

Micro fluidic Device for Cd⁺ Detection Using Gold Nano particles

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ABSTRACT

A power-free single channel microfluidic device was designed for rapid and sensitive detection of cadmium (Cd²⁺). Unmodified gold nanoparticles (AuNP) colloid was prepared by an electrochemical method to detect Cd²⁺ into water upon colorimetric assay and electric resistance. The detection method based on color changes resulted from AuNP aggregation and their impact on surface Plasmon resonance. Colloidal solutions of AuNPs have high extinction coefficients and absorption band in the visible region of the UV-Visible spectrum. Its position depends upon the Au particle size and inter-particles distance. Therefore, a well-designed chemical interaction between the analytic and AuNPs surroundings resulted in aggregates and changes in surface plasmon resonance band position and width that lead to visual detection of Cd²⁺. These visual results could be observed by the naked eye when the mixture color changed from red in blue with Cd²⁺ concentration. Optical property's changes with Cd²⁺ concentrations in water were studied via UV-Visible spectrometer. Using PDMS surface modified to construct microfluidic device supported to get stable electric resistance values for AuNP colloid and Cd aqueous solution mixture. Electric resistance results accomplished with UV-Visible results could be employed to detect low ion concentrations in water (10 μM) sensitively.

Keywords: Micro fluidic Device, Cd Detection, Aunp, Surface Plasmon Resonance.

معدة مايكروية لتحسس الكاديوم في الماء باستخدام جسيمات الذهب النانوية

الخلاصة

تم في هذا البحث تصنيع معدة مايكروية للموائع لا تحتاج الى أي مصدر للطاقة في عملها لغرض التحسس الدقيق والسريع للكاديوم في الماء. استخدم محلول الذهب النانوي الغروي المحضر مختبريا بالطريقة الكهروكيميائية والخالي من أي اضافات. اعتمد مبدأ التحسس على التغييرات اللونية والكهربائية المصاحبة لتغير نسبة الكاديوم في الماء. ان آلية التغير اللوني تعتمد على ظاهرة surface Plasmon resonance والتي تتأثر بشدة بمقدار كتل جسيمات الذهب النانوية. ان قيمة الطول الموجي الذي تظهر فيه حزمة surface Plasmon resonance تعتمد على حجم جسيمات الذهب النانوية وعلى المسافات البينية بينها. انعكست هذه الظاهرة على تغييرات لونية مصاحبة لتغير نسبة الكاديوم والتي يمكن ملاحظتها بالعين المجردة ومن تغير لون مزيج المحلول الغروي مع المحلول المائي الحاوي على الكاديوم من الاحمر الى البنفسجي المزرق. تمت دراسة طيف الامتصاص لمزيج المحلول الغروي مع المحلول المائي الحاوي على الكاديوم بمطياف الاشعة فوق البنفسجية – المرئية. الخواص الكهربائية درست باستخدام المعدة المايكروية والتي جرى ترسيب اوكسيد السليكون على سطح قناتها الداخلية لتحديد الامتصاص خلال جدرانها والذي كان يؤدي الى عدم استقرار قيم المقاومة الكهربائية للمزيج. من خلال النتائج المستحصلة يمكن القول ان التوافقية بين النتائج الطيفية والكهربائية يمكن توظيفها لتحسس نسب واطئة من الكاديوم في الماء.

INTRODUCTION

Heavy-metal ions (HMIs), such as lead (Pb^{2+}), cadmium (Cd^{2+}) and mercury (Hg^{2+}) represent significant hazards to the environment and human health, since they can contaminate the soil and water and enter the water supply and food chain [1]. Their toxicity caused serious and long-term effects. Many techniques have been developed to detect HMIs most of them are expensive and complicated [2]. Recently rapid and sensitive methods have become a very urgent need. This kind of work received much attention from many researchers to find fast, simple, non-expensive and reactive method. Their work focused on nanomaterials with specific optical properties employed in a colorimetric assay as chemical sensing strategy.

Gold nanoparticles (AuNPs) are one of the important nanomaterials used for chemical and biosensing applications due to their chemical and optical properties. Gold nanoparticles absorb and scatter light with extraordinary efficiency. Their strong interaction with light occurs because their metal surface conduction electrons undergo a collective oscillation when they are excited by specific wavelengths. This oscillation is known as a localized surface plasmon resonance (LSPR). As a result of this phenomenon strong absorption band(s) or increased radiation scattering intensity occurs at certain wavelengths [3]. LSPR of the AuNPs is mainly related with the particle size, shape, composition, inter-particle distance, and dielectric constant (the local refractive index near the particle surface) of the surrounding medium [4].

