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Recent progress in Prussian blue films: Methods used to control regular nanostructures for electrochemical biosensing applications

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ABSTRACT

In the last decade, Prussian blue (PB) has attracted increased scientific interest in various research fields, such as fuel cells, gas separation and pollution treatment. Due to its advanced catalysis, biocompatibility, selectivity and stability, PB has been widely used in biosensor construction. However, the formation of regular PB nanostructures is challenging due to its fast crystallization rate. Recently, developments in this research area have increased due to emerging novel synthesis methods in nanoscale technology. Various regular nanostructures of PB films that show superior biosensing performance have been prepared. In this review, recent research progress in PB nanostructures is summarized, with special emphasis on the methodology of nanostructure control. The mechanism and key factors in regular PB crystallization are also discussed for each synthesis method. The performance of PB nanostructure-based biosensors is compared with others to show the advantages of nanostructure control. The methodology discussed in this review not only include the regular growth of PB films, but also provides information on the nanostructure control of more crystalline materials, including PB analogues, noble metals, metal oxides and coordination compounds. In addition to biosensing applications and the development of more advanced nanostructures, PB has also shown increased advanced properties in other scientific areas.

1. Introduction

Prussian blue (PB), which is a typical hexacyanoferrate coordination compound (Fig. 1a), has attracted considerable attention in various scientific fields due to its unique properties (Ferlay et al., 1995; Karyakin et al., 1995; Buser et al., 1977; Lu et al., 2012). It was first synthesized for use as a dark blue pigment (Fig. 1b) by the German paint maker Diesbach in 1704 (Holtzman, 1945). This material has a face-centered cubic structure of the unit cell, the ideal edge length of the cell lattice is 10.143 Å and is composed of only three elements: iron, carbon and nitrogen (Itaya et al., 1986; Herren et al., 1980). Due to its cell structure and composition, it was known as a simple metal organic frameworks (MOFs) material by some researchers (Okubo et al., 2010; Xiao et al., 2015), but it is much more stable than MOFs, especially in water.

Interestingly, each neighboring iron in PB has two different valances, Fe(II) and Fe(III), for building the skeleton with the CN group. Every adjacent twelve Fe-CN-Fe edges of the unit cell can construct a large cavity which allows the entrance of alkali metal ions, such as Na^+ and K^+, to increase conductivity (Bleuzen et al., 2004; Karyakin, 2001; Crumbliss et al., 1984). Its standard chemical formula is $Fe_4[Fe(CN)_6]_3$, and the Fe(II) is hex-coordinated with CN and then combined with Fe(III). In addition to its nontoxicity and biocompatibility, PB can be easily excited to induce its catalytic function due to its low energy gap (Yamamoto et al., 2009). All the above characteristics provide the electrocatalytic function of PB which has been widely employed as an electrode material since 1978 (Neff et al., 1978; Karyakin et al., 1995; Ricci and Palleschi, 2005).

PB is a highly efficient electrode modifier in biosensor fabrication. To date, numerous researchers have adopted this material for the detection of various physiological activators (Haghighi et al., 2010). Since 1978, more than 2000 papers have been published in this field. From 2010 to now, more than 1110 of these papers have shown interest in the development of PB-based biosensors. However, with the development of nanoscience, a vital disadvantage of PB has been exposed, which is an obstacle in the further improvement of sensing performance. This disadvantage is control of the PB nanostructure. Traditional synthesis of PB mainly depends on the chemical reaction between ferrocyanide and iron ion (Coleby, 1939). Although this method results in the rapid preparation of PB, the obtained crystal

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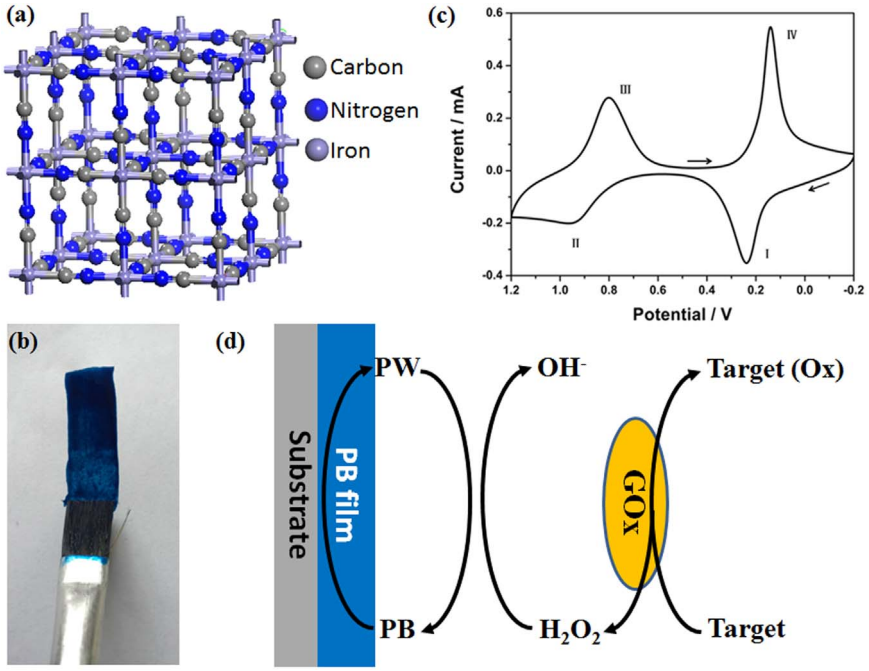

