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COMMUNICATION

Phototriggered growth of crystalline Au structures in the presence of a DNA–surfactant complex†

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A method for the preparation of complex anisotropic gold structures with potential uses in catalysis and photonics is presented based on the use of salmon sperm DNA and a photosensitizer to enable light triggered gold salt reduction.

Metallic nanoparticles (NPs) have, in recent years, found applications in many different fields due to their remarkable optical and electronic properties stemming from the free electrons confined in a small volume and the high surface to volume ratio.[1] Among them, gold NPs (Au NPs) have a wide application spectrum ranging from catalysis to photonics, nanoelectronics and nanomedicine.[2] Recently, anisotropic and multi-branched NPs such as nano-sea urchins, nanoflowers and nanostars have attracted lots of attention due to their strong two photon luminescence and plasmon resonance exhibited close to NIR.[3] Such structures can be prepared using different stabilising ligands, surfactants and changes under ambient conditions (temperature, ionic strength or pH).[4] Templated synthesis using either surfactant–polymer or surfactant–polyoctometalate assemblies was successfully used to obtain Au nanostructures of different shapes and there is lots of interest in the application of biotemplates for design of novel materials.[5] DNA being a robust biopolymer, which can enable precise structuring and nano-element design based on the high specificity of the base pairing, represents an interesting platform for the design of novel NP based materials. Small (up to 35 base pairs), double stranded DNA has recently been used as a template for the synthesis of highly fluorescent Cu and Ag NPs and chiral structures were prepared by precise immobilisation of Au NP onto DNA wires.[6] The interest for such DNA-hybrids is growing rapidly not only because of their use in preparation of biosensors,[7] but also due to their promising applications in photonics and in electronics.[8]

Here we present the use of DNA obtained from salmon sperm for growth of complex Au NP based structures with the help of light triggered reduction of the Au salt precursor. Salmon sperm DNA is an abundant and cheap source of DNA and previous studies have revealed that extracted DNA can be employed as a functional and robust optical material for electronics and photonics where larger amounts of materials are needed.[9] Light triggered reduction of the Au salt precursor enables the temporal control over the growth of the NPs, which could help in designing new materials whose properties change on demand as well as photonic devices in which light acts as a trigger of different processes. Furthermore, it has already been reported that light facilitates redistribution of ligands and charges on the surface of NPs, and therefore might influence the further aggregation and growth after initial NP seeds are formed.[10] It is believed that the size and shape-dependent photo-effect produced by light might break the stabilising effect of surface ligands and trigger clusterisation with other nanoparticles. A number of studies exploring the photo-activation of NP production have been reported,[11] but the effect of the irradiation has not been studied extensively, in particular, in the context of hybrid NP structure formation. To our knowledge this is the first example of light being used as a trigger to prepare complex Au structures in the presence of both the natural DNA and a surfactant. Such a facile technique, coupled with current advances in the field of DNA optoelectronics, can therefore open new routes for thin film modification for photonic applications.

DNA from salmon sperm was first rendered soluble in isopropanol (IPA) by addition of the CTMA surfactant in a 1 : 1 ratio. The DNA was sonicated before CTMA treatment to reduce the average molecular weight and obtain fragments of approx. 1500 kDa as this is a common procedure to improve the DNA film forming characteristics.[12] To the solution of DNA and CTMA in IPA, $HAuCl_4$ and the organic photosensitizer Irgacure-2959 (I-2959) were added followed by the irradiation with a 365 nm light source (Fig.1). DNA has a high affinity for metallic cations, which can coordinate within the double helix and act as NP seeds. A ketyl radical is formed upon irradiation of I-2959, which acts as a Au(III) reducing agent[13] and the solution first turns red (plasmon peak at 520 nm, data not shown) and then pale yellow. TEM analysis revealed that complex, crystalline structures of different sizes (100–200 nm) (Fig.2a) are formed after up to 30 min irradiation. HRTEM analysis showed that the crystal structure matches perfectly with Fm-3m gold (ESI, Fig S1†). When initially prepared solutions of 200–250 nm structures were left to age for 3 months, massive, branched flower-like structures with 200 nm core and 600 nm long petals of crystalline gold were observed (Fig. 2). Further growth could be avoided if the prepared solutions are centrifuged, washed and stored protected from light. Formation of complex Au nanoflowers and dendritic structures has been reported before.[4] The growth of such structures depends on the kinetics of the