The optical properties of AuNPs change when particles aggregate and the conduction electrons at surfaces of neighboring particles become delocalized and are shared among them. When this occurs, the localized surface plasmon resonance, LSPR shifts to lowering energies, causing the absorption and scattering peaks to be red-shift to longer wavelengths [4]. Thus UV-Visible spectroscopy can be used as a simple and reliable

method for monitoring the stability of nanoparticle solutions. As the particles aggregate, the original extinction peak will decrease in intensity (due to the depletion of stable nanoparticles), and often the peak will broaden or a secondary peak will form at longer wavelengths (due to the extent of aggregates) [5].

Previous works in HMIs detection employing AuNPs colloidal, which prepared in many methods and sizes. Many strategies were carried out based on aggregation of surface modified AuNPs, and the effect of this aggregation on surface plasmon resonance absorption [2]. AuNP modified with 4-MB and thiosulfate strategy built upon the fact of accelerating the leaching rate of AuNPs by Pb²⁺ and the colorimetric route [6]. Au (S₂O₃)₂ complexes on AuNP surfaces formed from their reactions with thiosulfate ions, with the zeta potential being more negative and leading to slight decreases in their surface plasmon resonance absorption. This method was highly selective toward Pb²⁺ detection at a low level in aqueous solution without using complicated chemosensors or sophisticated equipment. A new class of turn-on surface enhanced Raman scattering (SERS) sensors for the sensitive and selective detection of cadmium ion (Cd²⁺). The SERS-active nanoparticles consist of 41-nm gold nanoparticles, encoded with a Raman-active dye through a disulfide anchoring group, and a layer of Cd²⁺-chelating polymer brush coating grafted on the nanoparticle via surface-initiated atom transfer radical polymerization. Addition of Cd²⁺ leads to interparticle self-aggregation and immediately turns on the SERS fingerprint signal. In contrast to nanoparticle-based colorimetric assays, the SERS probe is also capable of detecting Cd²⁺ in heavily colored samples [7]. Chunhui Fan worked on detection of Pb²⁺ with AuNPs which were modified by MUA (MUA-AuNPs). The chelation between MUA and Pb²⁺ caused the aggregation of the MUA-AuNPs and color changes from red in purple caused by the effect of plasmonic coupling. That could be seen obviously under a microscope when a dark line resulted from the aggregations formed deposition on the surface of PDMS when using a power-free PDMS microfluidic device [8].

The aim of the present work is to detect Cd²⁺ using unmodified AuNPs colloidal, based on colorimetric assay and electric resistance. Obviously the mixture solution color changed from red in blue/purple caused by the effect of plasmonic coupling. The chelation between -COOH group and Cd²⁺ will cause the aggregation of the AuNPs and their mixtures color changes. On our PDMS microfluidic device, the aggregations formed a conductive media which can be employed to Figure out with colorimetric assay a sensitive method to detect Cd²⁺ in water.

EXPERIMENTAL WORK

Au Nanoparticles Preparation

A gold nanoparticle colloidal was prepared by developing electrochemical method used by Katherine et al [9]. HAuCl₃ produced by using 99% purity gold electrode with electrolyte solution, 0.75 g NaCl and 3 drops of hydrogen peroxide in water, stirring continued during DC applied voltage of about 30-60 min. The resultant gold chloride was reduced to gold colloidal by adding 1% trisodium citrate solution (4 mL) to the boiling solution of HAuCl₄ (99 mL deionized water and 1 mL 1% HAuCl₄). The mixture was continued boiling and stirring for about 30 min until the color of the aqueous changed from yellow to red, the resultant was combining of -COOH group with gold nano

particles. After that, the solution was cooled down to room temperature while being stirred continuously. The prepared AuNPs colloid was stored at room temperature. Au particle size was estimated from red color colloid and the wavelength of SRP according to previous works done by many groups [10, 11 and 12].

Reagents Preparation

Cd²⁺ aqueous solution prepared from dissolution of cadmium acetate with different concentrations in distill water. Two different ratios of Cd²⁺ aqueous solution mixed with AuNP colloid, 0.5 ml/0.5ml and 0.3ml/0.7 ml Cd²⁺ aqueous solution to AuNPs colloid.

