GOLD NANOROD ARRAYS: OPTICAL PROPERTIES
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Abstract
We present two- and three-dimensional arrays of aligned gold nanorods (GNRs) on the transparent substrates using the method of self-assembly by controlled drying from aqueous colloidal solution. Single domains are big enough to identify them under white-light in conventional microscope. The optical microscope images are correlated to scanning electron microscope (SEM) micrographs of the same area to distinguish between patches with different rod orientation and the far-field optical response of coupled plasmonic field. GNRs are synthesized by well-known seeded growth method and used in the form of colloidal solution with cetyltrimethylammonium bromid (CTAB) as stabilizing surfactant. We utilize self-assembly of GNRs in aqueous environment using simple system of GNR/CTAB/water. Our method does not require laborious chemical modifications of nanorods, e.g. the grafting of polymers onto GNRs, CTAB bilayer exchange, or use of co-assembly methodology with additives. This anisotropic metallo-dielectric composite is a step towards the preparation of three-dimensional metamaterial.

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

1. INTRODUCTION
It has recently been shown convincingly that self-assembly of anisometric metallic nanoparticles into superstructures would be viable way for mass production of metamaterials working in visible region [1]. We have developed the method of self-assembly of GNRs in aqueous environment using simple system of GNRs/surfactant/water [2]. Well defined 3D domains and 2D islands of aligned GNRs were prepared using controlled drying techniques. The domains are big enough to be examined by using a conventional optical microscope.

2. EXPERIMENTAL
We have exploited the basic principles described in work of Akbulut et al. [3] 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 [4]. Figure 1 demonstrates the coexistence of both voluminous colloidal crystals (Fig. 1b) and 2D arrays of standing rods (Fig. 1c). 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.

2.1. Observation of 2D GNR arrays in white-light transmission optical microscope
We have directly observed arrays of standing GNRs in white-light transmission microscope. The arrays appear red in colour that corresponds to the absorption by transversal LSPR mode of an individual GNR in the array. Interesting phenomena is observed, when the 2D arrays are heated (by intensive light illumination), the colour starts to change to blue. This phenomenon corresponds to the longitudinal LSPR
dominating the spectra and it can be explained by the idea, that the GNRs included in arrays start to lean away from their upward-standing positions. This was confirmed by FE-SEM imaging of selected 2D islands.

Fig. 1: Top-down white-light transmission microscope view on self-assembled GNR arrays (60x/0.7NA PLAN objective) (a) consisting both of voluminous assemblies (dark) and 2D mololayers of standing GNRs (blue – red). FE-SEM imaging confirms the declared GNR configurations (b,c)

Fig 2: Detailed white-light transmission microscope view (100x/0.9NA PLAN objective) on self-assembled 2D islands of GNRs (left). FE-SEM image of one of the islands (right.)

2.2. Observation of voluminous GNR arrays under white-light reflection microscope
The optical appearance of voluminous GNR arrays has been explored by white-light microscope in reflection mode, as the stacked layer of assembled rods already absorb most of the transmitted light. In Figure 3 can be seen reflection micrographs of voluminous GNR domains together with SEM micrograph depicting detailed view on part of the area of interest. The domains exhibit interesting behaviour under polarized light conditions – the domains of differently oriented rods change colour in dependence on incident light polarization and analyser settings (Fig. 3 – 2a, 2b).

**Fig 3.** Single domains are big enough for identification under white-light reflection microscope using 50x/0.80NA PLAN objective (1). The images can be correlated to SEM observation of the same area (3) to distinguish between different orientation of rods in respective domains and their response to polarized light (2a, 2b) (yellow arrow – incident polarization, red (green) arrow - polarization analyzer settings).
3. METHODS

3.1. Gold nanorods synthesis
Monodisperse nanorods samples were synthesized by seeded-growth method in the presence of silver nitrate [5]. 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. In described experiments we utilize GNRs with longitudinal LSPR at 650 and 750 nm (Fig. 4).

3.2 GNR self-assembly and deposition
The composites consisting of smectic-like arrays of parallel aligned nanorods in the CTAB environment were obtained. Interparticle distances were approximately three times as long as in the „solid“ colloidal crystal, where the aliphatic chains of inner solvation CTAB layers on neighbouring nanorods are interdigitated. By varying the length of aliphatic chains in surfactants, the distances between nanorods in colloidal crystal could be adjusted and thus coupling of localized surface plasmons could be tuned [4].

3.3. Instrumental setup
Wide-field white-light microscope images were acquired with Nikon Eclipse LV-100 microscope. Both transmission and reflection mode was used. Polarization settings were set using the standard microscope polarizer and analyser. 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
Large single-domain three dimensional colloidal crystals of GNRs with typical volumes about several hundred cubic micrometres were prepared. 2D islands of standing GNRs were prepared with sizes above 5 \( \mu \)m. Such areas already allow seeing the optical properties of GNR self-assemblies using conventional white-light microscope. Metallo-dielectric composites described in this study represent real steps towards the preparation of three-dimensional metamaterials.

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LITERATURE

