GOLD NANORODS AS MULTIPURPOSE BUILDING BLOCKS

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Abstract

Among all of the plasmonic noble metal nanoparticles the gold nanorod (GNR) retains a special place. Its elongated shape gives it unique anisotropic optical and physico-chemical properties. Owing to possibility to control the end-cap geometry, the GNR is the most tunable shape in the terms of localized surface plasmon resonance (LSPR) spectral range. Moreover, the possibility to synthesize GNRs in high yield as colloidal solution makes them cost-effective nanomaterial. The number of prospective applications for colloidal GNRs is still growing – from novel immunolabelling for both optical and electron microscopy, model nanoparticle for emerging field of theranostics, to building blocks of optical metamaterials, literally forming ordered arrays of nano-antennae. In this talk we sum up our results from extensive study of aqueous GNRs colloidal solutions stabilized by cetyltrimethylammonium bromide, synthesized by modified seeded growth approach. We use the strong LSPR dependence on rod aspect ratio to observe GNRs growth kinetics and tune the synthesis to produce high yield monodisperse colloidal solutions. The resulting quality allows us to easily apply the GNRs colloid as a cell-specific light-scattering label in confocal microscopy or to prepare both two- and three-dimensional colloidal crystals of GNRs by self-assembly. Using a state-of-the-art scanning electron microscopy we have directly observed such process at drop surface and we have obtained an original video supporting our findings in GNR colloidal crystal formations. We demonstrate visible LSPR coupling effects in optical properties of such ordered arrays.

Keywords:
Gold nanorods, localized surface plasmon resonance, self-assembly, metamaterial, theranostics

1. INTRODUCTION

Noble metal nanoparticles (NMPs) evoked great interest in past two decades, resulting in a number of different MNPs shapes synthesis and these methods refined to a point, where high-yield samples of non-spherical metallic MNPs can be obtained. The unique electro-optical properties of such MNPs induced number of applications spanning from fundamental studies of colloidal systems to application in biological systems as a biocompatible and addressable carrier. Since about 1980, an enormous effort has been devoted to the synthesis of uniform colloidal particles with tunable size and shape [1]. Colloidal particles of non-spherical shapes possess many peculiar physico-chemical properties which promise fundamentally new applications for optics, photovoltaics, chemical sensors, biomedicine and other areas [2, 3]. Among metallic nanoparticles the gold nanorods occupy a prominent position, especially for their excellent plasmonic tunability [4-6].
2. RESULTS

Fig. 1: Image of colloidal solutions of GNRs synthesized by seeded growth approach (left). Absorption spectra of the GNR solutions (right).

2.1. Self-Assembly of gold nanorods

Fig. 2: Self-assembly of GNRs from water solution using controlled drying technique. Our method allows us to prepare both voluminous domains of assembled GNRs, and 2D monolayer islands of standing GNRs.

In this work, seeded growth method in the presence of silver nitrate [7] was used for synthesis of monodisperse population of GNRs (Fig. 1).

Nearly twenty years of experience with self-assembly of spherical and quasi-spherical colloidal particles [8] inspires thoughts that “bottom-up” approach based on self-assembly of anisotropic colloidal particles might be a feasible route to obtain the composite materials with excellent three-dimensional periodicity, at least under some circumstances [9].

We have exploited the basic principles described in work of Akbulut et al. [10] and we have obtained high quality voluminous domains of several hundred cubic micrometres through the CTAB driven phase separation. By control of the thermodynamic parameters one can achieve the possibility of controlling both the level of self-alignment and the inter-particle distance [11]. Figure 2 demonstrates the coexistence of both voluminous colloidal crystals and 2D arrays of standing rods. The voluminous arrays are created from smectic-like liquid crystals of GNRs assembled by steric confinement achieved by increasing the concentration of GNRs near the meniscus of drying drop. The 2D islands on the other hand, are formed at the liquid/gas interface at the top surface of drying drop.
These findings have been confirmed in situ using high resolution scanning electron microscopy including state-of-the-art WET-STEM technique which allows one to observe the dynamics of GNR self-assembly in thin water/CTAB membrane formed under conditions of saturated water vapour (Fig. 3). Most importantly, our method allows us to explore the effect of inter-particle distance of GNRs in formed arrays. The particle separation ranges from 8 nm to 2 nm. This interval appears to be crucial crossover between weak plasmon interactions to strongly coupled plasmon modes in nanoparticle arrays.

The domains of aligned GNRs are big enough to explore their basic far-field optical properties by conventional white-light microscope (Figs. 2, 4). We utilize transmitted light mode for 2D GNRs arrays and reflection mode for 3D voluminous GNRs colloidal crystals. One can observe spectral changes in dependence of GNRs alignment in the crystal (Fig. 4). Such metallo-dielectric composites represent real steps towards the preparation of three-dimensional metamaterials.