Micro device Fabrication

Photolithography was used to get a single straight micro-channel, 300 μm in width, 50 μm in depth and 4 cm in length on Si wafer. Sylgard® 184 oligomer and curing agent were thoroughly mixed at 10:1 mass ratio degassed for 30 min and poured over cleaned patterned Si wafers. Poured PDMS was cured at 65 °C for 180 min. The master was kept then overnight inside an oven maintained at 60 °C. The cured PDMS layer was carefully peeled off from the wafer. The PDMS slab with microchannel feature was cleaned ultrasonically for 10 min with water, ethanol and water subsequently before drying by air. To hinder species absorption on PDMS surface, we found that, from our previous work on PDMS surface modification by SiO₂ deposition the good results can be obtained with increasing SiO₂ thickness. To deposit SiO₂, PDMS slab was firstly, plasma treated for 3 minutes using 124 watts RF power. Plasma treated PDMS was loaded on BMR Low Temp PECVD machine within 30 min after oxygen plasma treatment. After the chamber was evacuated to 10⁻⁶ mtorr, 4 nm amorphous silicon layer was deposited on it. By applying 1000 watts RF power and using H₂ and SiH₄ gases with flow rates of 50 and 25 sccm respectively. To precipitate SiO₂ thin film with 30 nm thickness over PDMS chip 25, 10, and 7 sccm gas flow rates for O₂, Ar, and SiH₄ respectively were used, maintaining chamber pressure at 10 mtorr and RF power at 1000 watt. Layers thicknesses were measured by ellipsometer in University of California Irvine. After the replicas were peeled off from the mold and before surface modification, reservoirs holes (d = 3 mm) punched at the two ends of the channel. Flat PDMS substrate (0.2–0.4mm height) was obtained by casting and curing the pre polymer mixture on a large flat glass slide. The PDMS layer with microchannel and thin flat PDMS were sealed together to form PDMS microchip by clamping them between two PMMA sheets as shown in Figure (1). The mixture solutions, AuNP colloidal and Cd²⁺ solutions, were inlet into the micro-channel by syringe. Two copper electrodes immersed into reservoirs at the both micro-channel ends to measure electrical resistance.

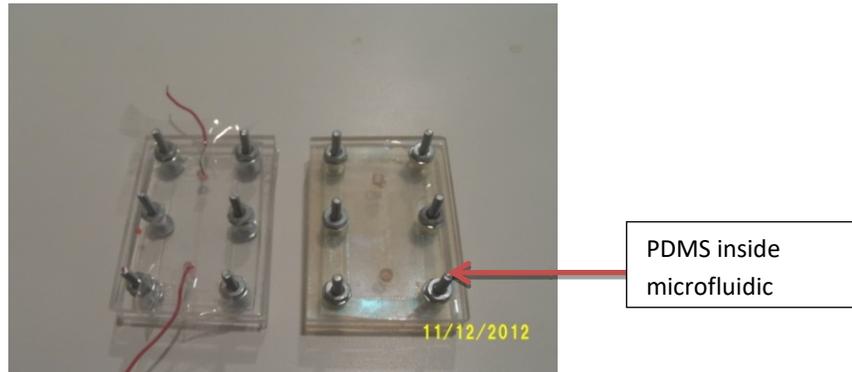


Figure (1) Photographic picture for microfluidic devices with native and coated with SiO₂ PDMS.

RESULTS AND DISCUSSION

The strategy based on using unmodified AuNP to study its aggregation caused by Cd²⁺. AuNP-heavy metal ions (HMIs) sensor is based on the colorimetric assay; color change resulted from localized surface plasmon resonance changes due to AuNP aggregation. It is well known that normal AuNPs with size between 10 nm to 50 nm appear red color in aqueous solution [9, 10]. Diana et al illustrated the chelation mechanism of Cd²⁺ ions and COOH-AuNPs as it can be seen in figure 2 [8]. When Cd²⁺ was added, chelate interaction with the carboxylate groups (–COOH) surrounding AuNPs occurred, which shortens the distance between the gold nanoparticles and formed aggregates. It was noted that the color solution changed from red in blue/purple and can progress to a clear solution with black precipitates caused by the effect of plasmonic coupling when inter-particle distance changes as shown in Figure (3).

