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A photoelectrochemical aptasensor based on a 3D flower-like TiO_2-MoS_2-gold nanoparticle heterostructure for detection of kanamycin

Xiaoqiang Liu[a,*], Peipei Liu[a], Yunfei Tang[a], Liwei Yang[a], Lele Li[a], Zhichong Qi[a], Deliang Li[a], Danny K.Y. Wong[b,*]

[a] Henan Joint International Research Laboratory of environmental pollution control materials, College of Chemistry and Chemical Engineering, Henan University, Kaifeng, Henan Province 475004, PR China
[b] Department of Molecular Sciences, Macquarie University, Sydney, NSW 2109, Australia

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ABSTRACT

In this work, a sensitive photoelectrochemical aptasensor was developed for kanamycin detection using an enhanced photocurrent response strategy, which is based on the surface plasmon resonance effect of gold nanoparticles deposited on a 3D TiO_2-MoS_2 flower-like heterostructure. A significant aspect of this development lies in the photoelectrochemical and morphological features of the unique ternary composite, which have contributed to the excellent performance of the sensor. To develop an aptasensor, mercapto-group modified aptamers were immobilised on the photoactive composite as a recognition unit for kanamycin. The TiO_2-MoS_2-AuNP composite was demonstrated to accelerate the electron transfer, increase the loading of aptamers and improve the visible light excitation of the sensor. Under optimal conditions, the aptasensor exhibited a dynamic range from 0.2 nM to 450 nM of kanamycin with a detection limit of 0.05 nM. Overall, we have successfully synergised both the electrical and the optical merits from individual components to form a ternary composite, which was then demonstrated as an effective scaffold for the development of PEC biosensors.

1. Introduction

As a new emerging analytical technique, photoelectrochemical (PEC) sensors have attracted increasing research interest (Li et al., 2015a; Wang et al., 2013). In this technique, an illumination is used to excite electrons in a photoactive material from the valence band to the conductive band, while a potential is applied to prevent the recombination of the photogenerated holes and electrons. An electroactive analyte is then oxidised by the photogenerated holes to produce a photocurrent (Gao et al., 2015; Li et al., 2015b). Hence, this is a technique with a unique capability of preventing the excitation source from interfering with the photocurrent signal to yield a high signal-to-noise ratio measurement response (Li et al., 2016). Unfortunately, PEC sensing is usually restricted by its poor specificity to the target analyte. This has stimulated studies of incorporating many recognition elements including molecular imprinted polymers, enzymes, antibodies and aptamers to improve its selectivity (Li et al., 2012; Whitcombe et al., 2011; Zhao et al., 2013, 2014a). Among them, aptamers (single-stranded oligonucleotides with specific sequences) are some of the strong competitors to the other biological recognition systems in analytical applications due to their low-cost in vitro synthesis, mass production, reduced immunogenic response, good selectivity, and inherent binding affinity (Huang et al., 2015; Xin et al., 2015). In addition, aptamers are known to be less sensitive to temperature and pH, and are therefore less prone to deactivation, compared to enzymes. Most importantly, aptamers can be used to detect both small molecules and biological macromolecules including proteins, nucleic acids, polypeptides, hormones, sugars, viral particles, enzymes, *etc*, while molecular imprinted polymers and enzymes are usually restricted to detection of small molecules (Ansari and Husain, 2012; Fuchs et al., 2012; Xue et al., 2012).

In general, the features of materials immobilised on an electrode surface will significantly affect the performance of the electrochemical and PEC biosensors. For example, TiO_2 was very often used in developing electrochemical and PEC sensors due to its strong photocatalytic activity, good stability, controllable morphology and excellent biocompatibility (Liu et al., 2017). Unfortunately, TiO_2 is only amenable to excitation by UV light, which will otherwise damage any biomolecules immobilised on a biosensor (Li et al., 2014a). In addition, the fast electron-hole recombination may significantly attenuate the PEC signal, which has also limited the applications of TiO_2 (Luo et al., 2012; Yildirim et al., 2012). To circumvent this problem, many narrow

* Corresponding authors.
E-mail addresses: 13781157777@163.com (X. Liu), Danny.Wong@mq.edu.au (D.K.Y. Wong).

