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A Platinum Nanostructure Electrode with an Iodine Coating to Measure the Bio-Electrochemical Behavior of Arctigenin Using Cyclic Voltammetry

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استخدام قطب جسيمات نانوية بلاتينيوم مع طلاء اليود لقياس السلوك الكهروكيميائي للأركتيجينين باستخدام فولتامترية الموجة المربعة

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ABSTRACT

The cyclic voltammetric method was utilized to build an iodine-modified platinum nanoparticle electrode for measuring arctigenin electrochemically. The findings of the experiments showed that this modified electrode had a considerable voltammetric response to arctigenin, which was due to the electrocatalysis properties of iodide and the strong conductivity and large specific surface area of the platinum nanostructure electrode. The proposed approach demonstrated a broad linear range, good sensitivity, low detection limit and high selectivity. The examination of the scan rate change revealed that the electrode process is adsorption-controlled. The oxidation of arctigenin was demonstrated to involve both protons and electrons. Finally, this method can be used to develop a sensitive arctigenin detection sensor.

Keywords: Volumetric sensor, Iodine-coated, Nanoparticle, Arctigenin, Platinum electrode, Iodide, Electrocatalytic ability.

المخلص

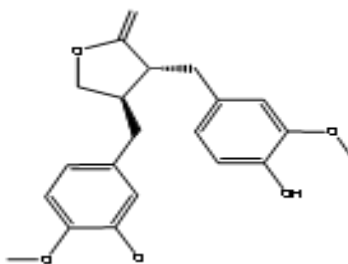
تم استخدام طريقة قياس الفولتامترية الحلقي لبناء قطب جسيم نانوي باليود معدّل باليود لقياس الاركتيجينين كهربائياً. أظهرت نتائج التجارب أن هذا القطب المعدل له استجابة فولتامترية كبيرة للأركتيجينين، والتي كانت بسبب خصائص التحفيز الكهربائي لليوديد والموصلية القوية ومساحة السطح المحددة الكبيرة لقطب البلاتين النانوي. أظهرت الطريقة المقترحة نطاقاً خطياً واسعاً وحساسية جيدة وحداً منخفضاً للكشف وانتقائية عالية. كشف فحص تغيير معدل المسح أن عملية القطب الكهربائي يتم التحكم فيها عن طريق الامتصاص. تم إثبات أن أكسدة الاركتيجينين تشمل كل من البروتونات والإلكترونات. أخيراً، يمكن استخدام هذه الطريقة لتطوير مستشعر حساس للكشف عن الاركتيجينين.

الكلمات الرئيسية: مستشعر حجمي، مغلف باليود، جسيمات نانوية، الاركتيجينين، قطب بلاتينيوم، يوديد، قدرة التحفيز الكهربائي.

1. Introduction

Arctigenin is extracted from the seeds of the traditional Chinese herb *Fructus Arctii* [1]. Arctigenin has been shown to have a variety of pharmacological effects, including anti-cancer, anti-asthmatic, anti-influenza, anti-austeric, anti-HIV, and anti-inflammatory activities [2-5]. Arctigenin has a wide range of pharmacological effects; hence quantifying it is crucial [6]. However, there are only a few analytical methods now available for arctigenin, including HPLC, LC-MS/MS, fluorescence, UPLC-ESI-MS/MS, and HPLC-UV [7-11]. Arctigenin electrochemical studies and electroanalytical methods have a large linear range, great sensitivity, and simplicity [12]. As a result, developing a sensitive and reliable electrochemical sensor for measurement and mechanism investigation of arctigenin remains an exciting prospect [13]. Among the numerous various ways for modifying electrode surfaces, the production of iodine on metallic electrode surfaces has attracted a lot of interest [14]. It is for reasons such as environmental friendliness, chemical stability, technological suitability on the electrode surface and low cost [15]. The ligand's significant surface activity on common solid-metal electrodes changes the redox chemistry of the iodine in the surface-bound state [16]. This is where the chemisorption species come in. Iodine adlayer modified electrodes have been widely used in various metallic electrodes [17], and the fabrication of nanoparticles is rich in anticipated properties [18]. Platinum nanoparticles electrode has a long history of application as electrode-modified materials [19-21]. Iodine adlayer modified electrodes have been widely used in various metallic electrodes [22-23], particularly in self-assembly electrodes [24] and the synthesis of nanoparticles rich in expected properties [25]. Only one article on iodine modified glassy carbon electrode (GCE) has been found so far [26]. By electrochemically depositing KI (10^{-3} mol.L⁻¹ in H₂SO₄ solution, pH 1.5), an iodine modified GCE was created. The deposition was carried out