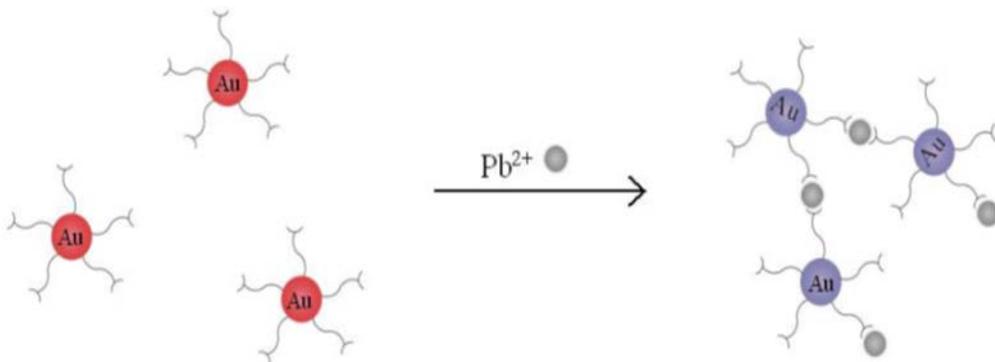


Figure (2) Schematic illustration of the chelation mechanism of Cd²⁺ ions and COOH-AuNPs [8].

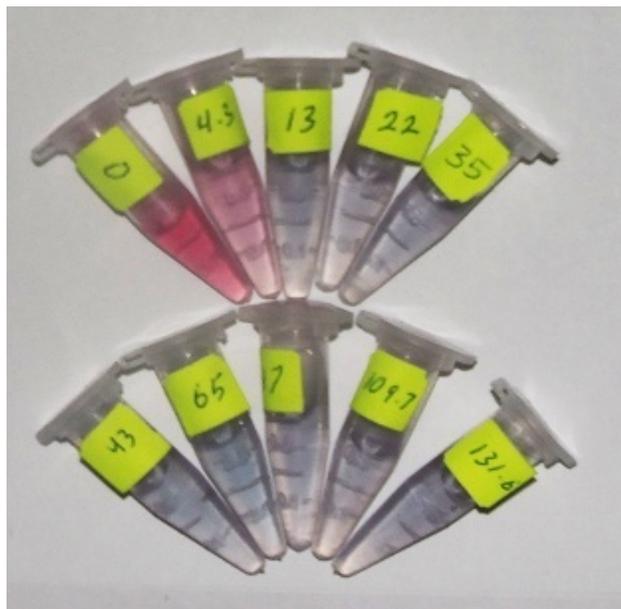
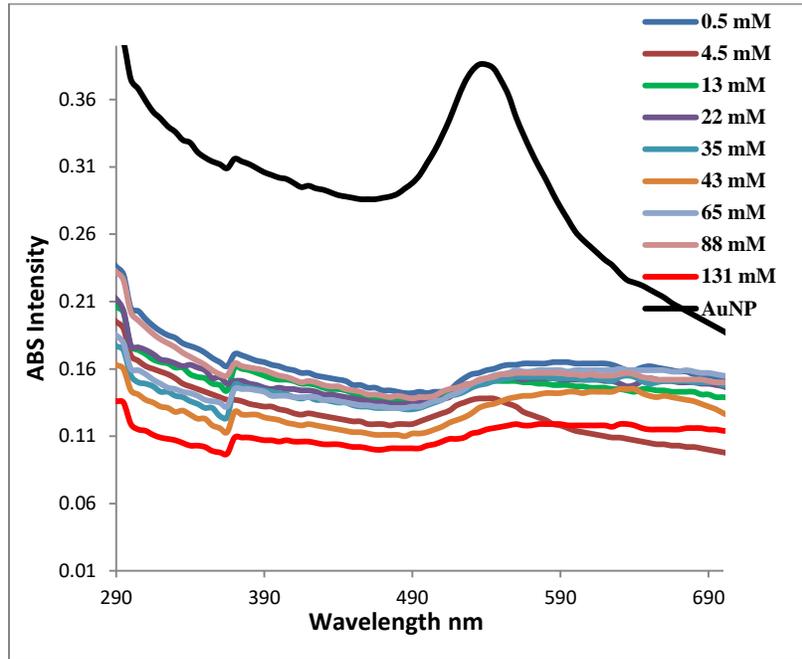


Figure (3) Photographic picture for AuNP colloid colors Changes with Cd²⁺ addition.

