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Controlled synthesis of Pt nanoparticles array through electroreduction of cisplatin bound at nucleobases terminated surface and application into H_2O_2 sensing

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ABSTRACT

Fabrication of sub-monolayer array of Pt nanoparticles (PtNPs) assembled at nucleobases terminated layers and their application into H_2O_2 and glucose sensing were reported. To prepare such a PtNPs assembly, 3-mercaptopropionic acid (MPA), Zr^{4+}, nucleotide-5′-monophosphate (NTMP including guanosine, adenosine, cytidine, uridine-5′-monophosphate, and abbreviations were GMP, AMP, CMP, UMP, respectively) were adsorbed onto Au substrate sequentially to form nucleobases terminated surface and Zr^{4+} acted as binder to link carboxylic and phosphoric groups (NTMP/Zr^{4+}/MPA/Au). Complexation of cisplatin, cis-Pt$(NH_3)_2Cl_2$, with terminated nucleobases and following electrochemical reduction of surface-bound cisplatin gave PtNPs attached surface. Different PtNPs coverage or particle density was obtained depending on the NTMP used and decreased in the order: PtNPs/GMP/Zr^{4+}/MPA/Au > PtNPs/AMP/Zr^{4+}/MPA/Au > PtNPs/CMP/Zr^{4+}/MPA/Au > PtNPs/UMP/Zr^{4+}/MPA/Au. The surface loading of Pt was between 160 and 16 ng/cm^2. The as prepared PtNPs can be used as electrocatalysts for H_2O_2 sensing (detection limit of H_2O_2 < 100 nM) and the sensitivity increased with decreasing PtNPs density. After adsorption of glucose oxidase, the modified electrode can be used as enzymatic electrode for glucose sensing and a detection limit of 38.5 μM was achieved. This study provided an example of fabricating PtNP arrays utilising surface complexation of cisplatin with nucleobases. The advantage of this method is that the NP density can be controlled through changing nucleobases or Pt complexes used to obtain suitable kinetics of the complexation reactions. Additionally, the PtNPs sub-monolayer as prepared has high sensitivity for H_2O_2 sensing even at a very low loading of Pt.

1. Introduction

Metal nanoparticles (NPs) are widely used for biological and chemical sensing and these works have been reviewed recently (Guo and Dong, 2009; Liu and Tang, 2010). Among the various metal nanomaterials, highly dispersed Pt or Pt-based alloys have special d-band electronic structures and have been attracting growing interest in fuel cell as electrocatalysts for oxygen reduction and methanol or formic acid oxidation (Hammer and Norskov, 1995; Jung et al., 2009; Stamenkovic et al., 2006a,b; Zhang et al., 2009b). Additionally, nanoscale Pt has been used widely for the detection of many electroactive species such as H_2O_2 (Chakraborty and Raj, 2009; Karam and Halaoui, 2008; Rong et al., 2007; Song et al., 2005; Wen et al., 2009a; You et al., 2003) and also used in direct glucose electrochemistry or in enzyme electrodes for the detection of glucose as electrochemical transducer (Bahshi et al., 2008; Cui et al., 2007; Hrapovic et al., 2004; Karam et al., 2008; Lu et al., 2008; Park et al., 2003; Sakslund and Wang, 1994; Shang et al., 2008; Wen et al., 2009a,b; Xie et al., 2007; Yuan et al., 2005).

To fabricate nanostructured Pt materials with optimum morphology including shape, size, crystal facets and coverage is of great importance to improve their catalytic and analytical properties. Various technologies have been developed to prepare PtNPs. McCreery and coworkers have developed a method to fabricate Pt clusters in glassy carbon (GC) by incorporation of Pt in a GC precursor followed by thermolysis (Callstrom et al., 1990; Hutton et al., 1993; Pocard et al., 1992a,b; Schueller et al., 1993). Niwa and coworkers reported radio frequency sputtering method to prepare nanoscale Pt particles highly dispersed in a graphite-like carbon film by co-sputtering Pt and carbon (You et al., 2002, 2003).

