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TiO_2: Au (Titanium Dioxide Conjugated Gold) Crystals as the Biomimetic Oxidase for Rapid and Sensitive Oxalate Detection Combining with Bionic E-Eye

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Abstract: ***TiO_2:Au (Titanium dioxide conjugated Gold) crystal is a new materials was grown from aqueous solution. Solubility of the crystal has a positive temperature coefficient facilitating growth by slow cooling. Transmission electron microscopy and scanning electron microscopy are used to study the morphological studies of the crystals. Second harmonic generation (SHG) conversion efficiency of up to 2.56 times that of a phase matched conjugate crystal was achieved when the (TiO_2:Au) crystal was rotated about c axis, by 9.1 in the clockwise direction. Furthermore, the method was tested by the artificial urine samples, indicating its greater performances for monitoring and diagnosis of urolithiasis in point-of-care applications.***

Keywords: oxalate, TiO_2-Au conjugate crystals, bionic E-eye and urolithiasis

1. Introduction

Titanium dioxide with Gold conjugate is excellent combination of physical and chemical properties is potential but less explored candidates for optical properties. They are a class of organic materials that crystallize in symmetric space groups. Due to multidirectional hydrogen bonding, the crystals can be grown to large sizes from solution. They also possess higher hardness and melting temperature than van der Waals bonded organic crystals [1]. Urinary tract infection for the human is due to the Urolithiasis gives the symptoms such as shivering, fatigue, dysuria and renal pain. Depending on where a stone is located, it may be called a kidney stone, ureteral stone, or bladder stone. The process of stone formation is called urolithiasis [2]. Therefore, to monitor this disease for the prevention and treatment, measuring the oxalate in the urine is of great significance. Here, a rapid and sensitive colorimetric method was developed based on Titanium dioxide with Gold conjugate (TDG) for oxalate detection. Titanium dioxide with Gold conjugate (TDG) acted as an efficient biomimetic oxidase to catalyze the reaction. Yellow TDG can be oxidized to blue oxide and oxalate can selectively inhibit this reaction by consuming and reacting with TDG, thus achieving the quantitative detection of oxalate. Moreover, a home-made bionic electronic-eye (E-eye) system was developed as a portable in-situ detection platform to efficiently measure the oxalate concentrations in 10 s by direct photographing [3]. By optimizing experimental conditions, this method shows a wide linear range (7.1 μM to 300 μM) and a low detection limit (0.89 μM) for oxalate detection. Besides, this method exhibits high selectivity even with 80-fold interfering chemicals [4].

The probability of stone formations varies with different countries of atmosphere, food and life syle. It varies from 1% to 10% in Asia, 5% to 9% in Europe, and 13% in North America [5]. It is formed due to the deposition of crystals in the kidney it consists of calcium phosphate, calcium oxalte and calcium carbonate, magnesium ammonium phosphate and cysteine [6]. It is worth stressing crystals in that 85% urolithiasis mainly contains calcium oxalate [7]. Normal oxalate levels in healthy people are 100-300 μM in urine [8] and 0.8-2.50 μM in plasma [9]. The excess concentration of oxalate in urine (>300 μM) indicates the high suspicion of urolithiasis. Therefore, an efficient method for measuring oxalate is of great necessity to prevent and diagnose urolithiasis in the early stage [10].

2. Experimental

The presence of Titanium in well known optical crystals, Titanium carbide (TiC) 99%, Auric chloride ($AuCl_3$) 0.5%, and Glycene 0.5% was added. Also such a metal organic compound is expected to combine superior physical properties of their counterparts. This combination was diluted in the 100 mL solution and it was grown as a single crystal within 21 days. This crystals was ground in the mortar and then annealed to 200º C for 1 hour and then characterized by using UV-Vis absorbance and Photoluminescence studies florescence and it was used to detect oxalate detection combining with a highly portable bionic E-eye system. Nacl, KCl, glucose, $Na_2HPO_4.12H_2O$, NH_4Cl, $AuCl_3$, TiC and Sodium citrate were purchased from Sigma Aldrich Chemical Reagent (Ltd). The kit for Oxalate detection was analyzed from Life Tech research Centre, Chennai. Bionic E-eye developed in Life Tech Research Centre, Chennai, laboratory.