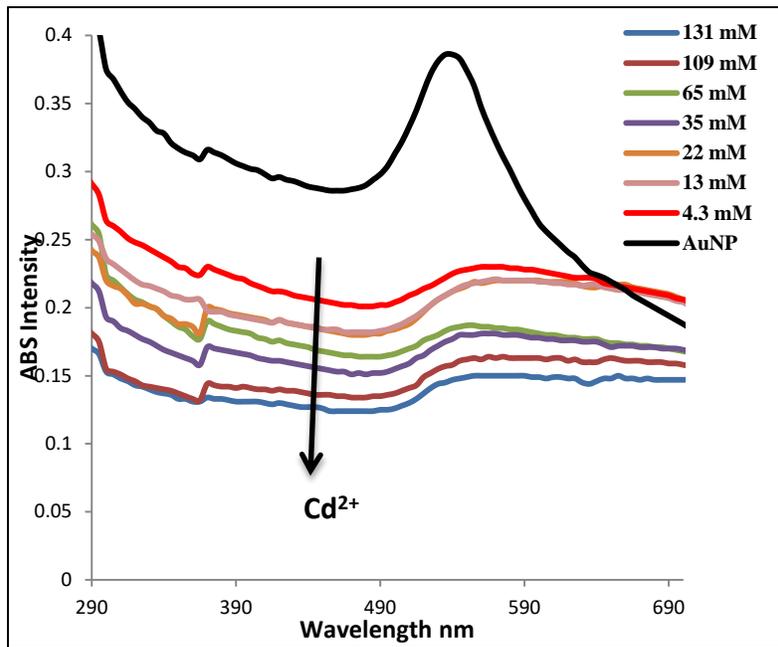
The UV-vis spectra in Figure 4 illustrates that the intensity of the original plasmon resonance peak, for AuNP colloid, appeared at 535 nm progressively and sharply decreases and broadness with Cd²⁺ addition. This is accompanied by a colorimetric red-to-blue transition. These results are in good agreement with Diana et al [2], Jun Yin et al [7] and Djibril et al [15]. The extinction spectrum of our unmodified AuNP with carboxy (COOH) groups surrounding their surfaces shows LSPR at 535 nm, figure 4. As the mixture solution becomes more acidic by carboxy (-COOH) groups, this comes from Cadmium acetate used, the carboxy group is protonated, and the zeta potential is reduced resulting in destabilized nanoparticles [2]. Cd ions chalet with carboxy (-COOH) groups and aggregate AUNP. This can be demonstrated from the rapid change across the extinction spectrum as the Cd²⁺ decreased, which referred to the nanoparticles agglomerating. UV-Visible spectroscopy was used here as a characterization technique that provides information on whether the nanoparticle solution has destabilized and aggregate as illustrate in Figure (4a and b).

Less sensitive results achieved with lower ratios of AuNP colloid /Cd²⁺ aqueous solution, 0.5/0.5, as shown in Figure (4b). Decreasing AuNP amount will decrease its opportunities to be aggregate by Cd ions more addition.

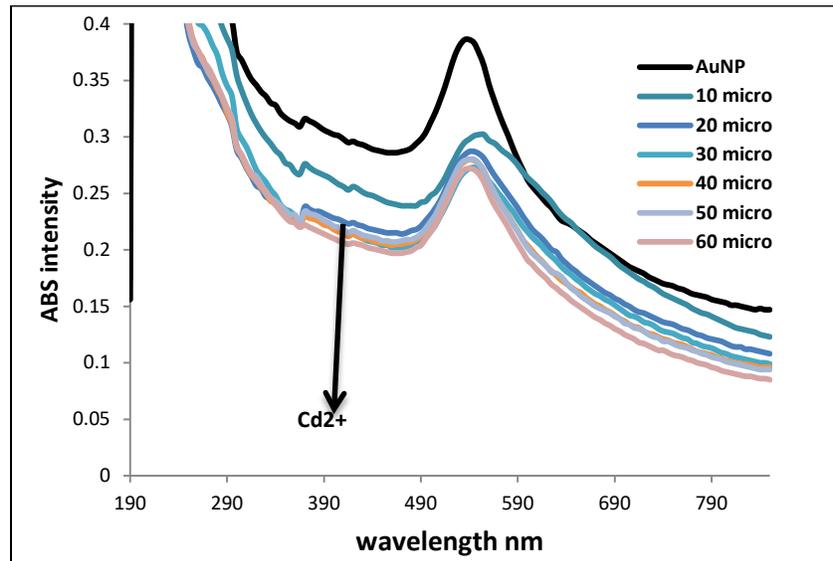
By this strategy, we achieved a universal colorimetric assay employing gold nanoparticles and water-soluble conjugated polyelectrolytes (inorganic ions dissolved in aqueous solution of polymer acid) to detect a wide range of Cd²⁺ 10-60 μ M and 4.3-131 mM.



