



Self-powered sensing platform equipped with Prussian blue electrochromic display driven by photoelectrochemical cell



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ABSTRACT

By incorporating the Prussian Blue (PB) electrochromic display as cathode, a solar-driven photoelectrochemical (PEC) cell was constructed through combining sandwich-structured graphite-like carbon nitride (g-C₃N₄)-Au-branched-titanium dioxide (B-TiO₂) nanorods as photoanode for self-powered hydrogen peroxide (H₂O₂) sensing, which exhibits both direct photoelectrochemical and electrochromic response. The gold nanoparticles (Au NPs) sandwiched between the B-TiO₂ nanorods and the g-C₃N₄ layer served as electron relay as well as plasmonic photosensitizer to enhance the solar-to-chemical energy conversion efficiency. Owing to the effective disproportionation of H₂O₂ and specific recognition of mannose on cell surface, concanavalin-A conjugated porous AuPd alloy nanoparticles were introduced as the catalytically active nanolabels promoting generation of hydroxyl radicals (\cdot OH). Based on the cleavage of DNA with the participation of \cdot OH radicals generated by the decomposition of H₂O₂ under the catalysis of AuPd alloy result in the disassembly of cancer cells to achieve further signal enhancement. The multiple-signal-output sensing response not only provides a promising strategy for different analytical purposes based on novel stimuli-responsive materials, but also enhances the reliability in the analyte detection.

1. Introduction

Hydrogen peroxide (H₂O₂) as a byproduct of biological and chemical processes and also generated by incomplete reduction of oxygen, plays critical roles in a diverse range of biological processes including biology, biomedicine, food security, and environmental protection (Rhee, 2006; Giorgio et al., 2007). In addition, in living systems, excess of H₂O₂ would lead to different kinds of disorders in the body, such as Parkinson's, Alzheimer's, atherosclerosis, heart attack, and cancer (Miller et al., 2005; Maji et al., 2014). Thus, there is a great desire to develop effective strategies for physiological H₂O₂ monitoring which has been proved a potential diagnostic marker for several diseases. Up to now, a number of sensing methods towards H₂O₂ detection have been explored, including fluorescence (Yuan et al., 2011), spectrophotometry (Matos et al., 2006), chemiluminescence (King et al., 2007), cell imaging (Srikun et al., 2010), electrochemical methods (Xu et al., 2010), and so on.

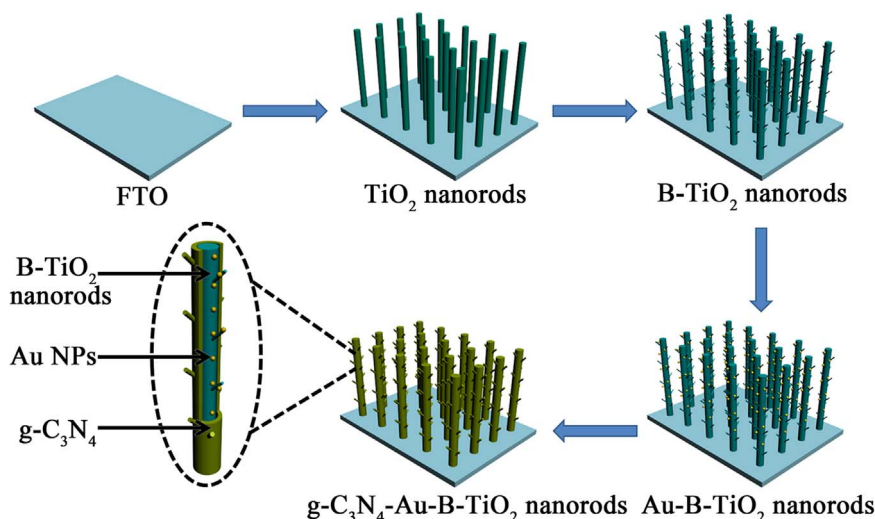
Aside from these traditional methods, recent studies on photoelectrochemical sensing with intrinsic advantages of simple devices, low price, simple operation, easy scaling and integration have produced a few new sensing approaches (Fan et al., 2016). Benefiting from the

separation of excitation source and detection signal, photoelectrochemical detection system could also provide excellent sensitivity (Liang et al., 2006). Undoubtedly, photoactive species play a vital role in analytical performances of photoelectrochemical sensors. And various n-type and p-type semiconductors such as TiO₂, ZnO, CdS, CdSe, PbS and NiO that can efficiently convert UV or visible light irradiation to anodic/cathodic current have been extensively explored to prepare photoelectrodes (photoanode/photocathode) (Bai and Zhou, 2014; Zhang et al., 2011).

Recently, titanium dioxide (TiO₂) has proved to be an excellent candidate material to develop photoelectrochemical assays due to its biocompatibility, photoelectric activity, high stability, environmental safety, and low cost. Moreover, TiO₂ with hierarchical structure has attracted considerable attention due to the high surface-to-volume ratios (Yu et al., 2015). However, TiO₂ with intrinsic large band gap (3.2 eV) could only be excited by ultraviolet light ($\lambda \leq 387$ nm), only about 4% of the incoming solar energy is utilized by TiO₂, limiting photoelectric effect further limited its direct applications (Shu et al., 2015). Until now, various approaches have been explored to overcome the drawbacks, including element doping (Xu et al., 2012), sensitizing with secondary semiconductors, such as dye-based compound or

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Scheme 1. Schematic representation of the procedure for formation of g-C₃N₄-Au-B-TiO₂ nanorods.

narrow-band-gap semiconductor (Liu et al., 2013), or coupling with plasmonic metal nanostructures as the photosensitizers (Zhu et al., 2015).

