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Bovine serum albumin-dependent photoelectrocatalytic oxidation of ascorbate on a cadmium sulfide/titanium dioxide electrode

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ABSTRACT

The photoelectrochemical oxidation of bovine serum albumin (BSA) at a cadmium sulfide/titanium dioxide (CdS/TiO_2) electrode and its influences on the photoelectrocatalytic oxidation of ascorbate (AA) have been investigated by combining a photocatalytic fuel cell. The UV-excited BSA/CdS/TiO_2 electrode exhibits direct oxidation peaks related to tryptophan (Trp) and other amino acid residues. The oxidation products of Trp on CdS/TiO_2 electrode exhibit a pair of well-defined quinonyl/hydroquinonyl-based redox peaks at the formal potential of 0.025 V (vs. SCE) controlled by surface-confined electrochemical processes. The BSA oxidation photocurrent linearly increases with increasing BSA or O_2 concentration. The AA oxidation is dependent on the UV irradiation, BSA concentration and photoanode materials. An appropriate amount of BSA leads to a 58% increase in the photocurrent response of AA oxidation on the CdS/TiO_2 electrode, and a 0.5-fold increase in the maximum power density of the proposed photocatalytic AA/O_2 fuel cell employing palladium(II) porphyrin Pd(II)TCPP (TCPP = meso-tetrakis(4-carboxyphenyl)porphyrin) modified carbon felt cathode. The present results provide a new platform for evaluating the effects of serum albumin on the antioxidative action of AA in the absence and presence of UV irradiation.

1. Introduction

Considerable interest has been focused on the oxidation of biomolecules by oxygen or other oxidizing agents under different environmental conditions [1,2]. Ascorbic acid or ascorbate (AA) from dietary intake is usually functioned as a biological fuel or antioxidant, for which its oxidation product, dehydroascorbic acid (DHAA), can be reversely regenerated to AA inside human body by chemical and enzymatic reduction pathways [3–5]. For this reason, there is a series of studies on the electrochemical oxidation of AA in the past decades using enzyme, microbe, redox mediator, conducting polymer, and metal and/or metal oxide nanoparticles as catalysts [6–9]. On the other hand, AA has a profound effect on cell functions by acting as enzyme cofactors in biochemical and physiological processes [10–12]. The DHAA reduction may be promoted by thioltransferase, protein disulfide isomerase and 3-α-hydroxysteroid dehydrogenase [13,14]. Serum albumin was known to play an essential role in the physiologic recycling of AA by glutathione-dependent DHAA reductase [15,16]. It is desired to know thoroughly the effects of serum albumin on the electrochemical oxidation of AA in vitro.

Serum albumin is the most abundant blood protein that is conserved in both amino acid sequence and three-dimensional structure [17], and involves in binding, transport and delivery processes for endogenous and exogenous compounds [18,19]. Bovine serum albumin (BSA) is one of the most well known proteins because of its widespread availability, high sequence homology to human serum albumin (HSA), and wide use for medical and biochemical assays [20,21]. BSA has a single chain globular protein consisting of 583 amino acid residues with a heart-like shape surrounded by three homologous domains, and stabilized by 17 disulfide bridges [22]. The binding interactions of BSA and other proteins with AA were known to cause the changes of protein conformation, which may affect the AA oxidation [23–26]. The disulfide bridge-based redox reactions can mediate the recycling reactions of AA by introducing glutathione in intact multifunctional albumins [27]. On the other hand, the two tryptophan (Trp) residues including Trp-134 and Trp-212 from BSA can be oxidized by various oxidants, in particular photogenerated reactive oxygen species, leading to the emission quenching and oxidative damage of BSA [28,29]. Recently, Özcan and Şahin have reported the oxidation of Trp on a pencil graphite electrode to form 2-amino-3-(5-oxo-3,5-dihydro-2*H*-indol-3-yl)propionic acid (Trp-O), which was reduced to produce 2-amino-3-(5-hydroxy-3,5-dihydro-2*H*-indol-3-yl)propionic acid (Trp-OH) for the determination of Trp in blood serum [30]. If BSA were oxidized to produce Trp-O/Trp-OH couples, it would act as unique mediators to influence the oxidation