using a cyclic scan potential between -0.75 V and 1.2 V for 30 cycles [26]. The proposed iodide modified electrode demonstrated the highest electrocatalytic activities in different buffer solutions for As (III) oxidation, CrO_4^{2-} , and IO_3^- reduction. Nonetheless, the conductivity of iodide-modified GCE is poor. As a result, the iodide modified GCE with improved conductivity is worth investigating [27]. The electrochemical determination of arctigenin was reported for the first time in this work using a biosensor Iodide/platinum nanostructure electrode.



Scheme(1): Chemical structure of arctigenin.

2. Experimental

2.1 Reagents, Apparatus and Instrumental

For the electrochemical procedures, a Model CHI650 electrochemical system (Chenhua Instrument Company, Shanghai, China) used Ag/AgCl reference electrode, a platinum auxiliary electrode, and a bare or modified platinum nanostructure as a working electrode employed in a typical three-electrode setup (diameter 3 mm). The remaining chemicals were all of the analytical quality and were utilized without further purification. Aladdin Co. Ltd. provided the KI powder and the arctigenin analytical standard (Shanghai, China). Arctigenin stock solution (1×10^{-4} M) was produced in methanol and stored in a refrigerator at 5 °C. When utilized, it was diluted to an appropriate concentration. 0.2 M phosphate buffer solution (PBS) was made by combining 0.15 M Na_2HPO_4 . For the experiments, double-distilled water was employed. X-ray

powder diffraction (EDX) and scanning electron microscopy (SEM) (Inspect F50 Company, Netherlands) were used.

2.2 Fabrication of Iodide/Pt nanostructure electrode

The platinum electrode (3 mm diameter) was polished to a mirror-like surface with 0.05 μm alumina slurry. The Pt (nano) was then cleaned in ethanol and water for 5 minutes using an ultrasonic treatment before drying at room temperature. The I-Pt (nano) electrode was created by sprinkling 1 L of iodine solution onto pre-cleaned Pt (nano) and drying it at room temperature. The Pt nanostructure surface was then electro-deposited with iodide by cyclic scanning between -0.2 V and 1.3 V with 100 mV/s for ten cycles in pH 7.5 PBS containing 1.0×10^{-4} M of KI.

The genuine sample arctigenin was used to assess the performance of the suggested voltammetric sensor in terms of practical application. Arctigenin powder was disseminated in 25 mL of methanol and super sonicated for 180 minutes. Finally, the filtrates were mixed and evaporated until just 10 ml of solution remained. As a detection sample, the solution was employed.

3. Results and Discussion

3.1 Morphological analysis of an I-Pt (nano) electrode

The SEM analysis was performed to identify and describe I-Pt (nano) electrode's precise microstructure. The SEM micrograph of the I-Pt (nano) surface may be seen in Figure 1. They could observe that iodide had effectively electrodeposited onto the platinum electrode. Another effective method for testing the interfacial characteristics of surface-modified electrodes is scanning electron microscopy (SEM). That is, for modified electrodes, the charge transfer rate at the electrode/electrolyte interface is kinetically fast.