Fig. 1. (a) Unit cell structure of PB; (b) Digital photo of painted PB ink; (c) CV diagram of PB modified Pt electrode in 0.1 M PBS with 50 mV/s scanning rate; (d) Mechanism of PB-based biosensor.

structure is always irregular, which may strongly affect the catalytic ability of the prepared biosensor. Therefore, in recent years, PB research has mainly focused on the development of methodology for nanostructure control (Puganova and Karyakin, 2005; Gimenez-Romero et al., 2007; Zhang et al., 2013). Various novel preparation strategies have been designed to synthesize regular PB crystals, and more importantly, these special nanostructures have been confirmed to possess stronger electrocatalysis and conductivity, which obviously improve the biosensing performance of PB films (Chu et al., 2011; Du et al., 2010; McHale et al., 2010; Roy et al., 2011). Moreover, PB is an important metal coordination compound with numerous family analogues (Tang et al., 2016; Kaye and Long, 2005; Aguila et al., 2016). The two Fe sites can both be changed to different metals (such as Co, Ni, Mn, Cr), and the CN group can be replaced by other organic groups. This type of compound has a multiple element composition and shows various characteristics, but retains the same cell structure (Han et al., 2016; Jiang et al., 2016). Therefore, understanding its growth behavior, electrochemical features and nanostructure control technologies is meaningful and beneficial in identifying more analogue materials and their nanostructures in the fabrication of new biosensors.

In this review, we will describe the mechanisms of PB-based electrochemical biosensors, introduce traditional preparation methods (such as chemical synthesis and electrodeposition methods) and their development history, and discuss the disadvantages of PB nanostructure control. Emphasis is given to the novel developed approaches for the successful production of various nanostructures, and the principles of crystallization control will be discussed to provide guidance on material synthesis. Finally, the advantages of these regular PB nanostructures and their applications in various biosensors are discussed. Using this approach, we hope to provide an overview of recent progress in PB nanostructure synthesis and the wide application of PB in electrochemical biosensors. A summary of nanocontrol methodology may provide new motivation for the development of other useful nanostructures of PB and its analogues.

2. Electrochemical behavior of PB

The electrochemical properties of PB are mainly derived from the iron elements. Due to the two different valances of iron in its unit cell, PB can produce electron movement for easy oxidation or reduction by the external potential. There are three common forms of PB with different valances: further oxidation of all Fe(II) to Fe(III) is called Berlin Green (BG); mixed coexistence of Fe(II) and Fe(III) is PB; transformation of all Fe(III) to Fe(II) can produce Prussian White (PW) (Liu et al., 2009a, 2009b; Zhang et al., 2016; Sgobbi et al., 2016). Normally, this behavior can be expressed by the cyclic voltammetry (CV) diagram of PB (Fig. 1c). The pair of redox peaks I and IV describe the change between PB and PW, and II and III represent the conversion between PB and BG. Normally, because the synthesis sources of PB contain alkali metal ions such as K^+ or Na^+, the prepared PB which has the ions in its lattice can show weak solubility (Doumic et al., 2016; Manivannan et al., 2016).

The electrochemical activity of PB was demonstrated to rely on the existence of alkali metal ions in the PB lattice (Du et al., 2016; Itaya et al., 1982). Researchers believe the electrochemical reaction of PB is always related to the quantitative change in alkali metal ions. However, to date, there has been no definite clarification of its redox mechanism. However, the electrocatalytic principle has been generally accepted. Accompanying the transformation from PW to PB, H_2O_2 can be quickly reduced to OH^- by the transferred electrons, and PB can again be reduced to PW under an appropriate potential (Qiu et al., 2007b). During this process, PB acts as the electron carrier to transport electrons from the electrode surface to H_2O_2. Due to the excellent electrocatalysis of H_2O_2, PB is known as the "artificial peroxidase" (Karyakin et al., 2000). In addition, because H_2O_2 is one product of most oxidase reactions, PB can be employed as the core biosensor material in the detection of various physiological activators (Fig. 1d), such as glucose, lactate and glutamate (Y Jiang et al., 2016; D Jiang et al., 2016; Xu et al., 2015; Imani et al., 2016; Salazar et al., 2016). PB has very low operation potential, normally lower than 0 V (*vs.* Ag/AgCl). Therefore, PB-based biosensors can possess excellent anti-interference ability regarding other co-existing substances in blood or serum, such as ascorbic acid and uric acid.

According to the band structure of PB, the band gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is approximately 1.43 eV which belongs to