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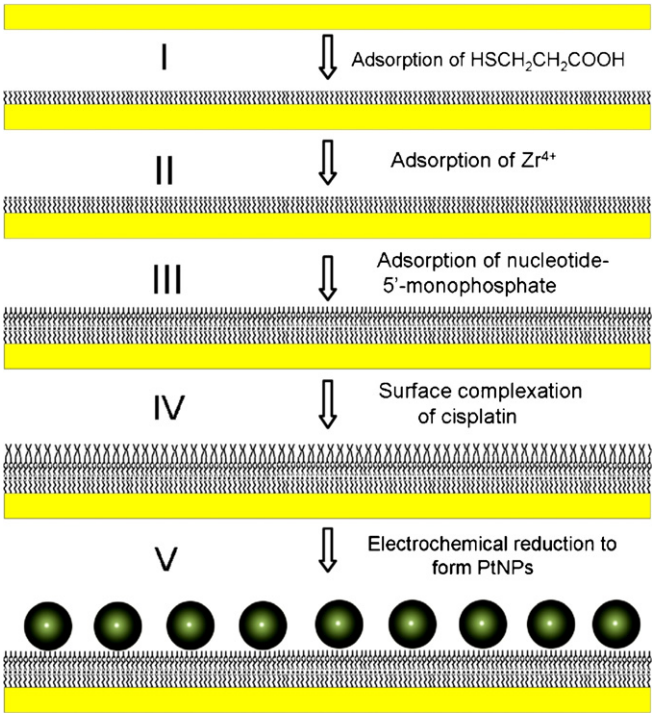
Komanicky et al. (2009) fabricated Pt multi-faceted crystal with a 30–40 nm diameter in ordered arrays on strontium titanate utilising electron beam lithography. Usually electrochemical deposition was also used to fabricate highly dispersed Pt or Pt based alloy materials for sensor use. The Pt precursor can also be adsorbed into the polymer layer onto electrode substrate and then electrochemically reduced to form NPs (Chakraborty and Raj, 2009; Du et al., 2009; Kost et al., 1990).

In fabrication of enzyme electrodes, the addition of PtNPs and formation of enzyme-capped PtNPs created a direct-linkage between NPs and enzyme during particle growth, thus leading to fast communication between enzymatic process and NPs response for signal transduction in biosensing (Karam et al., 2008; Katz and Willner, 2004). Different routes of addition of Pt to enzyme have been reported. The mixture of Pt salts and glucose oxidase (GOD) can be reduced electrochemically or chemically after they were coated onto the electrodes and then these modified electrodes were used for glucose detection (Karam et al., 2008; Sakslund and Wang, 1994). Alternatively, PtNPs can be deposited first on substrates and then covered with enzyme (Male et al., 2007). Recently, Willner and coworkers developed integrated PtNPs/GOD composite film for glucose detection (Bahshi et al., 2008), where the thioaniline-functionalized PtNPs and thioaniline-modified GOD were electropolymerized together onto the electrode and the resulting GOD/PtNPs stimulated the O_2 oxidation of glucose (Bahshi et al., 2008).

To control the morphology of the prepared Pt nanostructures, the physical technique, such as radio frequency sputtering or electron beam lithography can be used. However, these equipments are not easily available. In electrochemical or chemical preparation of metal NPs, usually the morphology are controlled through adjusting deposition time, step and potential, the ratio of metal salts to reductants and these parameters have been studied (Wang et al., 2009; Zhang et al., 2009a). To achieve an easily controlled dispersion of NPs on substrates, usually NPs with fixed size were synthesized first and then adsorbed on self assembled monolayer (SAM). Karam and Halaoui (2008) prepared random arrays of about 2.5 nm polyacrylate-capped PtNPs assembled in poly (diallyldimethylammonium) chloride (PDDA). The density or coverage of the NP submonolayer was adjusted by varying the adsorption time of PDDA-modified electrodes (e.g. indium tin oxide glass) in the NPs solution. The PtNPs/PDDA assemblies exhibited significant sensitivity and stability at small Pt mass for H_2O_2 detection (Karam and Halaoui, 2008) and oxygen electroreduction (Estephan et al., 2007).

