OPTICAL DETECTION SYSTEM BASED ON TITANIA QUANTUM DOTS MODIFIED WITH
GOLD NANOSHELLS

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Abstract

Luminescent quantum dots (QDs) are increasingly attracting the attention as possible optical detectors of
biomolecules, such as proteins, DNA, etc. Large amount of different factors influences the selection of
material for QDs synthesis when dealing with substances from living organisms. Non-toxic and biocompatible
titanium dioxide (TiO₂) and gold were chosen as a suitable material for QDs creation employing template
based non-lithographic technique. Namely, nanoporous alumina template was used for the fabrication of
TiO₂ QDs by anodic oxidation of sputtered Ti film on a silicon wafer followed with gold deposition by
electrochemical approach.

Self-ordered TiO₂ QDs modified with Au nanoshells were characterized by SEM, which confirmed that the
size of QDs satisfies the requirement of quantum confinement effect. Fluorescence spectroscopic study was
also performed, comparing the emission spectra of annealed and non-annealed QDs and showing that the
annealing is essential for achieving desired fluorescence properties of TiO₂ QDs. Even the gold nanoshells
did not enhance the intensity of TiO₂ QDs in our case; they provide an excellent platform for further
functionalization with biotinylated oligonucleotide or ssDNA. This functionalization step enables subsequent
hybridization reaction with detected nucleic acid resulting in the decrease of QDs luminescence intensity.

Keywords: porous anodized alumina, quantum dots, TiO₂, gold nanoshells, luminescence

1. INTRODUCTION

The coating of semiconducting QDs with metal plasmonic nanostructures, such as gold nanoshells, can lead
to the enhancement of QDs luminescence which opens new opportunities in sensing, imaging and medical
diagnostics [1, 2]. The thickness Au shell, its size and the distance between particular nanostructures can
tune the optical properties of whole system. However, the choice and geometry of semiconducting core
material also strongly influence its optical properties [3]. In an effort to avoid the usage of traditionally applied
toxic cadmium based QDs [4, 5], we designed new system based on biocompatible titanium dioxide QDs. So
far, the conjugation of nanosized gold with TiO₂ found the applications mainly in photocatalysis [6], as SERS
tags [7] etc. Nevertheless, the optical properties of system based on TiO₂ QDs with gold nanoshells,
especially in deposited form, have not been sufficiently investigated yet.

The photoluminescence (PL) of TiO₂ nanocrystals is usually observed in both ultraviolet (UV) and visible
(VIS) range of spectra, depending on the nanostructure size and state (colloidal or deposited). Zhang et al.
reported on the PL of colloidal TiO₂ nanocrystals with size below 10 nm around 550 nm after excitation at
477 nm (2.6 eV), which is lower than band gap energy for the bulk anatase (3.2 eV) [8]. This VIS
luminescence arose from a radiative recombination of electrons via intrinsic surface states of TiO₂
nanocrystals. The position of main emission peak did not change with annealing temperature (up to 400 °C),
but the intensity significantly increased. Liu et al. found two PL peaks of TiO₂ nanoparticles with size of
15 nm under excitation at 236 nm (4.71 eV), the first at 480 nm and the second with lower intensity at 580 nm [9]. Luo et al. observed size dependent strong UV PL located at 346 nm (4.71 eV) for TiO₂ nanodots with size of 48 nm [10]. The authors also examined the PL properties of Eu doped TiO₂ nanodots, which shifted from UV to VIS range (the main emission peak at about 614 nm under excitation at 300 nm) [11].

Recently, we reported on the PL luminescence of deposited TiO₂ QDs with the size below 10 nm in VIS range (maximum at 540 nm under excitation at 350 nm) [12]. In the following work, we studied the influence of different biomolecules (BSA, DNA) on the PL of TiO₂ QDs array after simple deposition of particular biomolecule solution on the QDs surface. We observed no change in the position of QDs emission peak after the biomolecules modification, while significant PL intensity decrease occurred depending on the biomolecules concentration [13]. Since the deposition of biomolecules on TiO₂ QDs surface was not specific in this case, we further aim at the preparation of TiO₂ QDs array covered with Au nanoshells, which enables the elimination of biomolecules nonspecific interactions due to the strong affinity of gold to thiol groups of biomolecules. This modification step should also lead to above mentioned increase of TiO₂ QDs luminescence. But the beneficial effect of Au nanoshells on TiO₂ luminescence is not always clear. For example, Li et al. showed the PL spectra of pure TiO₂ nanoparticles array as well as Au modified TiO₂ with maximal intensity located in both cases at about 420 nm after excitation at 350 nm [14]. While the position of main emission peak did not change after Au deposition, the PL intensity of TiO₂/Au system decreased compared to pure TiO₂.

2. EXPERIMENTAL

2.1 Preparation of TiO₂ QDs array covered with Au nanoshells

The fabrication procedure of TiO₂ QDs array is described in details in the previously published work [13]. Briefly, we employed the template based non-lithographic process, namely anodic oxidation of Ti layer through porous anodic alumina template in 3 M H₂SO₄ under constant potential of 5 V. In the second step, the original pores size in the range of 5–8 nm was widened to 10–12 nm using standard clean solution (SC1) to fully expose the QDs surface prior the deposition of Au nanoshells (see Fig. 1).

