TiO2 Optical Sensor for Amino Acid Detection

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TiO_2 Optical Sensor for Amino Acid Detection

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ABSTRACT

A novel optical sensor based on TiO_2 nanoparticles for Valine detection has been developed. In the presented work, commercial TiO_2 nanoparticles (Sigma Aldrich, particle size 32 nm) were used as sensor templates. The sensitive layer was formed by a porphyrin coating on a TiO_2 nanostructured surface. As a result, an amorphous layer between the TiO_2 nanostructure and porphyrin was formed. Photoluminescence (PL) spectra were measured in the range of 370-900 nm before and after porphyrin application. Porphyrin adsorption led to a decrease of the main TiO_2 peak at 510 nm and the emergence of an additional peak of high intensity at 700 nm. Absorption spectra (optical density vs. wavelenght, measured from 300 to 1100 nm) showed IR shift Sorret band of prophiryn after deposition on metal oxide. Adsorption of amino acid quenched PL emission, related to porphyrin and increased the intensity of the TiO_2 emission. The interaction between the sensor surface and the amino acid leads to the formation of new complexes on the surface and results in a reduction of the optical activity of porphyrin. Sensitivity of the sensor to different concentrations of Valine was calculated. The developed sensor can determine the concentration of Valine in the range of 0.04 to 0.16 mg/ml.

Titanium dioxide, nanoparticles, optical sensor, porphyrin, amino acid

1. INTRODUCTION

Amino acids are complex molecules forming building blocks of proteins and involved in metabolism as intermediates. There are twenty amino acids involved in protein construction. Each of them contains a unique functional group, which defines the fundamental properties such as size, shape, charge, capacity for hydrogen bonding, hydrophilicity/hydrophobicity and chemical reactivity. Valine ($C_5H_{11}NO_2$), the one of the most important amino acids, is a branched-chain essential amino acid, hydrophobic and usually localized inside of proteins. It is a stimulating agent which promotes muscle growth and tissue regeneration[2,3]. Valine can be used as food additive[4,5], nutrient and/or dietary supplement in animal drugs, feeds, and related products[6,7]. Because of the above mentioned properties, Valine is often used by bodybuilders (in conjunction with leucine and isoleucine) as stimulating agent. However, high concentrations of Valine can induce a crawling sensation on the skin and hallucinations[8], what is crucial for people with kidney or liver disease. Therefore, the determination of the Valine concentration in human body is an important task in medicine.

Titanium dioxide is chemically stable, non-toxic and a low-cost material which is well known for its good optical, photocatalytic and sensing properties[9-15]. Over the last decade, TiO_2 nanostructures have been widely used as a sensor platform due to quantum-size effects such as absorption edge shift and room temperature photoluminescence[16-26]. A growing interest to the development of a new class of hybrid systems TiO_2 -sensitizers, in which macrocycles (porphyrins, for example) used as sensitive layer has been raised in the recent years[24].

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Porphyrins are brightly colored pigments built by conjugated multiple-loop systems, based on sixteen-member microcycles, which composed of four pyrrole molecules and bridges. A porphyrin molecule contains a coordination cavity, bound by four nitrogen atoms, having a radius of about 2Å. This molecule is capable to coordinate with metal ions, which have different degree of oxidation. As a result, porphyrin-metal complexes (metalloporphyrins) with unique combinations of structural, physical and chemical features with high biological and catalytic activity could be formed.
It is known that porphyrins showed the enhanced photocatalytic activity. In[27], the role of metal and macrocycle in the photocatalytic processes has been studied by utilizing TiO_2 samples coated by porphyrins and metalloporphyrins. Significant changes in optical properties of nanoporous glass filled with TiO_2 and TiO_2 /porphyrin nanostructures have previously been found[28].
In this paper we report on the investigation of new optical sensor based on TiO_2 nanostructures coated with porhyrin for Valine detection.

