Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Detection of cyanide by etching-induced electrochemiluminescence recovery

Yingying Feng [a, c], Lei Shi [a], Haishan Wu [a], Lichan Chen [b, **], Yuwu Chi [a, *]

[a] Key Laboratory for Analytical Science of Food Safety and Biology, Ministry of Education, Fujian Provincial Key Laboratory of Analysis and Detection for Food Safety, College of Chemistry, Fuzhou University, Fuzhou, Fujian, 350108, PR China
[b] College of Chemical Engineering, Huaqiao University, Xiamen, 361021, PR China
[c] College of Chemical Engineering, Fuzhou, Fujian, 350108, PR China

ABSTRACT

Electrochemiluminescence (ECL) emission of gold nanoparticles (Au NPs) loaded graphitic carbon nitride nanosheets (Au-CNN nanohybrids) can be modulated by the Au content. On the basis, a signal-on ECL sensor for detecting cyanide, a widespread toxic chemical, has been developed in this work. The sensor utilizes cyanide-mediated etching of Au NPs to recover the ECL emission of Au-CNN nanohybrids initially inhibited by Förster resonance energy transfer (FRET) from CNNs to Au NPs. The ECL sensor has a sensitive response to cyanide in the range of 50 nM to 1 mM with a detection limit of 50 nM, and shows high specificity due to the high affinity of Au-cyanide complex. The proposed FRET modulated ECL sensor may prove valuable in future environmental monitoring.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Graphitic carbon nitride (g-CN) polymer, a semiconductor with an aromatic π-conjugated system, has attracted attention in the fields related to energy, environment and sensing, due to its unique electronic structure [1–11]. To promote its applications, considerable efforts have been devoted to modifying bulk g-CN into optimized nanostructures with improved electron and mass transport [10,12]. For examples, two dimensional g-CN nanosheets (CNNs) have been prepared through various exfoliation methods for improving their photocatalytic activities in water splitting and enriching their interfaces for further coupling biomolecules or metal ions in sensing applications [13–16]. However, CNNs inherit limitations of bulk g-CN, such as rapid rate of charge-carrier recombination and low electric conductivity, restricting their applications in such fields as photoelectrochemistry, electrocatalysis and ECL [5,17–19]. To address these issues, several strategies have been proposed through modulating electronic structure and energy band configuration of CNNs, including doping, copolymerization, sensitization, and hybridizing [2,12]. For example, hybridization of CNNs with noble metal could form a Schottky barrier at the interface of metal-CNN [19,20]. A Fermi level of noble metal nanoparticles with lower energy compared to that of the covalent band (CB) of CNNs accelerates the transfer of the excited electrons from CNNs to Au NPs; meanwhile, the energetic electrons generated at the surface of metal would partially transfer to the CB of CNN. In other words, the noble metals in metal-CNN junctions play influential role as conductive nanowires, thus reducing the rate of charge-carrier recombination as well as improving the electric conductivity. On the basis, our group has successfully prepared a gold nanoparticle-CNN nanohybrid film (Au-CNN film) with strong and stable ECL emission [19]. Addition of high energetic electrons to g-CN always results in unpredictable side reactions either with oxygen-rich air or with g-CN themselves, leading to a structural and chemical disintegration of g-CN and thus sharp decrease of ECL emission of g-CN film at subsequent potential scans. In contrast, Au-CNN film with enhanced conductivity could inhibit the disintegration, providing stable ECL emission. Interestingly, in such Au-CNN nanohybrids, once the Au content is more than a certain amount, the non-radiative energy transfer, Förster resonance energy transfer (FRET) will become predominant, quenching the ECL emission [19].

Cyanide is a widespread chemical and can be found in surface water, which originates not only from industrial waste but also

* Corresponding author.
** Corresponding author.
E-mail addresses: lchen@hqu.edu.cn (L. Chen), y.w.chi@fzu.edu.cn (Y. Chi).

from biological sources such as bacteria and fungi [21]. Cyanide is acutely toxic to mammals' cardiovascular, respiratory and central nervous systems by inactivation of many enzymes with a rate-dependent dose-response curve [22]. Owing to its extreme toxicity and wide distribution, sensor with high sensitivity, well selectivity, reliability and low cost is highly desirable for on-site and real-time detection of cyanide. Herein we present a signal-on ECL sensor for cyanide detection based on cyanide modulation of ECL emission of Au-CNN film. As mentioned above, with high Au content, the ECL intensity of Au-CNN film sharply decreases due to FRET from the excited state of CNN* to Au NPs. It is known that cyanide is able to dissolve Au in the presence of oxygen upon formation of the soluble metal-cyanide complex [23,24]. Inspired by this, we envision that cyanide-mediated etching of Au NPs could inhibit FERT and recover ECL emission of Au-CNN film containing high Au content, as shown in Fig. 1. In this work, Au-CNN films with different Au content have been firstly prepared, and their ECL performances in the absence and presence of cyanide have been studied. Then a signal-on ECL sensor for cyanide detection is developed by using Au-CNN film with optimized Au content. The present ECL sensor detects cyanide in a "two-step" procedure, i.e. specific cyanide recognition by the formation of Au-cyanide complex followed by ECL readout, enabling the sensor to be used in colored samples and complex mixtures. Furthermore, the present solid-state ECL sensor is easy to be fabricated in low cost. The present work suggests promising applications of the emerging Au-CNN films in environmental monitoring.