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bandgap photoactive materials such as g-C_3N_4 (~2.7 eV) and MoS_2 (~1.9 eV) nanomaterials have been hybridised with TiO_2 to form a composite with improved photocatalytic or PEC performance (Zhao et al., 2012; Zhou et al., 2013). For example, our group has previously synthesised a TiO_2 nanosheet-g-C_3N_4 heterostructure and applied it as a scaffold on an electrode to develop a PEC glucose sensor, which exhibited a 0.05 – 16 mM linear range and a 0.01 mM glucose detection limit under visible light (Liu et al., 2017). However, the need for exfoliating g-C_3N_4 by ultrasonication always resulted in micrometer-size sheets, which are insufficiently small to exhibit some of the nanomaterial properties (Zhang et al., 2014).

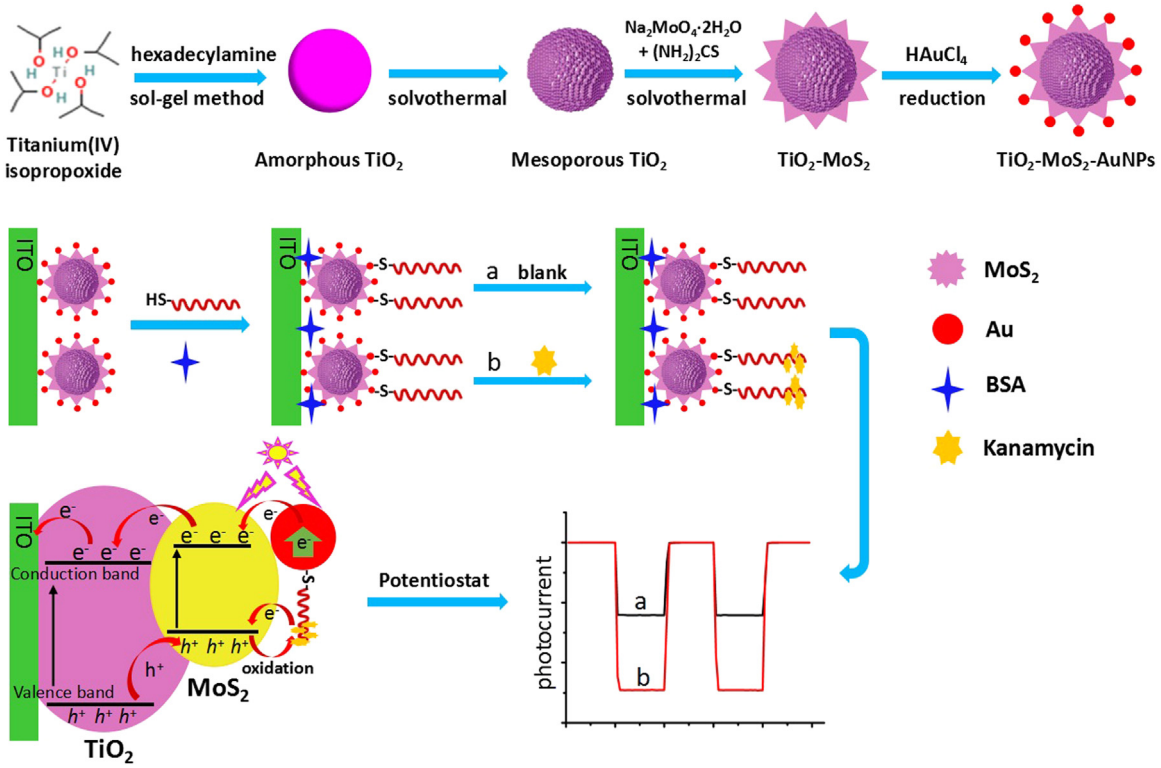
More recently, molybdenum disulfide (MoS_2) has received considerable attention due to its narrow bandgap, high thermal stability and special optical properties (Huang et al., 2014; Li et al., 2014b). In particular, the narrow bandgap of MoS_2 makes this material more suitable in PEC sensor development. In addition, MoS_2 is also regarded as a promising electrode material in battery developments owing to its 2D lamellar structure that is analogous to graphene (Ren et al., 2017). Accordingly, MoS_2 possesses many advantages similar to graphene such as large surface area and high conductivity (Sun et al., 2015). As an example, Zhou et al. synthesised a MoS_2-TiO_2 heterostructure with a few-layer MoS_2 nanosheets coated on TiO_2 nanobelts (Zhou et al., 2013). The heterostructure was demonstrated to significantly retard the recombination between photogenerated electrons and holes due to the energy band matching between TiO_2 and MoS_2. Therefore, the photocatalytic activity of the composite with 50 wt% of MoS_2 has increased by a factor of 3 under visible light irradiation, relative to TiO_2 nanobelts alone.