2. EXPERIMENTAL

Commercial TiO_2 nanoparticles (Sigma Aldrich, particle size 32 nm) were used as a sensor template. TiO_2 nanoparticles were dissolved in water to prepare sols. TiO_2 layers were formed on glass substrates by dropping TiO_2 sols on the substrate and drying it at room temperature[21]. Post annealing treatment at 300 ^{0}C for 1 hour was performed to remove water from the samples. Structural properties of the obtained samples were studied by SEM.
The fabrication of sensitive layers was performed by dropping of porphyrin "5,15-di(n-nonyl),10,20-di(4-pyridyl) porphynatotin dichloride" (chemical structure is shown in Figure 1) solution in chlorophorm on TiO_2 surface. Photoluminescence (PL) spectra were measured with the setup presented in Figure 2. The samples were excited by a UV laser (LCS-DTL-374QT, L_{ex}=355 nm) and PL spectra were recorded in the wavelength range of 370-900 nm. Absorbance spectra were measured with the use of a UV-VIS spectrophotometer (Shimadzu UV-1700) in the range of 300-1100 nm.
To check the sensitivity of porphyrin to Valine, PL spectra of porphyrin layer before and after interaction with Valine were studied. To study the sensor response, different concentrations of Valine in aqueous solution were deposited on TiO_2-porphyrin surfaces.
The spectra, measured after Valine deposition, showed no drastic changes in the PL intensity and peak position (see Fig.3 in sec.).

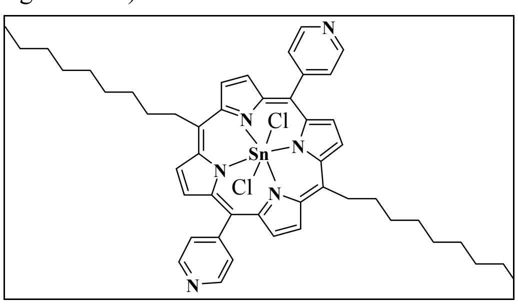

Fig.1. Chemical structure of porphyrin

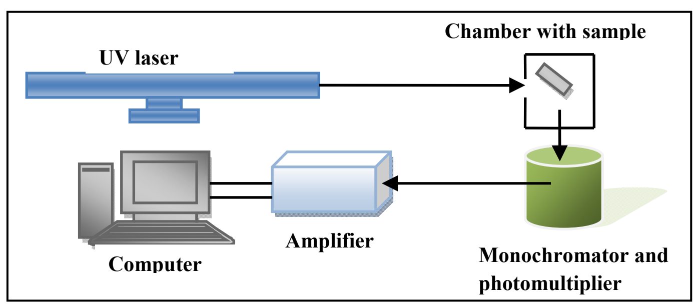

Fig.2. Experimental setup for photoluminescence measurements

3. RESULTS AND DISCUSSION

The obtained TiO_2 nanostructures were rough and porous as it is shown in Figure 3. Absorption spectra of initial porphyrin layer and porphyrin coated TiO_2 nanostructure are shown on Figure 4. The porphyrin demonstrated a Sorret band absorption, centered at 424 nm. It was found that after deposition of porhyrin on TiO_2, the Sorret band was shifted toward IR region, matching the interaction TiO_2-porphyrin.

Deposition of porphyrin layer resulted in significant changes in the PL spectrum of TiO_2-porhyrin nanostructure (Figure 4). Initially, TiO_2 emission spectrum showed wide peak, centered at 510 nm and the poprhyrin emission was centered at 693 nm (Figure 5).

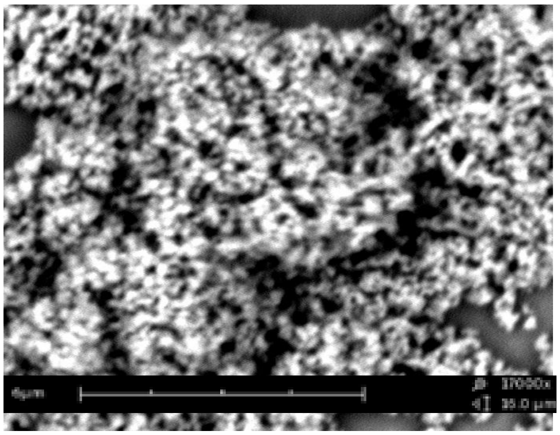

Fig.3. SEM image of TiO2 nanostructures

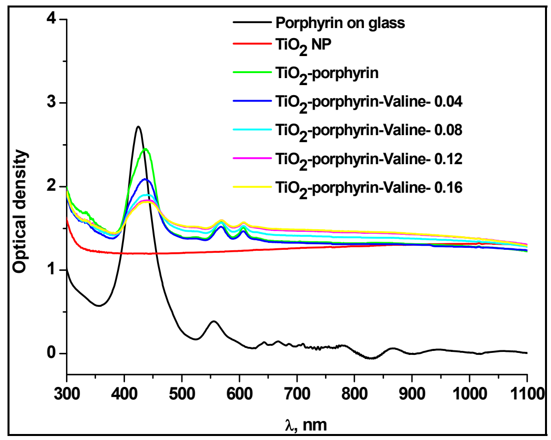

Fig.4. Absorption spectra of the studied samples

The peak, related to pure TiO_2 was quenched by a factor of three, while a peak, related to porphyrin, shifted to 700 nm after the formantion of TiO_2 - porphyrin complex (Fig. 5). The obtained PL data confirm the absorption results, matching to the interaction between metal oxide and porphyrin. The optical properties of porphyrin could change due to a special porphyrin complex containing both hydrophobic and hydrophilic parts as well as due to labile chlorine atoms associated with the central tin atom.

