

Euro Biosensors 2018- Using Nano-Arrayed Structures in Sol-Gel Derived Mn²⁺ Doped TiO₂ for High Sensitivity Urea Biosensor- Ravi R. Pandey- National Physical Laboratory

Ravi R. Pandey

National Physical Laboratory, India

Abstract

Ordered and self-organized nano-array structures have been developed by Mn²⁺ doping in TiO₂ thin films deposition on conducting substrates by dip coating technique. Mn doped TiO₂ thin films exhibits better bioactivity for enzyme immobilization and cyclic voltammetry measurement has been used for qualitative characterization of electrochemical induction of oxidation-reduction process in TiO₂ and Mn doped TiO₂ films. Due to presence of Mn²⁺ ions at film surface, current voltage characteristic of Mn doped TiO₂ matrix was enhanced by a factor of ten and it had also reduced the crystallite size and promoted transformation of anatase to rutile phase of TiO₂. Urea concentration in the electrolyte was determined by observing chronoamperometry response on urease immobilized working electrodes. The urea detection sensitivity of the Mn doped TiO₂ thin films base platform was 2.3 $\mu\text{A mM}^{-1} \text{cm}^{-2}$ which is about 15 times higher from only TiO₂ base platforms. Such kind of enzyme-TiO₂ /Mn nano-array electrode could contribute a potential prospect in low cost biomedical diagnosis..

Keywords: Nano-array structures; Mn doped TiO₂ ; Chronoamperometry; Cyclic voltammetry

Introduction:

Application of nanoscale materials for electrochemical biosensors has been grown exponentially due to high sensitivity and fast response time. These factors eventually controlled by the interaction effectiveness and determine selectivity and sensitivity of materials for potential application in the area of biomedical diagnosis. Extensively TiO₂ and TiO₂ with different polymer matrixes have been used for different applications such as DNA biosensor, enzyme immobilized platforms, detection of *Pseudomonas aeruginosa* and detection of toxic compounds. Stability and usefulness of structural modification for efficient immobilization of biomolecules in TiO₂ nanotube arrays based biosensor has been also discussed. It has been demonstrated that the large surface area, good chemical stability and nontoxicity of the TiO₂ have been achieved with different nanocomposite and 3D macroporous structures. Electrochemical synthesis of titanium oxide nanotubes (TiO₂) in different types of

electrolytes and applications for biosensors applications has showed great interest. The length and pore diameter of the TiO₂ layers have been tailored by varying electrolyte composition, applied potential, pH, and anodizing time. We report a new strategy for Mn²⁺ induced nano-arrayed structures in sol-gel derived TiO₂ platforms for biosensing applications. Previously, anatase-rutile phase transformation of TiO₂ in sol-gel method synthesized has been achieved by various amount of manganese (Mn) ions and has been reported to be among the most efficient transition-metal oxide catalysts for catalytic disposal of pollutants. However, using Mn doping with TiO₂ for biosensor applications has not been explored.

Experimental:

0.25 mole of HNO₃ was added to alcoholic solution of 0.5 M Ti(OBu)₄ in 1:2 molar ratio of HNO₃ : Ti(OBu)₄. After that 0.5 mole water was added to this solution drop wise using dropping funnel in 1:1 molar ratio of H₂O : Ti(OBu)₄. A clear yellowish, transparent and stable TiO₂ colloidal sol was obtained. A stock solution of 0.5M Manganese (II) acetylacetonate (Mn(acac)₂) was prepared in isopropanol. To prepare 5 mole % Mn²⁺ ion doped TiO₂ sols of stock solution was added respectively to TiO₂ sol. After 24 hours, the above solution used to coat the thin films by dip-coating technique at constant pulling speed 25cm/min on 2x4cm² ultrasonically cleaned glass substrates under controlled relative humidity (30-40%) condition and room temperature. These samples were further dried at 100°C in electric oven for 60 minutes followed by annealing at 550°C for five hours in programmable furnace. All chemicals were analytical grade and purchased from Sigma Aldrich otherwise were specified. The TiO₂ and TiO₂ /Mn electrodes were immersed in 50 g L⁻¹ urease prepared in 0.1M phosphate buffer solution for 12 h at 4°C. The enzyme immobilized electrodes were washed with phosphate buffer solution to remove unbounded sites.

Result and Discussion:

2 θ values of diffraction peaks observed in XRD spectra of undoped TiO₂ were at 25.28, 37.78, 48.02, 53.92, 55.06, 62.72, 68.80, 70.36, and 75.12. These peaks were assigned to reflections from (101), (004), (200), (105), (211), (204), (116), (220), and (215) crystal planes, which mainly

corresponds to anatase phase of TiO_2 . Prominent diffraction peaks of 5 mole % Mn^{2+} doped TiO_2 films 2θ values were at 25.41, 27.60, 36.13, 37.80, 39.24, 41.29, 44.13, 48.13, 54.46, 56.79, 62.59, 64.14, 68.79, and 75.12. These peaks were assigned to reflections from (101A), (110R), (101R) (004A), (200R), (111R), (210R), (200A), (211R), (220R), (204A), (310R), (116A), (215A) crystal planes, which corresponds to both anatase and rutile phase of TiO_2 and notation 'A' and 'R' were associated with anatase and rutile. After Mn^{2+} doping in TiO_2 the mix phase of anatase and rutile was obtained and a small shift in 2θ value was also observed. For analysis of particle size from XRD peak broadening, the strongest peak i.e. 101 was chosen and Debye-Scherrer's equation was used for calculation. The calculated value of average crystallite size in pure & 5 mole % Mn doped TiO_2 samples is 28 ± 2 nm & 20 ± 2 nm respectively. XRD studies showed decrease in crystallite size induced by the dopant ion, therefore more surface free energy in case of doped samples. Secondly, the incorporation of foreign atoms in a lattice of TiO_2 can create defects during formation of original crystal lattice. These results agree with other reported work in literature on effects of manganese to accelerate anatase-to-rutile transformation [19]. The most common effect of incorporation of foreign atoms in a lattice is the defect formation in the original crystal lattice which could develops regular patterns of nano-structures.

Conclusion:

Mn induced nano-arrayed structured TiO_2 platform has been developed by simple sol-gel process and dip coating techniques. Such types of platforms has demonstrated usefulness for biosensor which could provide more effective interaction areas and more feasible electron transfer interfaces to support amperometric response of electrode. On the base of enzyme catalysis and electrochemical reduction reaction under a potentiostatic condition, the biosensing application was achieved by applying the urease- TiO_2 /Mn electrode. This biosensor exhibited a very high sensitivity and low detection limit for urea detection. Such kind of enzyme- TiO_2 /Mn nanotube array electrode could contribute a potential prospect in low cost biomedical diagnosis.

This work is partly presented at 9th Euro Biosensors & Bioelectronics Congress November 29-30, 2018 Dublin, Ireland