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ORIGINAL PAPER

Self-enhancement photoelectrochemical strategy for kanamycin determination with amino functionalized MOFs

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Abstract

Based on the self-enhanced photoelectrochemical quality of Cu-MOF-NH_2, a photoelectrochemical biosensor for kanamycin detection with a Cu-MOF-NH_2 modified electrode was constructed. This biosensor took full advantage of the low electron hole recombination rate due to the ligand-to-metal charge-transfer mechanism of excited electron transfer in Cu-MOF-NH_2. The kanamycin aptamer was modified onto Cu-MOF-NH_2 by Schiff base reaction. In the presence of kanamycin, the holes on the amino group in Cu-MOF-NH_2 oxidize kanamycin, making kanamycin itself as a signal enhancement substance, and achieving the effect of self-enhancement. The dynamic monitoring range for kanamycin is 0.5 to 650 nM, and the detection limit is 0.1 nM. The sensor has been successfully applied to the determination of kanamycin in fish with recoveries of 95.7–105.0% and RSD of 1.5–4.0%. This work provides a broad path for the development of self-enhanced photoelectrochemical sensors.

Keywords Aptamer · Photocurrent · Antibiotic · Metal–organic frameworks · Self-enhancement · Copper sheet

Introduction

Photoelectrochemical (PEC) biosensor is a promising analytical technique, which combines the advantages of both optical and electrochemical analysis methods. The PEC biosensors separate the excitation light source and the current readout signal completely, and have the advantages of low cost, high sensitivity, simple operation, and simple design. [1–5] In the PEC detection and analysis process, the photoinduced formation of electron–hole pairs in photosensitive materials is used to initiate the oxidation–reduction reaction. Therefore, photosensitive materials play an important role in PEC biosensors. There are many kinds of photosensitive materials, such as two-dimensional (2D) layered nanomaterials that have the advantages of high specific surface area, easy preparation, good light harvesting performance, fast electron transfer rate, and good biocompatibility [6]. For example, Raghu et al. successfully synthesized Ni-doped ZnS-CdS hybrid composite using a simple chemical precipitation method, which improved the shortcomings of low photon efficiency and high photo corrosion of ZnS and CdS [7]. The Mn^{2+} doped ZNS-CdS composite nanopowder prepared by Jonnalagadda et al. can be used for optical sensors with good structural characteristics [8]. Doping metal oxides (such as TiO_2, ZnO, ZrO_2) with oxygen, sulfur, nitrogen, boron, phosphorus, and other non-metallic elements, due to the strong oxidation capacity of non-metallic elements, the photocatalytic efficiency is improved under visible light irradiation [9].

Metal–organic frameworks (MOFs) are a new type of hybrid porous materials with three-dimensional crystal frameworks formed by metal ions and organic ligands through coordination bonds. MOFs have the characteristics of extremely high specific surface area, ordered porous structure, high metal content, and adjustable composition metal and organic ligands [10]. In addition, electron transfer in most MOFs follows the ligand-to-metal charge-transfer mechanism (LMCT) after excitation by light, [11, 12] which makes holes and electrons reside on organic ligand and metal

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ion respectively. Therefore, compared with traditional semiconductor materials, MOFs have a lower charge recombination rate. These characteristics make MOF widely used in the field of energy conversion. Cao's team used Cu-BTC MOF/G-C_3N_4 nanosheet as the photosensitive material to build a PEC biosensor for the detection of glyphosate [13]. Zhang's team constructed a PEC biosensor based on PCN-222 material for the detection of phosphoprotein [14]. Vidyavathi et al. used a novel quinoline amino acid Schiff base ligand to prepare metal complexes (M = Fe (II), Co (II), Ni (II), Cu (II)) that can successfully cleave DNA by non-oxidation mechanisms under mild conditions by conventional reflow method [15].

Kanamycin is an aminoglycoside antibiotic that has been widely used to treat severe infections caused by gram-positive and gram-negative bacteria [16]. However, excessive intake of kanamycin has been associated with serious side effects, such as renal toxicity, hearing loss, and antibiotic resistance [17].