Sensor response to Valine is shown in Figures 4, 5. It was found that absorption of TiO_2-porphyrin decreased with increase of Valine concentration (Fig. 4).

It was found that the porphyrin showed low sensitivity to Valine (Figure 5, inserted plot). The significant changes of PL intensities and peak positions observed after adsorption of Valine on TiO_2-porphyrin surface (Fig. 5). Adsorption of Valine led to a quenching and a blue-shift of the porphyrin emission band. At the same time, an increase of the intensity of TiO_2 emission was observed.

The obtained results point to the irreversible interaction between porphyrin and amino acid, resulted in the formation of new complexes between them and a reduction of optical activity of porphyrin.

The sensor signal was calculated using photoluminescence and absorption data S_{lumin} (and S_{ads}):

$$S = \frac{S_0 - S_{Val}}{S_0}, (1)$$

where S_0 and S_{Val} are PL (and absorption) signals of TiO_2-porphyrin nanostructure related to porhyrin emission and absorption, measured before and after Valine adsorption, respectively. The sensitivity of the sensor was obtained as the ration of the sensor response S_{lumin} (and S_{ads}) due to (1) to the corresponding concentration of amino acid[29] C.

The sensitivity of the sensor vs Valine concentration is plotted in Figure 6. The obtained TiO_2 based sensor coated by porphyrin can detect Valine in the range of 0.04 to 0.16 mg/ml.

4. CONCLUSIONS

The TiO_2 and porphyrin form stable complex, proofed by the changes of absorption and PL of the porphyrin (IR shift) after deposition on TiO_2, matching to TiO_2 -porphyrin interaction. TiO_2 nanostructure coated by porphyrin showed good properties for Valine detection. The irreversible interaction between TiO_2 -porphyrin complex and Valine was confirmed by PL and absorption quenching after Valine adsorption and UV shift of PL peak position. The obtained results provide a basis for perspective applications of TiO_2 -porphyrin nanostructures for effective detection of Valine.

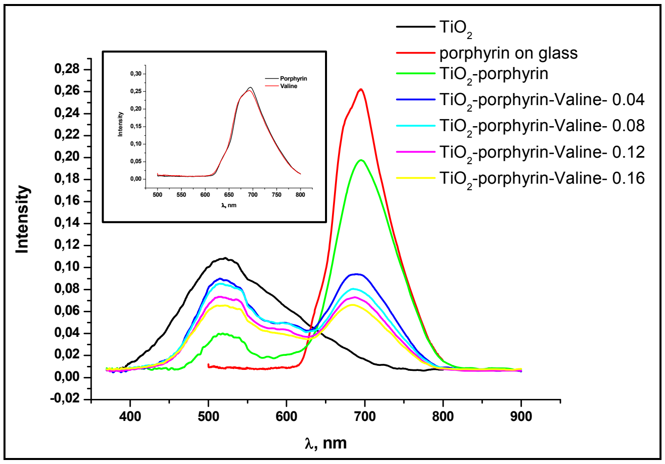

Fig.5.PL spectra of the TiO_2-porphyrin sensor measured at different concentrations of Valine

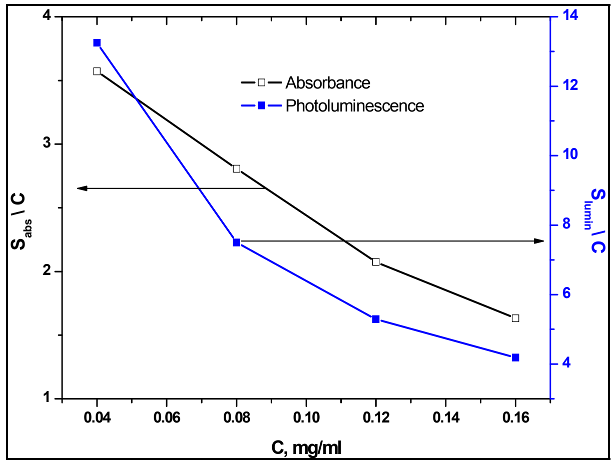

Fig.6. Response of sensor for different concentrations of Valine.

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