Fig. 3: Image of standing arrays of GNRs (approx. 20 x 60 nm) dynamically forming in thin water/CTAB membrane. The self-assembly process was observed using state-of-the-art WET-STEM microscopy in saturated water vapours. (In collaboration with Dr. Petr Wandrol, FEI Company, Czech Republic and Dr. Miroslav Slouf, IMC ASCR)

Fig. 4: Top-down view of self-assembled GNRs arrays by white-light reflection microscope (50x objective, scale bar = 10 μm) showing several differently oriented domains. The GNRs arrays exhibit colour switching when one is moving through the crossed polarizers setting (left). Image of large cleaved colloidal crystal of GNRs. Top surface is covered by excluded surfactant. Clean cross-sections, created by cleaving the crystal, reveal the well assembled nanorods which are uniform in size (middle). Detailed view on the same colloidal crystal (right).

2.2. Gold nanorods as biological markers

Gold nanorods are excellent candidate as addressable optical marker/carryer in biological systems. Strong optical absorption/scattering in visible and near-infrared region allows visualisation of the spatial distribution of GNRs in tissues using confocal microscopy. The non-bleaching and tunability of the optical spectral properties GNRs give them possible advantages over fluorescent dyes. Photothermal properties, especially
Heat generation in GNRs induced by light absorption, give rise a new application field of photothermal cancer therapy. In this study we utilize gold nanorods as light scattering probes in confocal microscope setup in order to explore their minute influence on human prostate carcinoma cells (line DU-145).

Two-photon fluorescence microscopy is conveniently used in imaging based on two-photon photoluminescence induced in GNRs. High spatial resolution and reduced background are the main advantages of the method. Unfortunately, undesired heat generation affects intracellular environment during continuous scanning with the femtosecond laser. To avoid this disadvantage, confocal reflectance microscopy was adopted as a method of non-destructive imaging in live cells based on strong scattering light by GNRs [12]. To overcome instability of the CTAB bilayer at the GNR surfaces, cytotoxic CTAB was replaced by covalently bound thiolated polyethylene glycol (PEG) or by thiolated analogue of CTAB, (16-mercaptohexadecyl)trimethylammonium bromide (MTAB) [13]. Both PEG or MTAB are non-toxic, biocompatible, covalently bound ligands, non-specifically targeted to cells (MTAB was synthesized by Dr. Kamil Musilek and Dr. Kamil Kuca, UHK).

Fig. 5: Confocal microscope image of DU-145 human prostate carcinoma cells after intake of GNRs. The gray channel corresponds to transmitted light, blue channel is fluorescence from HOECHST dye and red channel is backscattered light from GNR probes (633nm laser). The localization of GNRs in the cells can be resolved in great detail. (In collaboration with Dr. Zdenek Hodny and Dr. Zuzana Duchoslavova, IMG ASCR)

3 METHODS

3.1 Gold nanorods synthesis

Monodisperse nanorods samples were synthesized by seeded-growth method in the presence of silver nitrate [7]. This method was chosen because it leads to the best possible yield of nanorods (up to 99%). Moreover, by varying the amount of silver(I), one can fine tune the aspect ratio of the grown rods. The usual synthesis process involves preparation of monocrystalline gold seeds (2-4 nm) by fast reduction of gold(III) salt in the presence of CTAB and adding them into the growth solution of gold(I) complexed to CTAB in the presence of silver(I) in aqueous solution (pH 2-3). This starts the growth process where the amount of seeds added and the starting concentration of silver (I) influences the size and aspect ratio of rods produced.
3.2 Instrumental setup
Wide-field white-light microscope images were acquired with Nikon Eclipse LV-100 microscope. Both transmission and reflection modes were used. Polarization settings were used using the standard microscope polarizer and analyser.
Confocal microscope images under live-cell conditions were acquired by Leica TCS SP5 AOBS confocal microscope. Cells were imaged using transmitted light detector. GNRs backscatter was detected 633 nm laser in reflection mode. For colocalization analysis, cell nuclei were stained by Hoechst dye, visualized by excitation at 405 nm and 455 nm for collection of photoluminiscence.
SEM images were acquired by JEOL JSM-7500F FE-SEM utilizing upper secondary electron detector and 2 kV probe energy. Absorbance spectra of colloidal solutions of GNRs were measured by Shimadzu UV-1601 UV-VIS spectrophotometer.

4 CONCLUSION
We present recent aspects of our research in the field of anisotropic gold nanoparticles: Optimized synthesis for biological ultrastructure TEM imaging; the self-assembly of NPs, using state-of-the-art scanning electron microscopy including Wet-STEM imaging of self-assembly of gold nanorods in thin water membrane and confocal optical microscope imaging of GNRs as a scattering markers in biological systems.

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