We synthesized Cu-MOF-NH_2 using aminoterephthalic acid, and focus on the changes produced by the modification of amino groups. Because of the presence of amino groups, the Cu-MOF-NH_2 has a smaller band gap and a larger light absorption range, which is conducive to the improvement of PEC properties. On this basis, a self-enhancement PEC biosensor for detecting kanamycin was fabricated by connecting the kanamycin-binding DNA aptamer with the amine group of Cu-MOF-NH_2 by carboxymethyl chitosan and glutaraldehyde, and studied the electron flow inside the biosensor. The PEC biosensor made full use of the charge separation capability of MOFs. The PEC biosensor was successfully realized the detection of kanamycin based on self-enhancement photocurrent, and has the advantages of strong specificity and high sensitivity. It provides a new choice for kanamycin detection.

Experiment

Reagents

All reagents were analytical grade and were used directly without further purification. Copper (II) chloride dehydrate ($CuCl_2 \bullet 2H_2O$) and 2-aminoterephthalic acid ($C_8H_7NO_4$, BDC-NH_2) were ordered from Macleans Biochemical Technology Co., Ltd. (Shanghai China). Kanamycin sulfate (purity ≥ 94% Kana), ofloxacin (purity ≥ 98%), erythromycin (purity ≥ 99%), ciprofloxacin (purity ≥ 98%), chloramphenicol sulfate (purity ≥ 99%), neomycin (purity ≥ 95%), streptomycin (purity ≥ 90%), carboxymethyl chitosan (CMS), and glutaraldehyde (GLD) solution (50 wt. % in H_2O) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. N,N-Dimethylformamide (DMF) and absolute ethanol were obtained from J&K Chemical Ltd. (Shanghai, China). Copper sheets(CuSs, 99.9%)were provided by Tianjin Kemiou Chemical Reagent Co., Ltd. pH 7.4, 0.1 M phosphate buffer consisted of 0.1 M NaH_2PO_4, 0.1 M Na_2HPO_4, and 0.1 mM KCl, which was used for PEC measurement. Anamino group modified kanamycin-binding DNA aptamer with the sequence 5´-NH_2-$(CH_2)_6$-TGG GGG TTG AGG CTA AGC CGA-3´ was purchased from Shanghai Sangon Biotechnology Co., Ltd. (Shanghai, China).

Apparatus

All PEC and electrochemical measurements were performed on a CHI660E electrochemical workstation which contained a conventional three-electrode system (Shanghai Chenhua Instrument Co. Ltd, China). The characterizations of Cu-MOF-NH_2 were observed via a scanning electron microscope (JEM-F200, JEOL, Japan) and a transmission electron microscope (JSM-6700F, JEOL, Japan). UV–Vis and UV–Vis DRS were measured by a Cary5000 ultraviolet visible near-infrared spectrophotometer (Agilent Technologies, USA). Fourier transform infrared (FT-IR) spectra were recorded on an FT-IR spectrophotometer (VERTEX70, BRUKER, Germany) using the KBr disc technique. X-ray photoelectron spectroscopy (XPS) was recorded on the X-ray photoelectron spectroscopic instrument (model ESCALAB XI+, Thermo Fisher Scientific, China).

Preparation of Cu-MOF-NH_2/CuSs and fabrication of the PEC biosensor

Firstly, copper sheet (CuSs) was treated. Because of its water solubility and easy falling off after Cu-MOF-NH_2 being dropped onto the electrode, Cu-MOF-NH_2/CuSs was prepared in situ growth on CuSs substrate (S1). [18] Then, 10 μL 1% CMS solution (CMS dissolved in 1% acetic acid solution) was dropped onto the surface of Cu-MOF-NH_2/CuSs. After drying at 50 °C, it was washed several times with 0.1 M NaOH and deionized water. Then 5% GLD solution was dropped on the surface of modified Cu-MOF-NH_2/CuSs reaction at 40 °C for 1 h; the GLD molecules physically adsorbed on the electrode surface were removed with deionization water [19]. Then, 10 μL aptamer solution (2 μM) was dropped on the modified electrode and incubated at 4 °C for 12 h. For the detection of kanamycin (Scheme S1), different concentrations of kanamycin solution were first dropped on the electrode and incubated at 40 °C for 50 min, the electrode was cleaned with phosphate buffer, and the photocurrent response test was carried out in the next step.