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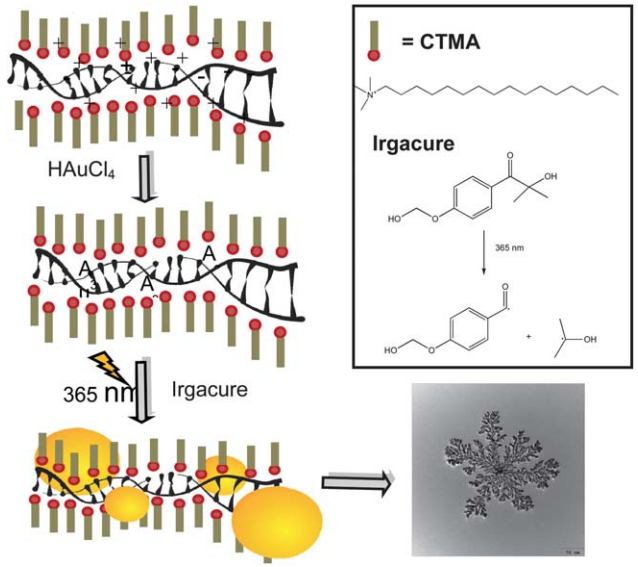

Fig. 1 Principle of phototriggered growth of Au structures using a DNA–surfactant (CTMA) complex as a template. Inset shows the structures of the surfactant and the Irgacure (I2959) photoinitiator.

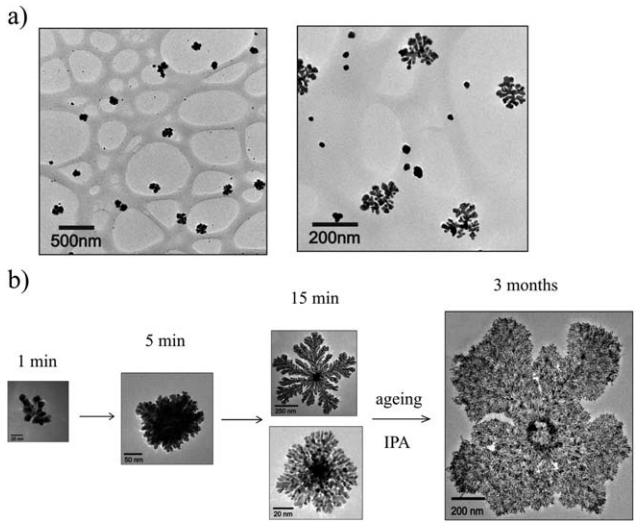

Fig. 2 TEM images of Au structures observed after irradiation of DNA–CTMA–$HAuCl_4$ in the presence of I-2959 for 15 min (a) and evolution of the structure formation after 1, 5 and 15 min irradiation and ageing for 3 months (b).

NP production, the amount of primary NP seeds, type of the surfactant and other directing surface ligands. In addition, it was shown that light has a certain effect on the formation of dendritic Ag structures and it can break stabilising bonds with ligand molecules and cause additional agglomeration and coalescence.[10]

In our case light also controls the amount of reducing ketyl radicals produced and in turn, the amount of primary Au NP seeds from which the complex structures can be formed by coalescence and agglomeration. We have followed the structure growth and observed that the shape and the size of the structures change with irradiation time (Fig. 2). First, small and irregularly shaped nanocrystals are formed, which act as seeds for further growth and agglomeration of freshly reduced Au atoms (Fig.2, 5 min). After 15 min both large flower-like and snowflake-like structures of different sizes but with distinguishable darker, denser cores of 70–120 nm and lighter outer boundaries and dendrites of up to 400 nm were observed. Similar dendritic structures have been described previously and it was suggested that they are a result of a slow and dense aggregation of elongated gold nanoparticles formed by fusion and reorganisation of Au atoms.[14] The observed polydisperse mix of grown structures was partially attributed to a finite size distribution of DNA resulting from the sonication process. Interestingly, light alone, without the presence of the photosensitizer can induce the growth of nanometer sized anisotropic seeds which, however, do not result in the dense core dendritic structures observed when a photoinitiator is present (ESI, Fig. S2†). This indicates that light itself, in the presence of DNA–CTMA can induce some Au salt reduction and coalescence. However, without the ketyl radical the rate of production of Au atoms is slow and there are not enough freshly produced NPs for complex structure formation. The importance of the light/photosensitiser was further confirmed by a control experiment in which use of $NaBH_4$ as a reducing agent resulted in formation of 10–15 nm spherical Au NP only (ESI, Fig. S3†).

Next, we were interested in exploring the significance of individual components on the formation of anisotropic structures. No flower-like and snowflake-like structures were observed in the experiments in which each of the components was irradiated separately in the presence of Au salt and photosensitizers (ESI, Fig S4†). 3 nm spherical NPs and larger agglomerates were obtained in the presence of only CTMA and DNA, respectively, and irregularly shaped NP (70–100 nm) and rods (400 nm) in the absence of both. This confirms that the presence of both DNA and CTMA is crucial for the formation of the larger dendrite structures. We believe that DNA acts as a soft template for formation of NP seeds. If the surfactant is not used, irregularly shaped large agglomerates are formed (ESI, Fig. S4d†), most probably due to the aggregation of NP seeds on coiled, non-stabilised DNA templates. When CTMA is added to the DNA solution, the structural changes in the DNA backbone – together with the effect of light irradiation – direct the growth of the branched crystalline structures. This cooperative, structure-directing effect is further confirmed by a remarkable change of DNA–CTMA grown Au structures upon addition of the anionic surfactant SDS. Depending on the DNA–CTMA to SDS ratio, large branched structures and worm-like structures – instead of compact dendritic shapes – were obtained (Fig. 3).