2. Experimental

2.1. Materials

Dicyanamide, potassium cyanide, hydrogen tetrachloroaurate trihydrate ($HAuCl_4 \cdot 3H_2O$) were purchased from Sigma. Metal salts, potassium persulfate ($K_2S_2O_8$), sodium borohydride ($NaBH_4$, 96.0%) and sodium citrate were obtained from Fuchen Chemical Reagent Co. (Tianjin, China). All of the chemicals were used as received. Doubly distilled water was used throughout this work.

2.2. Apparatus

The preparation of bulky g-CN was carried out in a tube furnace (GSL 1400X, Kejing Materials Technology Lt. Co., Hefei, China). Electrochemical (EC) and ECL measurements were carried out on an ECL detection system (MPI-E, Remex Electronic Instrument Lt. Co., Xi'an, China) with a three-electrode system. The working electrode was a GC disc working electrode (3 mm in diameter) modified with Au-CNN nanohybrids. The counter electrode was a Pt wire, and the reference electrode was an Ag/AgCl (3 M KCl) electrode. TEM images of Au-CNN were recorded on an electronic microscope (TecnaiG2 F20S-TWIN 200 kV). The field emission scanning electron microscopic (FE SEM) images of the Au_{30}-CNN film coated on glassy carbon electrode (GCE) were captured by a Nova NanoSEM 230 field-emission microscope (FEI, USA).

2.3. Synthesis of Au-CNN nanohybrids

The synthesis of Au-CNN nanohybrids was adapted from our previous work [19]. Briefly, different volume amount of 0.01 M $HAuCl_4$ solution was added to 2 mL of the as-prepared CNNs suspension with concentration of 1 mg mL^{-1}, under stirring. The suspension was sonicated for 10 min followed by a 2 h stirring period at room temperature, and this process was repeated 3 times to ensure the formation of highly dispersed AuNPs on the surface of CNNs. Afterward, 25 μL of 0.01 M freshly prepared $NaBH_4$ solution was added quickly to the suspension to reduce the $AuCl_4^-$, followed by continuous stirring for 20 min. Then, 10 μL of 0.01 M sodium citrate solution was added dropwise into the above suspension to improve the stability of as-prepared Au-CNN nanohybrids, and the stirring was maintained for 30 min. To remove excess $NaBH_4$, sodium citrate, and unbound gold nanoparticles, the obtained nanohybrid materials were centrifuged, washed thoroughly with distilled water, and finally redispersed into 1 mL of water for further use and characterization. The as-obtained Au-CNN nanohybrids were denoted as Au_{10}-CNN, Au_{20}-CNN, Au_{30}-CNN, Au_{40}-CNN, and Au_{50}-CNN when 10, 20, 30, 40 and 50 μL of 0.01 M $HAuCl_4$ was added, respectively, during the synthesis process.

2.4. Coating GCE with Au-CNN nanohybrids

GCEs were polished in turn with 0.3 and 0.05 μm alumina slurry and then washed ultrasonically in water. 3 μL of the as prepared Au-CNN nanohybrid suspension was dropped onto the pretreated GCE and dried at room temperature.

2.5. Etching of Au NPs in cyanide solution

Various concentrations of cyanide solution were prepared in the reaction buffer (100 mM PBS, pH 8.0). The as-prepared Au-CNN/GCE was immersed in the cyanide solution for 30 min followed by rinsed throughout with water and kept in 10 mM PBS (pH 7.0) prior to ECL experiments. (*Precautions must be taken to prevent any accidental release, since cyanide is a dangerous toxic compound. All the cyanide solutions were disposed of by adding an excess of sodium hypochlorite.*)
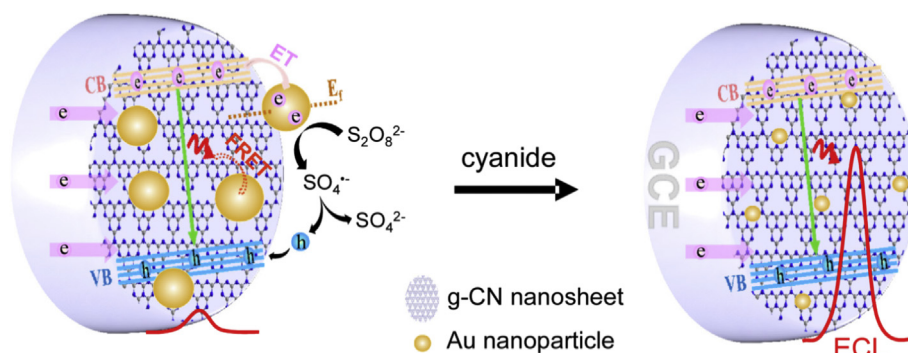

Fig. 1. Schematic illustration of ECL cyanide assay by turning on ECL emission of Au-CNN film upon cyanide-mediated etching of gold nanoparticles to inhibit Förster resonance energy transfer.