PEC measurement

In order to characterize the modification process of the PEC biosensor, the electrochemical impedance spectroscopy (EIS) response of the PEC biosensor was measured under the condition of 5.0 mM $[Fe(CN)_6]^{3-/4-}$ containing 0.1 M KCl. The Mott-Schottky curve of Cu-MOF-NH_2/CuSs was measured in 0.1 M Na_2SO_4 solution with a scanning range of − 0.5 ~ 0.9 V and a scanning speed of 1000 Hz. PEC signals were measured in 0.1 M phosphate buffer at pH 7.4. At a potential of 0.4 V, white LED light was used as the irradiation source, and the light was turned on and off every 10 s. Three parallel samples were set for each group and repeated three times.

Results and discussion

Morphology, composition, and elemental analysis characterization of Cu-MOF-NH_2/CuSs

To investigate the morphology and structure characteristics of Cu-MOF-NH_2/CuSs, SEM and TEM images were measured. As shown in Fig. 1B, Cu-MOF-NH_2 has an approximate cuboid morphology, and the size is about 400 nm ($n = 100$). As can be seen from Fig. 1A, the size of Cu-MOF-NH_2 growing on the copper sheet is uniform, which is about 200 nm. There is no larger size Cu-MOF-NH_2 growing, and the distribution of Cu-MOF-NH_2 on the copper sheet is very uniform. In addition, the lattice fringes of 0.21 and 0.26 nm in Fig. 1C and Fig. 1D can be attributed to the (200) and (201) crystal planes of Cu-MOF-NH_2, respectively [20]. Figure 1E presents the element mapping images of Cu-MOF-NH_2, and the Cu, C, N, and O elements in Cu-MOF-NH_2 are uniformly and continuously distributed. In addition, as shown in Figure S1 and Figure S2, the chemical composition and valence states of Cu-MOF-NH_2 were studied by XPS and FT-IR spectra. It can be seen from XPS analysis that the central metal ions and organic ligands of Cu-MOF-NH_2 have been linked together through Cu–O, which supports each other with the infrared analysis results. The results of SEM, TEM, and element mapping images, the XPS and FT-IR spectra showed that the Cu-MOF-NH_2/CuSs was successfully synthesized.

PEC properties of Cu-MOF-NH_2/CuSs

When Cu-MOF-NH_2 was grown on the copper sheet, the photocurrent response was significantly increased compared with the copper sheet (Fig. 2A). This is because Cu-MOF-NH_2/CuSs has a huge specific surface area. After modification with aptamer, the photoelectric response of the electrode was slightly reduced due to the relatively weak conductivity of CMC, GLD, and DNA strand. After the introduction of kanamycin, the photocurrent response was significantly enhanced. This is because kanamycin is oxidized and acts like an electron donor, providing electrons to the electrode and enhancing the PEC signal.

In $[Fe(CN)_6]^{3-/4-}$ solution (5 mM) containing 0.1 M KCl, EIS was used to characterize the assembly process of the electrode. The Ret value of the Cu-MOF-NH_2/CuSs electrode is smaller than that of the copper sheet (Fig. 2B). This is due to the huge specific surface area [21] and strong conductivity of Cu-MOF-NH_2/CuSs. As CMC, GLD, and aptamer were sequentially modified onto the Cu-MOF-NH_2/CuSs, the Ret value gradually increased because of their weak electron transfer ability and steric hindrance. The photocurrent response and EIS indicate that the biosensor has been successfully prepared.