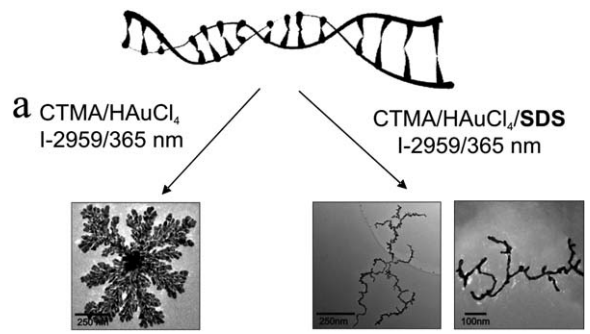

Fig. 3 TEM images of Au structures prepared by a 15 min irradiation of DNA–CTMA–$HAuCl_4$ in the presence of I-2959 in the absence (left) and the presence of SDS surfactant (right).

The effect of SDS can be observed both when the SDS is added to the solution prior or after the 15 min irradiation (ESI, Fig S5†). SDS as a linear, anionic surfactant causes decomposition of the CTMA–DNA complex through CTMA displacement, which in turn induces the changes in the DNA template structures and the growth of large nano-wire-like structures composed of NP grown along the double stranded DNA. When SDS is used instead of CTMA, spherically shaped Au NPs, similar to those obtained with Au salt only, are observed (ESI, Fig. S6†).

Finally, we explored the spectroscopic properties of the prepared structures. Interestingly, there was broadening of the plasmon band, but no significant shift when the absorbance spectra were recorded with different irradiation times (Fig. 4). This is in agreement with simulations done on metal tripods,[15] which showed that predominant contribution to the plasmon resonance comes from the tips of the branches and there is negligible effect of the heterogeneity and shape of the structures. However, the samples became more transparent with the prolonged irradiation (Fig. 4, inset) indicating the formation of larger particles, which scattered broadband light.

The photoluminescence (PL) was investigated by irradiating samples with 300 nm wavelength, which leads to an excitation of the interband transition and collective oscillation of conduction electrons.[16] The PL spectra of Au structures are shown in Fig.4b and several peaks between 350 and 600 nm can be observed. The intensity of PL increases with the irradiation time, which indicates that there is an increase in nanocrystal size. A similar effect was reported for spiked Au nanourchins. There are clear differences in the PL spectra of Au flowers when compared to other types of Au NPs such as spheres and rods (ESI, Fig.S7†). However, a peak at 380 nm resembles the broad peak observed for diamond shaped Au structures. Au diamond structures (Fig. S7c†) are highly anisotropic with well defined rugged spikes, which we believe contribute to the PL in the same way as the edges of the large branched DNA templated structures. We are currently exploring the use of such structures for the design of surface plasmon resonance hot spots, which might be of particular interest for surface resonance Raman scattering applications.

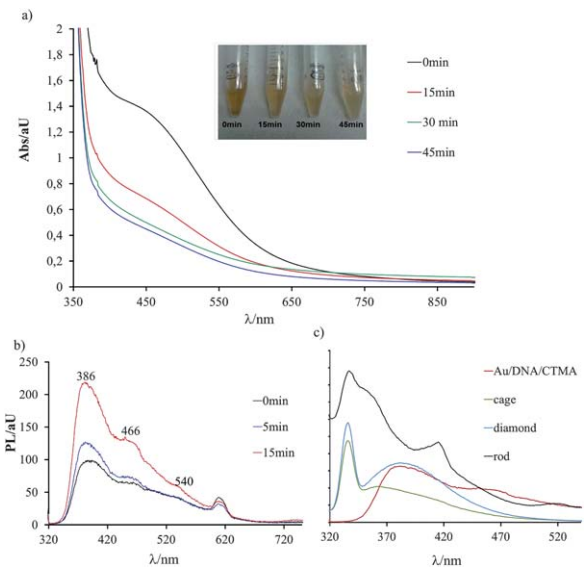

Fig. 4 Uv-Vis (a) and photoluminescence (b) spectra of the solutions after different times and (c) the comparison of PL spectra of differently shaped Au nanostructures.

In conclusion, complex anisotropic Au crystalline structures were prepared for the first time using a salmon sperm DNA–surfactant complex and light induced reduction of Au salt precursor. The structure growth was followed over time and the first spectroscopic analyses performed to pave the way for future applications. We believe that these results could inspire the preparation of novel DNA based materials. Our future efforts will be focused on the preparation of thin DNA films with temporal control over the growth of complex structures to be explored in the fields of catalysis and DNA photonics.

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