red box) of TEM micrograph.

S5: <u>UV-Vis measurements</u>

The green and the red curves characteristically show the UV-Vis absorption of the 5 nm gold nanoparticles at about 525 nm peak maximum. Without the stabilizer the 5 nm gold nanoparticles undergoes a continuous process of self-assembly.



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