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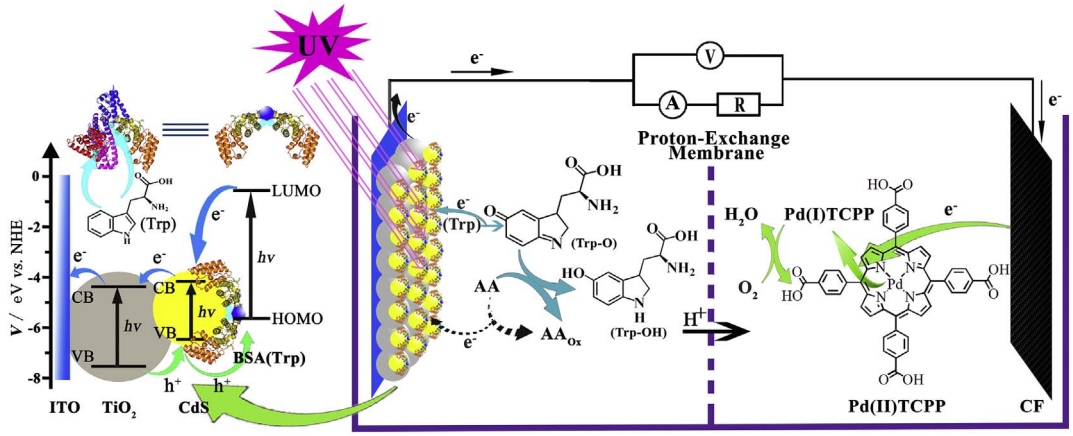

Fig. 1. Schematic diagrams for illustrating the photoelectrochemical oxidation of BSA assembled on UV-excited CdS/TiO_2 electrode accompanied by the formation of electroactive products and its synergistic effects on the photoelectrocatalytic oxidation of AA in a photocatalytic AA/O_2 fuel cell employing Pd(II)TCPP modified carbon felt (CF) cathode. Inset shows structures of Trp, Trp-O, Trp-OH and Pd(II)TCPP.