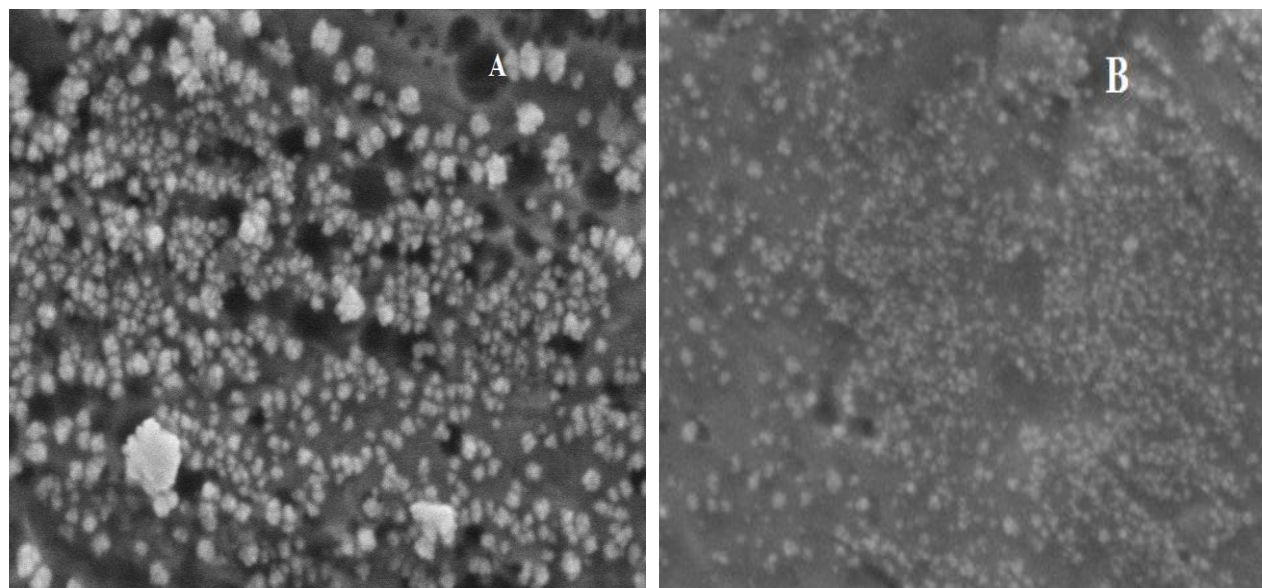


Figure (1): (A) SEM micrograph of platinum nanostructured electrode unmodified, (B) SEM micrograph of Iodine-modified platinum nanostructured electrode.

The identity of the deposited particles was confirmed by energy-dispersive X-spectroscopy. The EDX spectra in Figure 2 indisputably confirm the identity of the deposited platinum nanostructures. Thus, SEM, EDX spectra on the one hand, and cyclic voltammetry on the other, show that for the formation of pt (nano).

Spectrum: Acquisition 6372

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [%]
I	53	L-series	9.49	11.82	17.08	0.7
Pt	78	M-series	70.80	88.18	82.92	2.9
Total:			80.29	100.00	100.00	

Figure (2): EDX spectra of I-Pt (nano) electrode.

3.2 Electrochemical character of platinum nanostructure electrode modified by iodine

Using cyclic voltammetry at a scan rate of 100 mV/s, the electrochemical behavior of a Pt nanoparticle electrode modified by iodine was investigated. Figure 3 depicts the iodine coated

platinum nanoparticles electrode representative voltammograms recorded in 0.5 M H₂SO₄ (dashed line) superposed to the bare platinum electrode nanoparticles process voltammograms (solid line). The lack of redox (oxidation/reduction) activity, specifically oxygen and hydrogen adsorption, suggests a near total surface suppression between the hydrogen production limits (around -0.2 V) and surface iodine suppression levels (around 0.95 V). When the potential of the electrode with iodine-coated scans exceeds 0.95 V, the iodine is partially desorbed.

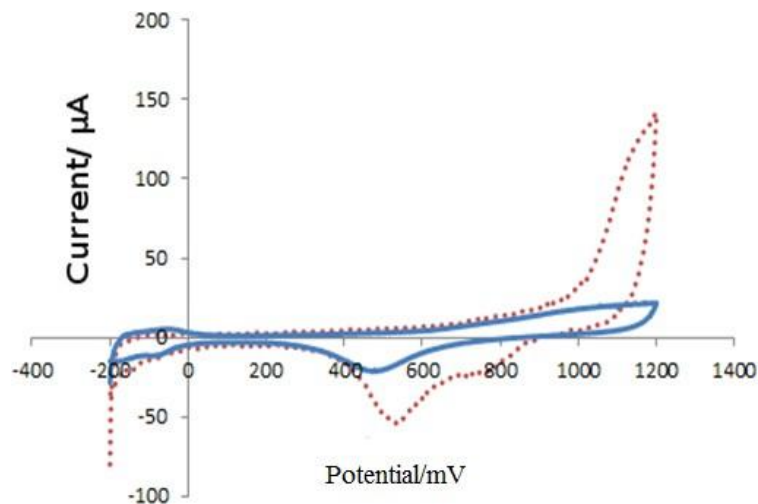


Figure (3): Voltammograms of platinum nanoparticle electrode (solid line) and iodine-coated platinum nanoparticle electrode (dashed line). At a scanning rate of 100 mV/s.