In this work, we report an approach to prepare PtNPs array through electrochemical reduction of Pt complex, e.g. cisplatin, which was covalently bound onto the SAM of nucleotide-5′-monophosphate (NTMP) and the details of preparation are shown in Scheme 1. Firstly, SAM of 3-mercaptopropionic acid (MPA) was formed onto the sputtered Au nanofilm by chemisorption; secondly, Zr^{4+} was adsorbed onto the terminated carboxylic acid of MPA layer and then acted as a binder to link the phosphonic group of the NTMP, thus forming SAM of NTMP with the nucleobases at the outside of SAM; thirdly, cisplatin was bound onto SAM of NTMP through covalent interaction between nucleobases and Pt complexes. Upon negative potential scanning, bound Pt complexes were reduced to form PtNPs array. So the preparation of PtNPs array here involved *zirconium coordination* and *platinum-nucleic acid* chemistry, respectively.

In *zirconium coordination* chemistry, the carboxylic or phosphoric group exhibits strong reaction affinity to Zr^{4+} by forming a complex bond. So, zirconated surface can form monolayer or multilayer assembly and used for photoelectronic device or electrical and electrochemical sensing (Fang et al., 2008). In *platinum-nucleic acid* chemistry, cisplatin, cis-$Pt(NH_3)_2Cl_2$, a metal-based chemotherapeutic drug, is well known to coordinate to DNA or RNA bases and proteins but the nature of these Pt adducts is still a topic of intense investigation (Sherman and Lippard, 1987). Mass spectrometry (Sar et al., 2009) scanning tunneling microscopy (Jeffrey et al., 1993) and electrochemistry (Yoshimoto et al., 2009) have been used to study the binding reaction of cisplatin with DNA, RNA and proteins. Cisplatin reacts with nucleobases and preferentially binds to nitrogen atoms of the purines and platination occurred at N(7) of guanosine, N(l) and N(7) of adenosine and N(3) of cytidine and uridine (Eastman, 1982; Mansy et al., 1978). The order of reactivity in competitive reactions of the four NTMPs with cisplatin has been established as GMP > AMP ≫ CMP > UMP (Mansy et al., 1978).



Scheme 1. Preparation of nucleotide-5′-monophosphate/Zr^{4+}/3-mercaptopropionic acid/Au multilayer assembly, binding of cisplatin at the outlayer of nucleobases and electrochemical reducing of cisplatin to form Pt nanoparticles array. Details are in text. Not drawn in real scale.

Here, we demonstrate NTMP/Zr^{4+}/MPA directional coordination multilayer assemblies (Scheme 1), onto which cisplatin was bound and then reduced electrochemically to form PtNPs upon negatively potential scanning. Different NTMP SAMs have different kinetics to bind cisplatin and the coverage of bound cisplatin and morphology of the obtained PtNPs depend on the characteristics of the NTMP SAMs. Atomic force microscopy (AFM), X-ray photoelectrospectrocopy (XPS), electrochemical characterization including cyclic voltammetry (CV) and impedence spectroscopy (EIS) were conducted to characterize the PtNPs. Finally, this PtNPs array was applied to detect H_2O_2 and glucose.

2. Material and methods

2.1. Materials

Guanosine-5′-monophosphate disodium salt hydrate (GMP) (Merck), $ZrCl_4$ (30% solution in hydrochloric acid), adenosine-5′-monophosphate disodium salt (AMP), cytidine-5′-monophosphate (CMP), uridine-5′-monophosphate disodium salt (UMP), 3-mercaptopropionic acid (MPA) (Aladdin Reagents Co., Shanghai) were of analytical grade. Dilute solution of Zr^{4+} was prepared immediately before use from a stock solution prepared by disso-