In this paper, we reported the development of a PEC aptasensor consisting of a novel TiO_2-MoS_2-gold nanoparticle (AuNP) flower-like nanocomposite using kanamycin as a model analyte. Notably, kanamycin has been widely used to treat serious infections caused by Gram-positive and Gram-negative bacteria during protein synthesis (Xu et al., 2015b). However, an overdose or residue of this drug in animal-derived foods can cause ototoxicity, nephrotoxicity and antibiotic resistance in human (Song et al., 2011). In our work, the ternary composite design was developed using multi-step solution chemistry illustrated in Scheme 1. We have firstly synthesised mesoporous TiO_2 microspheres with a large and rough surface, which acted as an effective platform for depositing an enhanced quantity of MoS_2 nanosheets. AuNPs were then deliberately decorated on the surface of the 3D TiO_2-MoS_2 heterostructure to produce the ternary composite. In this way, plasmonic AuNPs will directly transform the incident visible light into electrical energy by injecting photogenerated electrons into the conduction band of MoS_2, which will thus improve the photoelectric conversion efficiency. As demonstrated below, compared with a previously reported AuNP functionalised TiO_2 nanotube array-based PEC aptasensor (Xin et al., 2015), the presence of MoS_2 has increased the conductivity and visible light absorption. Finally, SH-functionalised kanamycin aptamers were immobilised on the modified electrode to develop an aptasensor. The specific interaction between the aptamer and kanamycin is expected to yield an increase in photocurrent response owing to the oxidation of kanamycin by photogenerated holes.

2. Experimental

2.1. Materials and reagents

All reagents were of analytical reagent grade and were used without any further purification. Titanium(IV) isopropoxide (TTIP, 97 + % purity) was purchased from Alfa Aesar Chemical Co. Ltd Tianjin, China. Sodium molybdite dihydrate, thiourea, hexadecylamine (HDA, 90%), acetic acid, chloramphenicol, erythromycin, streptomycin, doxycycline, ciprofloxacin and ofloxacin were purchased from Aladdin Reagent Co., Ltd., Shanghai, PR China. Gold(III) chloride trihydrate, chitosan (85% deacetylation) and bovine serum albumin (BSA) were acquired from Sigma-Aldrich Chemical Co. (St. Louis, MO). Sodium borohydride, sodium citrate, potassium ferricyanide, potassium ferrocyanide and potassium chloride were obtained from Sinopharm Chemical Reagent Co., Ltd., China. Kanamycin sulfate and a mercapto group modified



Scheme 1. Synthesis of TiO_2-MoS_2-AuNP composite; fabrication steps of a kanamycin aptasensor and its PEC mechanism for detection.