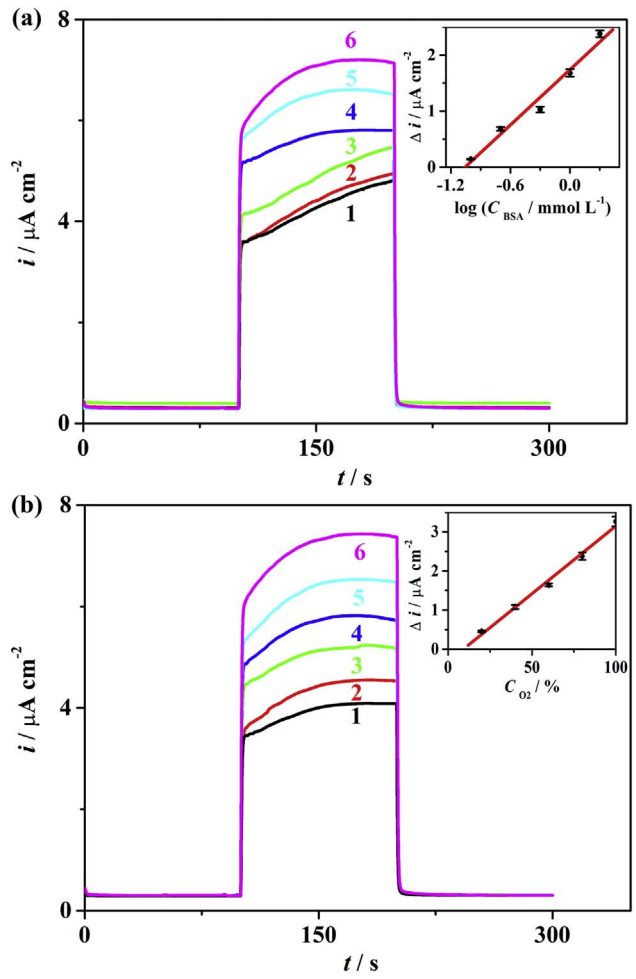

Fig. 2. Photocurrent responses from "fuel" cell employing Pd(II)TCPP/carbon felt cathode and UV-excited CdS/TiO_2 anode with keeping 100% O_2 and increasing C_{BSA}: (1) 0, (2) 0.1, (3) 0.2, (4) 0.5, (5) 1.0 and (6) 2.0 mmol L^{-1} (a), or with keeping 2.0 mmol L^{-1} BSA and increasing C_{O2}: (1) 0, (2) 20%, (3) 40%, (4) 60%, (5) 80% and (6) 100% (b). Inset shows photocurrent responses (Δi) enhanced by increasing C_{BSA} (a) or C_{O2} (b).

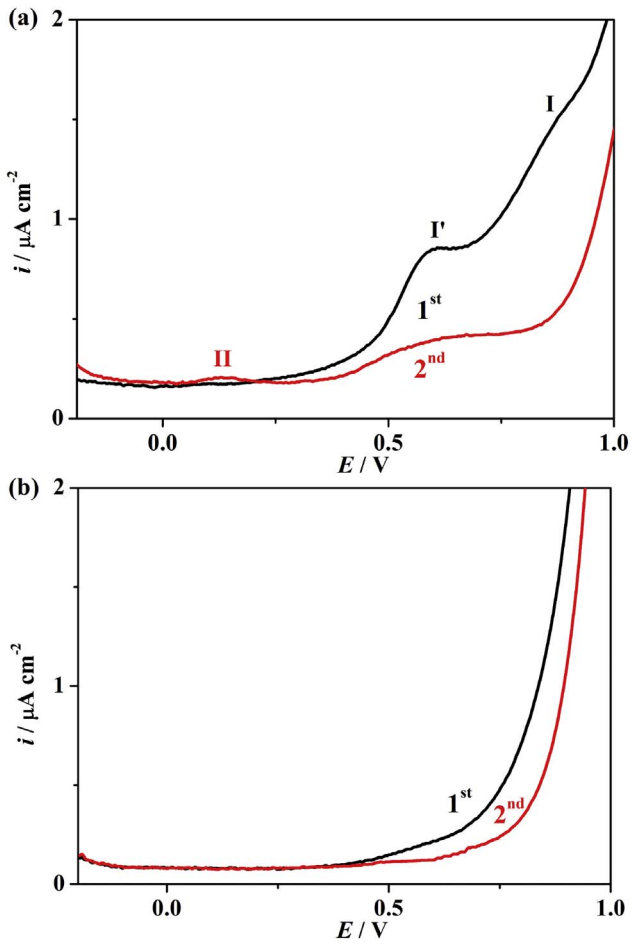

Fig. 3. The 1st and 2nd differential pulse voltammograms of BSA/CdS/TiO_2 electrode in buffer solutions for 5 min under UV irradiation (a) or dark (b) conditions.

of AA.

However, as a multifunctional transport non-metalloprotein, BSA is usually difficult to involve in the direct electrochemical reaction at a conventional electrode because of its deeply embedded amino acid residues and unfavorable orientation [31,32]. The oxidation nature of BSA is highly dependent on its conformational changes and initiation methods [33,34]. So far, despite the fact that many researchers have focused on the oxidation damage of BSA [35], there are no reports on the formation of Trp residue-based redox-active mediators. Although BSA is a common type of biomolecules that occur in living organisms, the formation of special mediators may require additional assistance of nanomaterials and light irradiation [36]. Therefore, it is beneficial to explore the photoelectrochemical oxidation of BSA and its synergistic effects on the oxidation of AA antioxidants by introducing