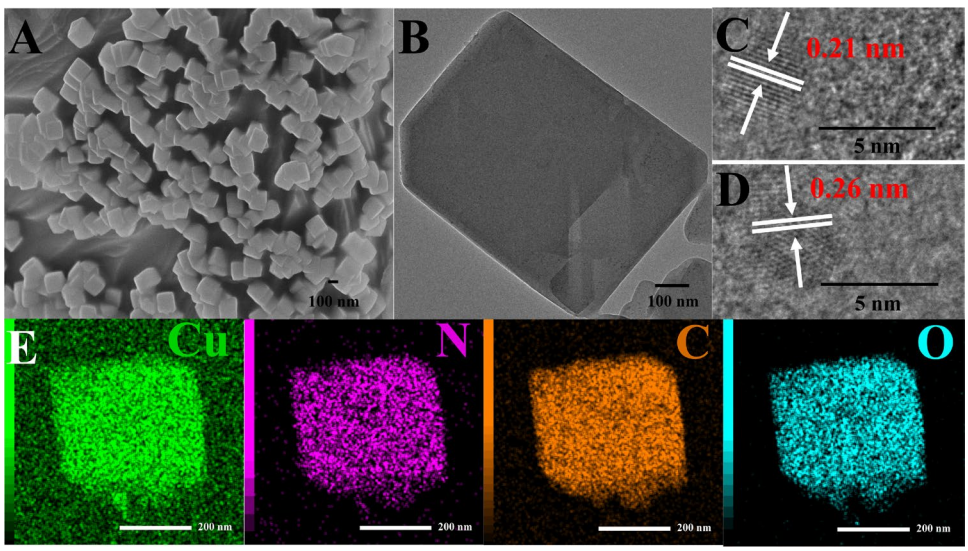

Fig. 1 SEM (**A**), TEM (**B**), and HRTEM (**C**, **D**) of Cu-MOF-NH_2. Elemental mapping image (**E**)

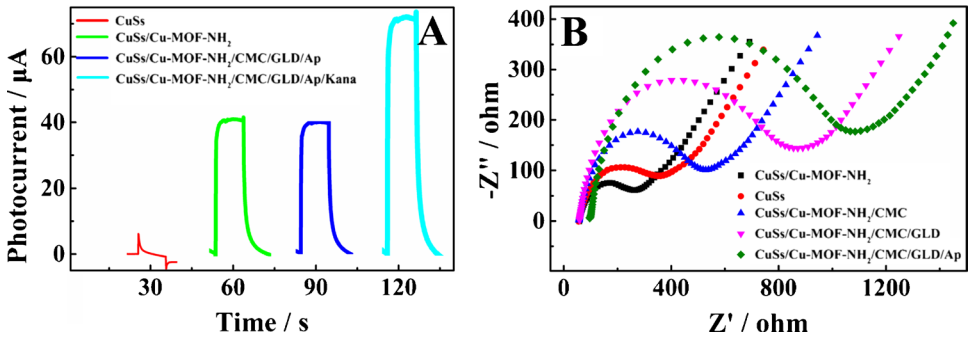

Fig. 2 Photocurrent (**A**) and EIS (**B**) responses of the electrode stepwise modification process

MOFs are generally considered to be insulating materials with high band gaps [22], so many attempts have been made to reduce the band gaps of MOFs. It is considered a feasible and effective method to modify organic ligands with various functional groups such as NH_2, OH, CH_3, and Cl. For example, the study of Civalleri et al. [23] showed that when the amino group was modified to the organic linker, the lone pair electron of N in the amine group interacted with the π*-orbitals of the benzene ring, providing the electron density for the antibonding orbital, which caused the energy band shift, resulting in higher HOMO energy, thus reducing the band gap. The study of C. H. Hendon and his colleagues also demonstrated this method [24].

