Copper Nanoparticles/Polyaniline/Graphene Composite as a Highly Sensitive Electrochemical Glucose Sensor

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Abstract

A highly sensitive non-enzymatic glucose sensor based on Cu nanoparticles (CuNPs)/polyaniline (PANI)/graphene nanocomposite was fabricated *via* simple *in-situ* reduction of Cu precursor in polyaniline nanofibers under mild conditions followed by mechanical mixing with graphene suspension to form the composites with different graphene contents (0.5 %, 1 %, and 2 %). The properties of nanocomposites were characterized by SEM, TEM, XRD, UV-Vis, and XPS. The CuNPs (d = 2-4 nm) only slightly altered the ordered structure of PANI. It was found that CuNPs have direct electronic interaction with PANI *via* the N atoms on the polymer backbone, which enabled fast electrons transfer from electrode to CuNPs through graphene and PANI. The CuNPs/PANI/graphene nanocomposites were coated on a glassy carbon electrode for the investigation of their electrochemical properties. Both CuNPs/PANI and CuNPs/PANI/graphene showed high sensitivity towards glucose oxidation which occurred at ~ 0.5 V *vs* SCE. The best performance was achieved by the CuNPs/PANI/1% graphene-modified electrode which showed sensitivity of ~150 μ A cm⁻² M⁻¹, detection limit of 0.27 μ M (S/N = 3), and response time of about 3 s. This system was also highly selective towards glucose oxidation that almost no signal was detected from the interferents such as ascorbic acid and dopamine, demonstrating its great potential as a non-enzymatic glucose sensor.

Keywords: Copper nanoparticles, polyaniline, non-enzymatic sensor, glucose electrooxidation, graphene

1 Introduction

Exploring highly sensitive glucose sensor has been a hot topic for a few decades due to its wide application such as medical diagnosis, bioprocess, and environmental monitoring.[1,2] Enzyme-based sensors using glucose oxidase (GOx) are among the first to be discovered and broadly used because of its selectivity and sensitivity, while non-enzymatic sensors are gaining research interests only in the last decade. Similar to enzyme-base ones, non-enzymatic sensors also require catalytic active sites for glucose adsorption before oxidation,[3] but they offer the advantages in production cost, ease of synthetic procedure, and better stabilities towards temperature, pH, humidity, and toxic chemicals.[3,4]

Various materials have been explored for the development of non-enzymatic sensors, including polymers, [5,6] metal[7] and metal oxide[8–11] nanoparticles (NPs), carbon-based materials and their composites. [9,12–14] In particular, metal and metal oxide NPs, such as Pt, [15] Cu, [16,17] CuO, [8,18] and Pd[19] NPs, have attracted significant attention because of their high surface energy and large surface area, thus high electrochemical catalytic activity in numerous electrochemical processes, including glucose electrocoxidation. Normally, these NPs are loaded onto the inorganic/organic support for practical use as electrochemical catalysts. It is of critical importance to ensure both even dispersion and good electron transfer between the surface of NPs and electrode in order to realize high sensitivity and low detection limit. In recent years, conductive polymers have gained wide attention as both a good electrocatalyst support and metal NP stabilizer due to their excellent electronic conductivity and versatile functionality.[20-23]

Polyaniline (PANI) is among one of the most widely investigated conductive polymers because of its interesting redox properties, high stability, and ease of preparation.[24] Several materials including metal or metal oxide supported on PANI have been reported to have high sensitivity towards glucose. It has been demonstrated that NiCo₂O₄@PANI core-shell nanocomposite can be used to detect the oxidation of glucose with very high sensitivity and reasonably low detection limits.[25] Nanoporous PtPb networks and CuNPs on mesoporous PANI also showed similar high reactivity towards glucose oxidation.[7,16] However, the sizes of NPs used in those reports are relatively large (d >15 nm), which might limit the number of active sites. In principle, more catalytically active sites become available as the size of NPs decreases. Also, it should be noted that the morphology of PANI is an important factor that can alter the conductivity of the polymer,[26,27] which could enable higher catalytic glucose oxidation. Some researchers have demonstrated that CuNPs electronically deposited on vertically well-aligned multi-walled carbon nanotube arrays showed fast electron transfer and very short response time (<1 s), mainly due to the high conductivity.[28] CuO NPs dispersed on graphene also showed similar conductivity improvements and high sensitivity to glucose oxidation.[9] Faster electron transfer rate in the metal NP/PANI composite will

effectively improve the electrooxidation of glucose. Thus careful design of NP/PANI interfacial morphology as well as smaller NP size is much desired.