Alternatively, construction of hybrid heterojunction structures with narrow band gap semiconductors provides significant advantages extending the light absorption range as well as improving the efficiency of energy conversion (Kronawitter et al., 2011; Shiyonovskaya and Hapel, 1999). Construction of a heterojunction between TiO₂ and other semiconductors with a suitable band gap could greatly enhance light absorption and accelerate photogenerated electron-hole separation, thus enhancing the photoelectric conversion efficiency and further improving sensitivity (Reece et al., 2011). The graphite-like carbon nitride (g-C₃N₄) is an ideal candidate because of its suitable energy band gap (2.7 eV), high thermal and chemical stability, and good electrical and optical properties (Niu et al., 2012). However, the slow electron injection and high charge recombination rates at the interfaces often remain (Berea et al., 2010). It is essential to promote efficient interfacial charge transfer from the heterojunction to enable high efficiency energy conversion.

Fortunately, plasmonic nanostructures of noble metal especially gold nanoparticles (Au NPs) have been demonstrated to be promising for photocurrent enhancement due to their tunable interactions with visible and infrared light through localized surface-plasmon resonance (SPR) (Linic et al., 2011). It also has been reported that the formation of ternary heterostructures composed of narrow-gap semiconductor, Au NPs, and metal-oxide semiconductor could greatly enhance photocurrent response (Yu et al., 2013). Thus, a g-C₃N₄-Au-branched-TiO₂ (B-TiO₂) nanorods heterojunction was prepared and used as photoanode, the Au NPs play a dual role in enhancing photovoltaic conversion efficiency (electron relay and plasmonic photosensitizer).

Traditional PEC analytical system can hardly do without the reading system which departed from miniaturization and portable development. Prussian Blue (PB) is known to possess excellent electrochromic properties and a suitable redox reaction region, which make it a prominent candidate for electrochromic displays (Han et al., 2014). Herein, a novel PEC sensing platform was constructed by introducing PB into a PEC model as cathode and electrochromic display for the first time. When the PB electrode was connected with the photoanode, the generated photoelectrons could be transported to PB via the external circuit to convert PB into its reduced form Prussian White (PW), while the color of the PB was also changed from blue to transparent.

In this work, a dual-response self-powered sensing platform based on photoelectrochemical cell was developed for solar-driven, real-time, and selective sensing of H₂O₂ in the living cells, and it was further applied to highly sensitive detection of cancer cells. To this purpose, a

sandwich-structured g-C₃N₄-Au-B-TiO₂ nanorods probe was constructed as the photoanode, and PB-modified FTO as cathode. Cell-targeting aptamers modified photoanode was fabricated as the working electrode. Cancer cells were captured via the aptamer, hindered the electron donor to the electrode surface, decreasing the PEC response that could be used for sensitive assay of cancer cells. Meanwhile, AuPd alloy NPs labeled concanavalin A (AuPd@Con-A) was used as bioprobe captured on cancer cell surface. The aptamer can be cleaved by hydroxyl radical (\cdot OH) under the catalysis of AuPd alloy NPs toward the H₂O₂. This cleavage can further disassemble cancer cells and thus achieve H₂O₂ detection at lower concentration. Moreover, by monitoring photocurrent response or read-out electrochromic display, we can qualitatively or quantitatively determine the H₂O₂ and cancer cells. The dual-response sensing platform can serve as a template for the creation of cheap, miniaturizable sensors, and also provide a new exciting avenue for other relevant analytes.

2. Experimental section

2.1. Fabrication of graphitic carbon nitride (g-C₃N₄)-Au-B-TiO₂ nanorods sandwich structure

Scheme 1 illustrates the preparation of the g-C₃N₄-Au-B-TiO₂ nanorods sandwich structure. TiO₂ nanorod arrays were first grown over FTO substrates (Pathak et al., 2015). A total of 10 mL ultrapure water was mixed with 10 mL concentrated hydrochloric acid and to form a homogeneous solution. After 10 min ultrasonication, 0.4 mL aliquot of titanium butoxide was added to this solution under stirring for 30 min. After that, the homogeneous solution was transferred into a steellined Teflon autoclave (25 mL capacity) and pieces of the FTO substrates were placed at an angle against the inner wall of the autoclave, with the conductive side facing down. Then the autoclave was sealed and heated to 150 °C in an oven, held at the temperature for 4 h to facilitate the growth of the nanorods. After the reaction, the autoclave was cooled to room temperature. Then washed with ultrapure water followed by absolute ethanol, followed by drying in ambient air, TiO₂ nanorods formed on the FTO were obtained.

TiO₂ branched architecture was grown directly on the surface of the TiO₂ nanorods by the reported hydrothermal method with some modifications (Liao et al., 2012). Briefly, 0.25 mL of TiCl₃ was added into a mixed solution that contained 20 mL ultrapure water and 0.25 mL of HCl dropwise to prepare a branch forming solution vigorous stirring for 30 min. The pre-prepared TiO₂ nanorods were placed at an angle against the wall of the beaker, supporting each other at the base with the conductive side facing up, and containing the

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