Functionalisation of gold nanorods and its application to optical data storage

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Abstract—In this report we show the application of silica coated gold nanorods to optical data storage. We show controlled growth of a thick silica shell onto gold nanorods. The coated nanorods are transferred into a PVA matrix and data patterns are recorded. A silica layer on the nanorods dissipates the heat and the matrix does not melt, allowing reliable data storage.

Keywords-component; gold nanorods; silica coating; optical data storage; heat dissipation.

I. INTRODUCTION

A special class of nanoparticles is formed by the non-spherical geometries such as nanorods, which exhibit two absorption bands in their absorption spectrum. The transverse absorption band is associated with electron oscillation along the short axis of the particle while the longitudinal band corresponds to the aspect ratio of the rod. The longitudinal absorption band of gold nanorods can be tuned from the visible to near-infrared frequencies.

We explore the application of gold nanorods to high density optical data storage. Here we report on the synthesis, functionalisation and application of CTAB stabilized gold nanorods doped in a silica/polymer hybrid matrix. When rods without a silica shell are dispersed in polymer, melting of the matrix under strongly focused illumination was observed. We did not observe melting of a matrix without nanorods. We therefore attribute the melting of the PVA matrix to local heating of the PVA by the nanorods. For that purpose we show the controlled growth of a thick silica shell on the nanorod. A silica layer on the nanorods dissipates the heat and the matrix does not melt, allowing reliable data storage.

Recently controlled growth of a silica shell on CTAB stabilized gold nanorods has been shown by Pastoriza-Santos et al. [1]. The method they adopted to coat gold nanorods with silica involves an initial coating with polystyrene sulfonate, poly-(allylamine hydrochloride), and poly-(vinylpyrrolidone). The PVP coated particles were redispersed in 2-propanol and further growth of the silica shell was achieved by the Stöber method [2]. The much simpler method we adopted to coat gold nanorods is based on the method used to silica coat citrate stabilized gold nanospheres as reported by Liz-Marzan et al. [3], resulting in a general method to coat gold nanoparticles of arbitrary shape and size.

II. MATERIALS

We start by describing the preparation of the gold nanorods by wet chemical synthesis. We continue with the procedure we used to silica coat the gold nanorods with a controllable shell thickness. Finally we describe the preparation of poly-vinyl alcohol (PVA) films doped with silica coated gold nanorods for use in data storage applications.

A. Nanorod preparation

Gold nanorods were prepared using Ag⁺ assisted, seed mediated growth based on the method developed by El-Sayed et al. [4]. A 500 mL aqueous solution containing CTAB (0.1 M), HAuCl₄ (0.5 mM), and AgNO₃ (0.12 mM) was prepared. Au(III) was reduced to Au(I) by adding 3 mL of an ascorbic acid solution (0.1 M) while stirring. A seed solution (3 mL) containing CTAB capped gold particles (estimated 1.5-2 nm in diameter) is added to the growth solution. The absorption spectrum of the as prepared nanorods is shown in Fig 1. A clear transverse and longitudinal absorption band can be distinguished at 515 and 835 nm, respectively. The inset shows a TEM image of the nanorods.

![Figure 1. Absorption spectrum of the Au nanorods. The inset shows a TEM image of the sample. The scalebar indicates 50 nm.](image)

B. Silica coating

Controlled growth of a thick silica shell on gold particles has been shown previously on gold spheres [2] and we apply this method to gold nanorods. Controlled silica coating of the as prepared nanorods is achieved in two steps. First a thin silica
layer is formed on the nanorods [3, 5], followed by controlled
growth of a thicker shell using the Stöber method [2, 3].

Figure 2. Evolution of the longitudinal surface plasmon peak as a function of
TEOS concentration.

As prepared nanorods are first surface modified with a
silane coupling agent (MPS, (3-mercaptopropyl)trimethoxysilane) before purification by centrifugation. The
nanorods are redispersed in distilled water and coated with a
thin silica layer by mixing with an excess of sodium silicate.

Silicate treated rods can be transferred into ethanol to allow
growth of a thicker silica shell using the Stöber method. After
centrifugation the nanorods are redispersed in a mixture of
water (10 M), ethanol, NH4OH (0.5 M) and tetra-ethoxysilane
(TEOS). Silica shell thickness can be readily controlled by
varying the TEOS concentration. As a result of the silica
coating the dielectric function of the environment of the
nanorods changes and the longitudinal absorption band will
show a red-shift. In Fig. 2 we show the shift of the longitudinal
absorption band as a function of TEOS concentration. A red
shift of more than 30 nanometers is observed for the highest
TEOS concentration.

C. Transfer into PVA

The silica coated nanorods were dispersed in a poly vinyl-
alcohol (PVA) film by mixing a nanorod solution with peak
absorption of ~10 with a 10 % PVA solution in a 1:1 volume
fraction. We do not observe a noticeable change in the
absorption spectra, indicating that the particles are stable in the
matrix.

III. APPLICATION: HIGH DENSITY OPTICAL DATA STORAGE

A novel application of nanorods dispersed in a silica/polymer hybrid matrix is high-density optical data
storage. Recording of data is achieved by femtosecond pulsed laser induced melting of gold nanorods [6]. The pulse train (80
fs pulses, 82 MHz, 0.12 nJ per pulse) passes through a
computer controlled shutter to control the exposure time of the
individual bits (10 ns). The pulse train is focussed to an area of
about 1 μm² through a 0.4 NA objective. Nanorod melting in
the focal volume will decrease the absorption maximum in the
associated longitudinal absorption band. The recorded data is
read out in transmission by monitoring the change in
absorption at the recording wavelength.

In Fig. 3 (a) we show a data pattern recorded in a nanorod
based storage medium. The nanorods do not have a silica shell.
As can be clearly seen deformation of the PVA matrix material is
observed. The deformation is not observed in PVA films
which are not doped with nanorods. We therefore attributed the
deformation of the matrix material to heat transfer of the
nanorods into the medium. In Fig. 3 b) we show the pattern
recorded in nanorods coated with an 18 nm thick silica shell,
dispersed in PVA. The recording conditions are identical to
Fig. 3 (a). When the nanorods are coated with a silica shell we
do not observe deformation of the matrix material. The silica
shell dissipates the heat generated by the gold nanorods,
causing a significant decrease temperature at the silica/PVA
interface.

IV. CONCLUSION

We developed a procedure to silica coat CTAB stabilized
gold nanorods with a silica shell of controllable thickness. We
demonstrated the use of silica coated gold nanorods in optical
data storage. Data was recorded by pulsed laser induced shape
transformation of gold nanorods. We used the silica shell
around the gold nanorods to dissipate heat from the particle and
prevent the PVA matrix from deforming.

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"Synthesis of Nanosized Gold-Silica Core-Shell

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