Herein, we describe a simple synthetic method of CuNPs/PANI nanocomposites where the Cu precursors are reduced *in-situ* on PANI nanofibers. The morphology of as-synthesized nanocomposites was studied using electron microscopy and the interaction between CuNPs and PANI was investigated with several spectroscopic techniques. Graphene was introduced to promote the electron transfer process further and alter the morphology of CuNPs/PANI to expose more active sites.

2 Materials and Methods

2.1 Chemicals and synthesis

Graphene was purchased from GrapheneallTM Korea and dispersed in water (1 mg/mL) for future uses. Glucose, sodium hydroxide (NaOH), aniline, ammonium persulfate (APS), copper sulfate (CuSO₄), hydrochloric acid (37%), dimethylformamide (DMF), sodium borohydride (NaBH₄), and ammonium hydroxide solution (28.0-30.0% NH₃ basis) were purchased from Sigma-Aldrich, and used as received. All aqueous solutions were prepared by using high-purity water from MilliQ Water System (Millipore, USA, $R>18.2 \text{ M}\Omega \text{ cm}^{-1}$).

Synthesis of PANI nanofiber: PANI nanofiber was prepared according to Huang's report.[29] In brief, aniline (16 mmol) and APS (4 mmol) were dispersed in HCl aqueous solutions (0.5 M, 50 mL) separately, and mixed rapidly under continuous stirring at 1000 rpm. The solution was kept in an ice bath for 24 h. The color of the reaction mixture changed from light yellow to dark green. Crude product was obtained as green residue by filtration, which was washed with water several times, followed by rinsing with excessive amount of 1 M NH₃·H₂O aqueous solution until the color changed to dark blue (the de-doping process of PANI). The product was then further washed with water until it turned colorless. The solid was collected and dried in an oven at 100 °C overnight.

Synthesis of CuNPs/PANI: CuNPs/PANI was synthesized by the *in-situ* reduction of Cu²⁺ in DMF solution of PANI. CuSO₄ (17.5 mg) was dissolved in 10 mL DMF solution of PANI (1 mg/mL), to yield 1:1 molar ratio of Cu²⁺ to N atoms on PANI backbone. Then, NaBH₄ DMF solution (10 mg/mL) was added (NaBH₄:Cu²⁺ = 15:1) to the reaction solution which was kept at room temperature for 2 h before filtered and washed with water. The residue was collected and dried at 100 °C overnight.

Synthesis of CuNPs/PANI/graphene: CuNPs/PANI/graphene composite was prepared by mixing graphene aqueous solution with the ethanolic solution of CuNPs/PANI, followed by sonication. The proportion of graphene was 0.5 %, 1 %, and 2 % by weight.

2.2 Preparation of modified electrode

The CuNPs/PANI- and CuNPs/PANI/graphene-modified electrodes were fabricated by the following steps: the glassy carbon electrode (GCE, 3 mm diameter, area = 0.071 cm^2) was first polished with 1.0, 0.3, and 0.05 µm α -Al₂O₃ powders (CH Instruments), followed by the alternate rinses with deionized water and acetone. The cleaned electrode was dried in air at room temperature before use. CuNPs/PANI and CuNPs/PANI/graphene were dispersed in ethanol with a concentration of 2 mg/mL. For the of modification GCE surface, 5 µL of each ethanolic solution of samples was used to drop-cast and dried at room temperature for 2 h.

2.3 Apparatus and characterizations

All electrochemical measurements, including cyclic voltammetry and amperometry, were performed on a CHI 1030A electrochemical analyzer (CH Instruments, Inc., USA). A three electrode system was used with saturated calomel electrode (SCE) as the reference electrode and Pt wire as the counter electrode. The morphologies of the products were examined using transmission electron microscopy (TEM, JEOL Model JEM-2100F) and scanning electron microscopy (SEM, JEOL Model JEOLSM-31010). X-ray diffraction (XRD) results were collected from a PANalytical X'Pert Pro diffractometer operating in the Bragg– Brentano focusing geometry with Cu-K_a radiation ($\lambda = 1.5418$ Å) from a generator operating at 40 kV and 40 mA. X-ray photoelectron spectroscopy (XPS) experiments were performed on an ESCA 3400 X-ray photoelectron spectrometers provided by SHIMADZU. Ultraviolet–visible spectra (UV-Vis) were measured on a Perkin Elmer Lambda 750S instrument.