![Diagram of sample preparation](image)

**Fig. 1** Schematic illustration of sample preparation: a) TiO₂ QDs array in porous anodic alumina (PAA); b) widening of the pore size in PAA template prior the Au deposition; c) TiO₂ QDs array with deposited Au nanoshells after final template removing.
The modification of TiO$_2$ QDS with Au nanoshells was performed by galvanic deposition process through PAA template from hot solution containing K[Au(CN)$_2$] and H$_3$BO$_3$. The Au deposition time was set up to 1 s to avoid the growth of long Au nanowires instead of thin nanoshells. The deposition current up to 10 mA ensured the homogeneity of TiO$_2$ QDs surface coverage. Finally, the PAA template was selectively removed in the hot mixture of CrO$_3$ and H$_3$PO$_4$ solutions.

2.2 Characterization of physical and chemical properties

The size and distribution analysis of TiO$_2$ QDs covered with Au nanoshells was performed using scanning electron microscopy (FE Tescan Mira II LMU) under following conditions: work distance of about 3 mm, high vacuum mode (10$^{-3}$ Pa), voltage of 15 kV, and spot size of 2.4 nm.

The chemical composition of TiO$_2$ QDs before and after annealing in vacuum at 500 °C for 1 hour was characterized using X-ray photoelectron spectroscopy (XPS). The analysis was performed in a UHV chamber using a commercial instrument (Omicron DAR400 X-ray source and EA125 electron spectrometer). All the measurements were carried out at room temperature using Al K$_\alpha$ radiation and emission angle of 50° has been used.

The luminescence (fluorescence) properties of TiO$_2$ QDs with or without Au nanoshells were characterized by fluorescence spectroscopy (Horiba, Jobin-Yvon) under laser diode excitation at 350 nm and using photomultiplier (T1 PMT) detector.

3. RESULTS AND DISCUSSION

3.1 SEM characterization

SEM analysis confirmed the creation of hexagonally ordered TiO$_2$ QDs array as well as the presence of Au nanoshells on QD surface after galvanic deposition (see Fig. 2). We observed the size of TiO$_2$ QD in the range of 10–12 nm while the diameter of deposited Au nanostructure varied from 15 to 20 nm. This approved that TiO$_2$ QD surface was fully covered with Au nanoshells. The density of Au coverage slightly varied from place to place indicating the appearance of certain inhomogeneities in the PAA template, eventually in the originate aluminium layer.

![Fig. 2 SEM images of TiO$_2$ QD array (left) and TiO$_2$ QDs covered with Au nanoshells (right).](image-url)
3.2 XPS characterization

XPS analysis revealed the presence of TiO$_2$ in the pristine sample in amorphous state and its conversion to crystalline form (anatase) after sample annealing at 500 °C. The photoelectron lines (see Fig. 3) associated with titanium (left) and aluminium (right) are presented for as prepared sample (black) and sample annealed at 500 °C under vacuum conditions for 1 hour (red). Both TiO$_2$ and Al$_2$O$_3$ are present in the pristine sample. However, a small portion of both Ti and Al is present in a metallic form which is associated with the area in between the dots which is also analysed.

![Fig. 3](image3.png)

**Fig. 3** XPS spectra of TiO$_2$ QDs before and after annealing in vacuum: titanium (left) and aluminium (right).

3.3 Characterization of fluorescence properties

The emission spectra corresponding to TiO$_2$ QDs before (pristine sample) and after annealing in vacuum at 500 °C showed one narrow and symmetric peak located at 425 nm (Fig. 4). The fluorescence intensity of non-annealed TiO$_2$ QDs was about 11 times lower than the one of annealed QDs in anatase phase. Even we expected the enhancement of QDs luminescence properties after Au nanoshells deposition, this effect was not confirmed. In contrary, the fluorescence intensity of Au modified QDs was only 3 times higher than the intensity of pristine sample and the maximum intensity did not change the position. This observation was in agreement with the results found by Li et al. [14] as mentioned above.

![Fig. 4](image4.png)

**Fig. 4** Emission spectra of TiO$_2$ QDs before and after annealing and after modification with Au nanoshells.
CONCLUSION

The presented research work revealed the strong visible luminescence of highly ordered TiO$_2$ QDs array. We observed the multiply magnification of luminescence intensity after QDs annealing in vacuum at 500 °C, during which the transformation of amorphous titania into anatase phase occurred according to XPS analysis. Contrary to our expectations, the intensity enhancement was not noticed after galvanic deposition of thin Au shells onto TiO$_2$ QDs surface. However, this step is crucial for further QDs surface functionalization with thiol-group containing biomolecules (e.g. biotinylated oligonucleotides) which provide the platform for subsequent detection of nucleic acids via hybridization process.

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LITERATURE