a- 0.5/0.5, AuNP colloid to Cd²⁺ solution



B- 0.7/0.3 AuNP colloid to Cd²⁺ solution

C- 0.7/0.3 AuNP colloid to low Cd²⁺ concentration solution**Figure (4) The Effect of Aggregation on Optical Properties with Cd²⁺ addition.**

It is well known that PDMS surfaces are hydrophobic, making them difficult to wet and hydrophobic analytes can easily adsorb onto the PDMS surface [16]. These drawbacks make modification of the PDMS an important method to prevent species absorption [17]. Addition of Cd²⁺ to the dielectric AuNP colloid makes its conductive media. Since cadmium acetate is classified coordination polymer, featuring acetate ligands interconnecting cadmium centers. It exhibits conductive media of gold nanoparticles and water-soluble conjugated polyelectrolytes; inorganic ions dissolved in aqueous solution of polymer acid. In another world, carboxylate groups on AuNP surface chelated Cd²⁺, allowing the nanoparticles aggregating and networking. Unstable electric resistance values were measured by a native PDMS micro device due to continuous absorptions of species into PDMS surface [17]. While stable values got directly after the mixture inlet into microchannel constructed from PDMS surface modified with SiO₂ as an inert layer. The mixtures electric resistance decreases with Cd ions via using micro device constructed from PDMS surface modified with SiO₂ demonstrate in figure 5 for the two mixture ratios of AuNP colloid /Cd²⁺ aqueous solution, 0.5/0.5. These results accomplished with UV-Visible results can be employed to detect Cd ion in water sensitively.

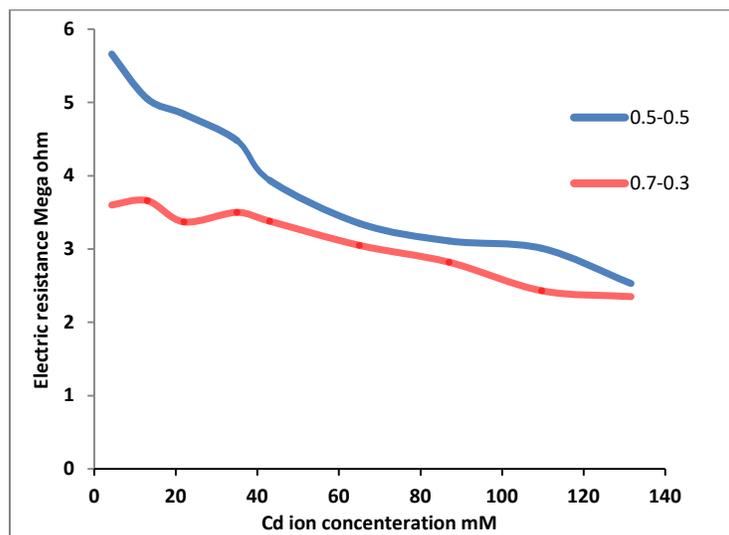


Figure (5) Electric properties of AuNPs with Cd²⁺ addition.

CONCLUSIONS

In the present work a simple, power free and portable microfluidic chip based on AuNPs colloid and their electrical properties change that compliant with colorimetric assay was developed. Synthesis of polyelectrolyte, AuNP colloidal of Au into the formic carboxyl groups, in simple method to get unmodified AuNP chaleted by the addition of HMIs is the main goal of this work. The detection limit of 10 μM Cd²⁺ by this work was satisfied competitive with the traditional physico-chemical quantitative methods. Among the numerous methods that focus on metal ions detection, such as fluorescence and colorimetric methods, electrical detection based on reduced grapheme, surface enhanced Ramans scattering (SERS) sensors and so on. Our device has obvious advantages. Firstly, it is considerably more convenient because it is power-free and reusable, and analysis results can be read simply by a voltmeter. Secondly, it is an effective and fast detection method. Thirdly, it is a low-cost analysis because no expensive and complicated reagents or equipment are needed. Thus, we believe our strategy offers a Cd²⁺ sensor with great potential popularity and with proper probes and condition optimization, many other targets can be achieved.

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