2.4 Electrochemical measurement

All electrochemical measurements were performed in 10 mL of 0.1 M NaOH aqueous solution at room temperature. Electrochemical behaviors of CuNPs/PANI and CuNPs/PANI/graphene-modified electrode were investigated by cyclic voltammetry within the potential range of 0 and 0.8 V vs. SCE. Amperometry was performed at 0.5 V vs. SCE with stirring at 1070 rpm. After the stabilization of background current, aliquots of aqueous glucose solution were injected (10 μ L, 20 μ L, and 50 μ L of 1 mM, 10 mM, and 100 mM glucose solution in 0.1 M NaOH) every 50 s and the current due to glucose oxidation was recorded.

3 Results and Discussion



3.1 Morphology of PANI, CuNPs/PANI and CuNPs/PANI/graphene

Figure 1 (a-d) SEM images of (a) PANI, (b) CuNPs/PANI, (c) CuNPs/PANI/1% graphene and (d) CuNPs/PANI/2% graphene; (e) TEM image of CuNPs in CuNPs/PANI/1% graphene; (f) illustration of CuNPs/PANI/graphene composite.

The morphologies of as-synthesized PANI, CuNPs/PANI, and CuNPs/PANI/graphene were studied with SEM and TEM, and the results are shown in **Figure 1**. PANI adopts nanofiber shape with a diameter ranging from 100 to 200 nm, which is in good agreement with the literature reported results.[29] The fibers are intertwined with each other due to DMF treatment. Upon *in-situ* reduction of Cu²⁺ ion, the CuNPs were formed and embedded in the PANI nanofibers, without causing significant morphology changes (**Figure 1b**). As shown in **Figure 1e**, the monodispersed CuNPs show diameter of 2-4 nm, which is considerably smaller than those previously reported.[16,30]

With the addition of graphene (Figure 1c and Figure 1d), CuNPs/PANI was found to adhere to the surface of graphene, as illustrated in Figure 1f. This behavior is attributed to the π - π interaction between graphene surface and the conjugate structure of PANI.[31,32] When the proportion of graphene was increased from 1 % to 2 %, more uncovered graphene was exposed to the surface.

3.2 Interaction between CuNPs and PANI

The interaction between CuNPs and PANI was studied with several characterization methods, including XPS, UV-Vis, and XRD. The interaction of PANI with metal NPs had been widely explored, and there are numerous reports on the case of Pt/PANI, Pd/PANI, Ag/PANI, and Cu/PANI.[16,33-35] The XPS spectra (N_{1s} region) of PANI and CuNPs/PANI are shown in **Figure 2a**. The binding energy of C_{1s} was set at 284.5 eV as reference. Three nitrogen-containing groups within PANI were found: imine (-N= at 398.4 eV), amine (-NH- at 399.6 eV), and a small amount of positively charged nitrogen (-NH+- at 400.1 eV).[36] With CuNPs embedded, both peaks of imine (398.3 eV) and positively charged nitrogen (400.6 eV) have been shifted compared to those of PANI, suggesting interaction between Cu and N atoms. Such electronic interaction is most significant on the positively charged nitrogen atoms, which is in good agreement with previous studies.[33] Moreover, the proportion of imine (24.4 % on PANI and 18.6 % on CuNPs/PANI) and charged nitrogen groups (18.5 % on PANI and 8.4 % on CuNPs/PANI) decreased, whereas that of amine groups (57.1 % on PANI and 73.0 % on CuNPs/PANI) increased upon the introduction of CuNPs, indicating that the PANI backbone was reduced by CuNPs (taking electrons from CuNPs).[16,34] However, it should be noted that XPS is sensitive for surface only, and the majority of N atoms on PANI backbone are not in direct contact with CuNPs.



Figure 2 (a) XPS spectra of N_{1s} region of PANI and CuNPs/PANI; (b) UV-Vis spectra of PANI and CuNPs/PANI, insert is the schematic energy level diagram of PANI; (c) XRD pattern of PANI and CuNPs/PANI.