In the first cycle, anodic peaks at 0.510 V and cathodic peaks at -0.4585 V were found (Figure 4). At the platinum nanostructure electrode modified by iodine, a pair of reversible redox peaks with $i_{pa} = 15.6$ A and $i_{pc} = 12.8$ A was discovered. In succeeding cycles, the anodic peaks at 0.481 V moved negatively, peak currents increased first then fell, and all other peaks grew. The results showed that the electroactive area was enlarged with the use of platinum nanostructure electrodes and Iodide modified electrode surfaces, which would increase electrochemical activity and enhance electrochemical sensing.

Figure 4 shows cyclic voltammograms for an iodine-Pt (nano) electrode and a Pt (nano) electrode with a variable surface area generated under the same experimental conditions. The identity of the nanostructured electrode is demonstrated by the striking similarity of the two electrodes' cyclic voltammograms and the appearance of the well-known typical voltammetric characteristics of platinum electrodes.

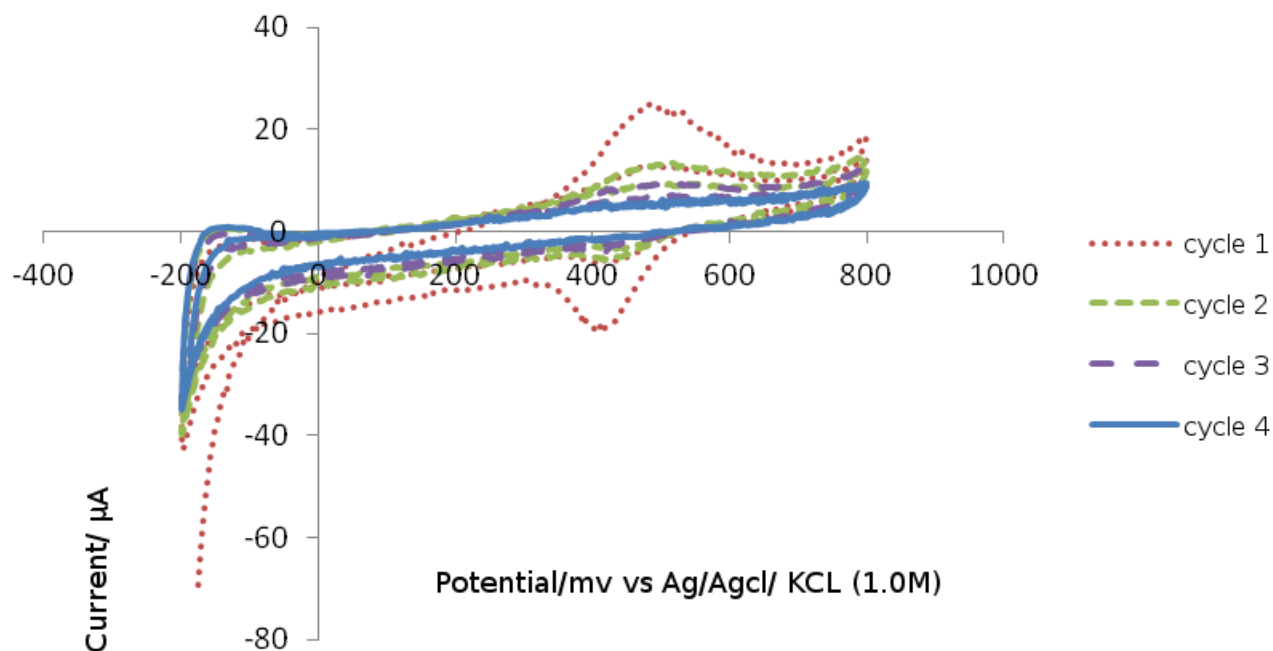


Figure (4): Cyclic voltammograms for the iodine-Pt (nano) electrode at different scan times.