We synthesized Cu-MOF-NH_2 using aminoterephthalic acid. As can be seen from Figure S3C, the band gap decreased from 3.5 to 2.6 eV due to the presence of amine groups, and the narrowed band gap was more conducive to electron transition (S4). At the same time, it can be seen from Figure S3D that the absorption intensity of Cu-MOF-NH_2 is significantly stronger than Cu-MOF because of the presence of amine groups, which indicates that Cu-MOF-NH_2 can generate more photoelectric charges [25]. In addition, Cu-MOF-NH_2 also has an absorption peak at 330 nm indicating that Cu-MOF-NH_2 has a wider range of wavelength utilization [26].

The fabrication of self-enhancement PEC biosensor and the PEC response mechanism

Firstly, Cu-MOF-NH_2/CuSs was prepared by using copper sheet as substrate. With hydrothermal method Cu-MOF-NH_2, was deposited onto the copper sheet formed Cu-MOF-NH_2/CuSs. Then aptamer was immobilized onto with glutaraldehyde cross-linking method. In the absence of target, the blank signal was achieved. After the target was added, it was captured by the aptamer and it was oxidized by the holes produced from the illumination of LED. The photocurrent was enhanced. In this self-enhancement PEC detection method, the PEC signal indicator is generated from the oxidation of target (Scheme S1). Thus, it is expected to achieve highly sensitive detection of kanamycin.

Scheme S2 illustrates the electron transfer mechanism of Cu-MOF-NH_2/CuSs. For Cu-MOF-NH_2, the charge excitation under illumination follows the LMCT mechanism, that is, electrons transfer from the organic linkers to the central metals. This results in holes left at the N atom in the organic linkers, while electrons reside on the central metals [26]. Therefore, the central copper ion exhibits two valence states, which is consistent with the HRTEM and XPS analysis results. The electron transfer mechanism of LMCT results in the superior charge separation capability of Cu-MOF-NH_2 compared to traditional semiconductors. Kanamycin is an antibiotic and is easily oxidized [27]. The aptamer was connected to the amine groups through CMC and GLD. After kanamycin is captured by the aptamer and then oxidized by the hole at the N atom, which makes full use of the excellent charge separation ability of Cu-MOF-NH_2. Meanwhile, kanamycin acts like an electron donor and significantly enhances the photocurrent response of the biosensor.

Analytical performance of self-enhancement PEC biosensor

The PEC biosensor was used to detect kanamycin under the optimal experimental conditions (Figure S4). As shown in Fig. 3, within the range of 0.5 to 650 nM, kanamycin concentration has a linear relationship with the photocurrent response of the PEC biosensor, $I = 0.064\ c\ (nM) + 40.85$, with the correlation coefficient 0.9998, and LOD is calculated to be 0.1 nM (S/N = 3. S, standard deviation; *N*, slope) ($n = 9$). Compared to the previously reported work on kanamycin detection, as shown in Table 1, this PEC biosensor we prepared exhibited a lower detection limit and a wider detection range.

Selectivity, reproducibility, and stability

The photocurrent response of six kanamycin analogues (ofloxacin, erythromycin, ciprofloxacin, chloramphenicol, neomycin sulfate, and streptomycin) and their mixtures with kanamycin was investigated to study the selectivity of PEC biosensor. As shown in Figure S5A, the PEC biosensor has