3. Results and Discussion

The pH and the depth of the color is positively correlated with the concentration of oxalate solution and artificial urine solution. The absorbance was measured at 325 nm using a plate reader, and the oxalate content in the sample was calculated based on the standard curve. The florescence peaks observed for this oxalate solution is nearly 450 nm. The absorbance was measured 360 nm and florescence peak was nearly 440 nm also correlated with this same concentration. Absorbance and Florescence spectra values were compared with the results of Figures 1 and 2 for oxalate and artificial urine solution [11].

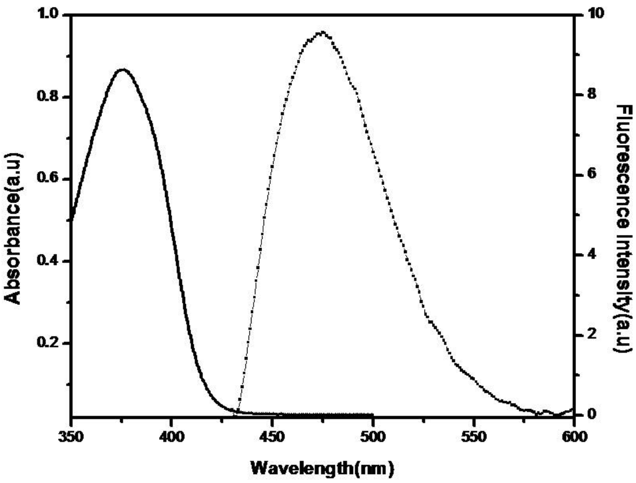

Figure 1: Absorbance and Florescence spectra of TiO_2-Au crystal in oxalate solution

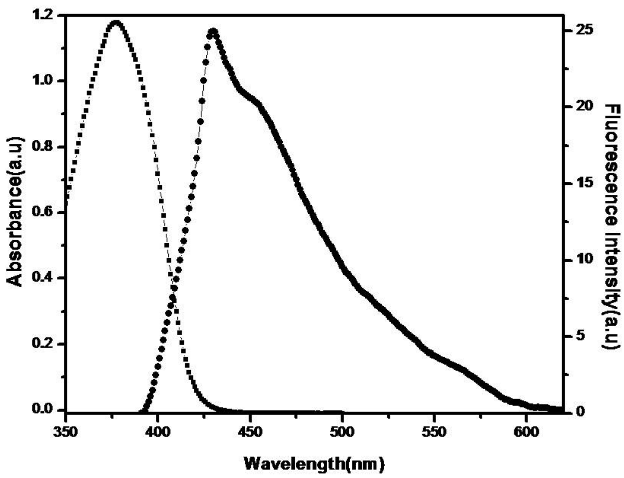

Figure 2: Absorbance and Florescence spectra of TiO_2- Au crystal in artificial Urine Solution

Compared to other materials/methods for oxalate detection (Table 1), TiO_2-Au single crystals demonstrate the lowest LOD and the shortest time cost. In plate reader, 96 wells are measured sequentially with a relatively long time cost. Home-made bionic E-eye can measure 96 wells which significantly shorten the plate reading time and ensure that all wells are detected simultaneously. Furthermore, the bionic E-eye with small size features and high portability, which is more suitable for on-site detection and point of care application [12].

Table 1: TiO_2-Au (average time required for one sample is 30 min)

Material	Artificial Urine Solution (LOD/μM)	Oxalate Solution (LOD/μM)
(TiO_2-Au) crystals (Plate reader)	31.80	26.23

4. Conclusion

In this work, we developed a simple, rapid and sensitive colorimetric method using based on TDG crystals for oxalate detection combining with a highly portable bionic E-eye system. Experimental conditions including the amount of TDG, interaction time of color reaction time, and pH have been optimized to ensure the ideal performance. The method shows a low LOD of 0.89 μM and a wide detection range from 6.9 μM to 300 μM with very good repeatability, long-term stability and high selectivity. Artificial urine samples were measured with good recovery to validate the performance for real sample analysis. Compared to other methods, the bionic E-eye based method shows the lowest LOD and the shortest time cost with high portability.

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