They used an electrochemical probe to examine the properties of the many changing layers by CV. These were the charging currents: an unmodified platinum electrode with a platinum nanostructure electrode with iodine alteration. Furthermore, the considerable increase of these peaks indicates the sequential building of the iodide monolayer on the surface of the platinum nanostructure.

3.3 Voltammetric behavior of arctigenin at Iodide- Pt (nano) electrode

Cyclic voltammograms for an iodine-coated Pt (nano) electrode 1×10^{-4} M of arctigenin in 0.1 M PBS buffer solution were investigated at a scan rate of 100 mV/s is shown in Figure 5. The voltammograms show anodic arctigenin oxidation peaks from 0.6 to 1.1 V. As a result, its behavior is irreversible. A small fluctuation in peak potentials for varying concentrations is to be expected for the various electrochemical processes. The iodine monolayer did not decay during the studies, although due to the ease of production of the iodine-coated electrode, the surface was re-coated frequently.

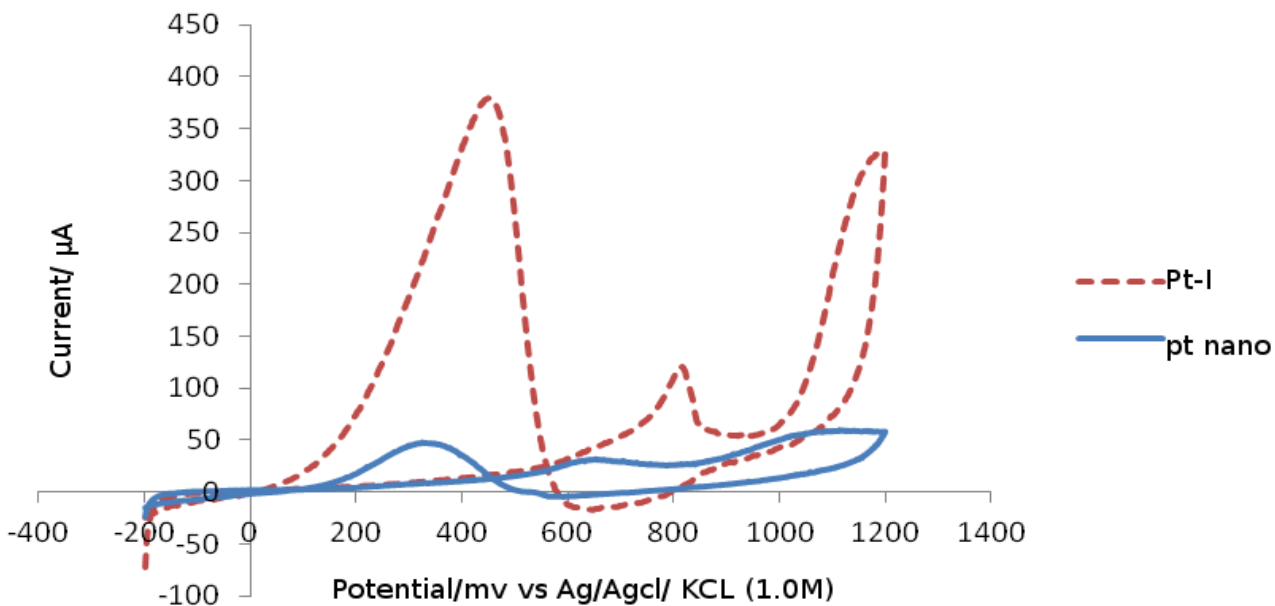


Figure (5): Cyclic voltammogram of iodine-Pt (nano) electrode with 1×10^{-4} M of arctigenin.

It lowered resistance to the bare Pt (nano) electrode significantly at Iodide-Pt (nano) electrode, attributing to the function of nanostructure and iodide working together. These findings agreed with the debate in cyclic voltammetry. The voltammograms contour matched the current peak order of arctigenin. Arctigenin showed one oxidation peak around 0.8 V and one reduction peak at -0.6 V during the first cyclic scan. The potential window was varied to better understand the

electrochemical behavior of arctigenin at the Iodide-Pt(nano) electrode. There were no redox peaks identified when the potential window was set between 0.1 V and 0.55 V for the cyclic scan.