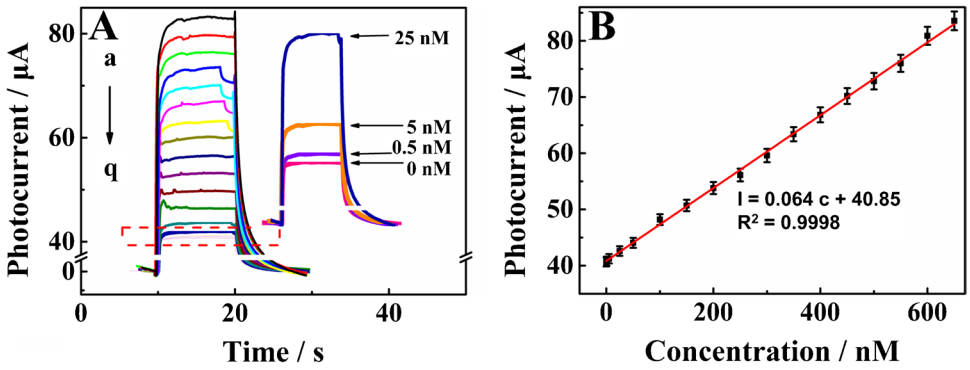

Fig. 3 PEC responses of biosensor to different concentrations of kanamycin. From a to q: 650 nM, 600 nM, 550 nM, 500 nM, 450 nM, 400 nM, 350 nM, 300 nM, 250 nM, 200 nM, 150 nM, 100 nM, 50 nM, 25 nM, 5 nM, 0.5 nM, 0 nM (**A**). The linear relationship between PEC response of biosensor and kanamycin concentration (**B**)

Table 1 Comparison of different detection methods for kanamycin

Method	Material	Linear range [b]	LOD[c]	Ref
CL [a]	Pt complex	200–1.5×10^5	143	[28]
Col	AuNPs	1–100	1.49	[29]
Flu	MoS_2 NSs	4×10^3–2.5×10^4	1100	[30]
Flu	GO	200–2×10^5	26	[31]
PEC	UiO-66	25–900	13	[32]
PEC	Cu-MOF-NH_2	0.5–650	0.1	This work

[a] *CL*, chemiluminescence; *Col*, colorimetry; *Flu*, fluorometry; *MoS_2 NSs*, MoS_2 nanosheets; *GO*, graphene oxide; *UiO*, UiO-66-NH_2/MCA/MWCNT@rGONR

[b] nM

[c] nM

good selectivity to kanamycin. In order to measure long-term stability, the PEC biosensors were kept at 4 °C, and three biosensors were taken from them every 5 days for measurement. As shown in Figure S5B, the photoelectric response of PEC biosensor was reduced by only 5%. The results indicate that the PEC biosensor has good stability. To evaluate the reproducibility of the PEC biosensors, the photoelectric response of five independent PEC biosensors was tested. As shown in Figure S5C, the RSD of the five PEC biosensors were 2.15%, which indicates that the PEC biosensor has good reproducibility.

Determination of kanamycin in real samples

Fish was purchased from local seafood market. The concentration of kanamycin in fish was detected and this method was evaluated with standard addition method (S6) and compared with the fluorescence detection [33]. As shown in Table S1, the addition concentrations of kanamycin in groups 1 to 5 were 0.20 nM, 5.00 nM, 20.00 nM, 50.00 nM, and 100.00 nM respectively. The recovery rate was between 95.7 and 105.0%, and RSD was between 1.5 and 4.0%. The results are in good agreement with those of standard method. This verified the feasibility and accuracy of the PEC biosensor in the actual sample analysis.

Conclusions

A self-enhancement PEC biosensor for kanamycin detection was established based on Cu-MOF-NH_2 photosensitive material modified copper sheet electrode. The detection photocurrent was produced from the kanamycin oxidization caused by electron hole pairs. This is the first time of the application of MOF for target with the self-enhancement PEC strategy. The biosensor has been successfully applied in the detection of kanamycin content in fish, and it broadens the application of MOF materials in the construction of PEC biosensors. The PEC biosensor is detected by combining the aptamer specifically with kanamycin. In the later stage, other antibiotics that are easily oxidized and can be used as electron donors can be detected by adjusting the type of aptamer, such as tobramycin. The PEC biosensor also has the limitation that the copper sheet here may be corroded under extreme conditions, such as strong acid and alkali medium. It may be considered to be replaced by inert electrodes in the further.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s00604-022-05266-w.

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Declarations

Conflict of interest We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work; there is no professional or other personal interest of any nature or kind in any product, service, and/or company that could be construed as influencing the position presented in, or the review of, the manuscript.

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