In the complex electrochemical reaction process of arctigenin at the Iodide-Pt (nano) electrode, triple potential step chronoamperometry was used to measure the diffusion coefficient and adsorption capacity. Experiments were carried out in an arctigenin solution (1×10^{-4} M) and blank PBS. The sensor was immersed in the solution for 5 minutes before the potential step to obtain saturation adsorption.

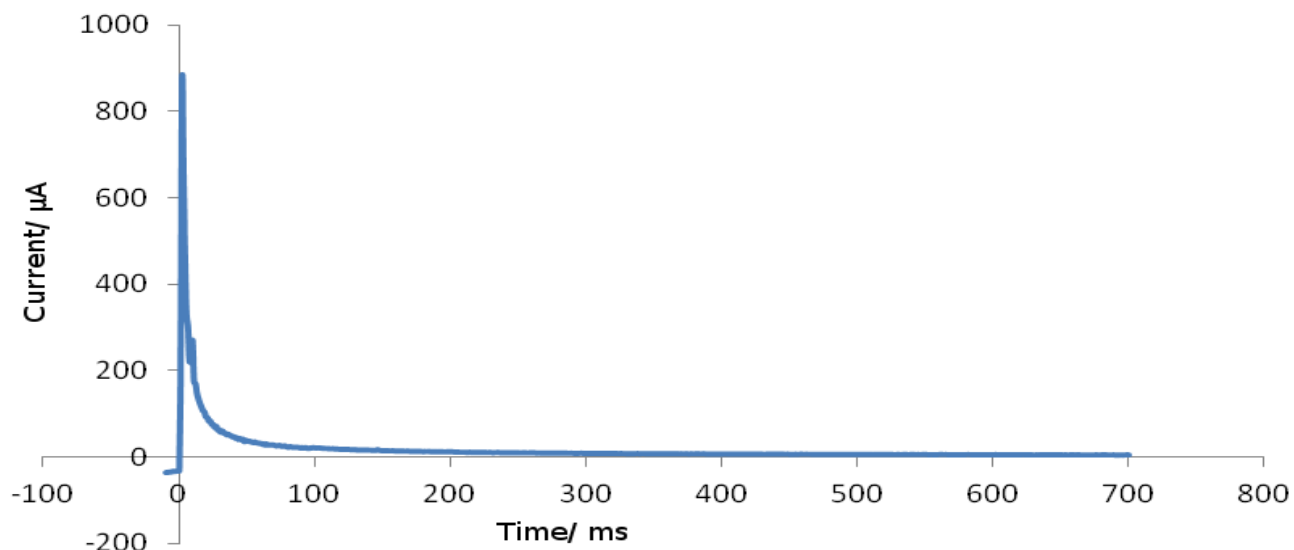


Figure (6): Chronoamperometric of iodine-Pt (nano) electrode with 1×10^{-4} M of arctigenin.

Figure 6 depicts the charge together with the time curve. The potentials were stepped from 0.6 V to 1.1 V, matching the arctigenin oxidation peak, implying that arctigenin oxidation is controlled by adsorption. According to Anson's CC theory (equation 1) [21].

$$Q = nFA\Gamma^* \quad (1)$$

Where D is the diffusion coefficient, Q is the double-layer charge, Γ^* is the adsorption capacity, A is current, and F is the Faradaic charge owing to arctigenin oxidation.

The saturating adsorption capacity was predicted to be 3.21×10^{-9} mol.cm⁻² of oxidation peak.

4. Conclusion

A volumetric sensor based on electrochemical iodide deposition and simple dipping-drying of platinum nanostructure electrode was successfully developed and employed for high-sensitivity arctigenin detection. The proposed approach demonstrated outstanding effectiveness against arctigenin, which was attributed to iodide's electrocatalytic capacity, large specific surface area, and platinum nanostructure electrode's excellent electric conductivity. It performed particularly well for arctigenin detection, with a wide linear range, low detection limit, high sensitivity, selectivity, and good stability. Finally, the current approach was applied to real-world samples with positive results.

List of Abbreviations and Symbols

A	Current
CV	Cyclic voltammograms
D	Diffusion coefficient
EDX	X-ray powder diffraction
F	Faradaic charge owing
GCE	Glassy carbon electrode
Nano	Nanoparticle
PBS	Phosphate buffer solution
Q	Double-layer charges
SEM	Scanning electron microscopy
Γ^*	Adsorption capacity

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