Electron exchange between CuNPs and PANI was also supported by their UV-Vis spectra, as shown in **Figure 2b**. The spectrum of PANI shows two peaks at 334 and 653 nm, which are assigned to the π_b - π_q electron transfer and π - π^* electron transfer, respectively.[37,38] When CuNPs were embedded in PANI, both peaks showed red-shift features, indicating that CuNPs have lifted the π_b energy level. Such energy level change is due to the electron transfer from CuNPs to PANI that would lead to the changes in peak intensity.[39] The effect of CuNPs on the structure of PANI was investigated by XRD (**Figure 2c**). The XRD pattern of PANI shows a broad peak at 20°, an indicative of ordered structure, and can be assigned to (110) crystallographic planes.[27] For CuNPs/PANI samples, the broad peak was positioned at 25°, which is assigned to (200) crystallographic planes of PANI. It clearly shows that CuNPs can alter the ordered structure of PANI. The pattern from CuNPs/PANI samples also shows a broad peak at 43° which is in agreement with the Cu (111) peak position. It should be noted that the diameter of CuNPs is too small (2-4 nm) to exhibit intensive signals from XRD.

3.3 Electrochemical measurements of CuNPs/PANI and Cu/PANI/graphene

Prior to fabricating the modified electrode for glucose sensing, the electrochemical properties of the composites were investigated. **Figure 3a** shows the cyclic voltammograms of PANI, CuNPs/PANI, and CuNPs/PANI/graphene composites measured in 0.1 M NaOH aqueous solution. PANI showed nearly no signal apart from the charging current since it is not in its acid-doped form.[40] With the CuNPs embedded, the electrochemical oxidative current becomes larger, due to the oxidation of Cu^{2+} to Cu^{3+} at around 0.58 V and the conductivity has been increased because of metal doping.[16,30,41-44] The peak current was further increased to ~12 and 14 µA by introducing 1 % and 2 % graphene to CuNPs/PANI, respectively, which suggests potentially high sensitivity when employed as a sensor.



Figure 3 Cyclic voltammograms of (a) PANI, CuNPs/PANI, and CuNPs/PANI/graphene in 0.1 M NaOH aqueous solution; (b) Cu/PANI/1% graphene in 0.1 M NaOH aqueous solution containing various concentrations of glucose. Scan rate is 50 mV s⁻¹ and reference electrode is SCE.

The electrooxidation of glucose at the surface of the CuNPs/PANI/graphene-modified GCE in an alkaline solution was investigated by cyclic voltammetry. **Figure 3b** displays the cyclic voltammograms of

CuNPs/PANI/1 % graphene in 0.1 M NaOH aqueous solution in the absence and presence of 5 mM, 10 mM, 25 mM, and 50 mM glucose. The electrooxidation of glucose involves the following steps[30,45]:

$Cu + 2OH^- \rightarrow CuO + H_2O + 2e^-$	(Reaction 1)
$CuO + OH^- \rightarrow CuOOH + e^-$	(Reaction 2)
$Cu^{3+} + Glucose \rightarrow Gluconic acid + Cu^{2+}$	(Reaction 3)

As the Cu⁰ is being oxidized to Cu²⁺ at 0.30 V (Reaction 1) and further to Cu³⁺ at 0.52 V (Reaction 2), the surface of CuNPs becomes more active for taking electrons from glucose, oxidizing it to gluconic acid (Reaction 3). The Cu²⁺ produced during glucose oxidation would be oxidized back to Cu³⁺ (Reaction 2) regenerating the active sites on NPs. As shown in **Figure 3b**, no significant signal was observed in the absence of glucose. Once glucose was added, a peak appeared around at 0.5 V, which was assigned to glucose electrooxidation. This peak current increased with glucose concentration.: an increase of peak current from 51 to 174 μ A was observed as the glucose concentration was changed from 5 to 50 mM. It is noted that the current increment when the glucose concentration from 0 to 25 mM. The peak position has also slightly shifted towards the anodic direction. This could be due to the limited total number of active sites on CuNPs. At a relatively lower glucose concentration, there are enough active sites on CuNPs that can readily oxidize glucose molecules have to overcome molecular repulsion and compete for active sites, thus resulting in smaller increment of peak current, as well as anodic peak shift and slower response time.[16]

3.4 CuNPs/PANI and Cu/PANI/graphene as glucose sensor



Figure 4 (a) Amperometric response of GCE, PANI, CuNPs/PANI, and CuNPs/PANI/graphene. Inset is the zoom of low concentration region as shown with the box. Insert values are the concentration change; (b) Calibration curve for glucose detection using CuNPs/PANI/1% graphene. Inset is the low concentration range from 1.0 µM to 0.96 mM.

The modified electrodes were further used to study their current responses for the successive injection of glucose to 0.1 M NaOH aqueous solution at an applied potential of 0.5 V. Stirring speed was fixed at 1070 rpm to achieve stable background current. The amperometric response of all samples including bare GCE are shown in Figure 4a. Both bare GCE and PANI-modified GCE showed nearly no responds to glucose addition. For CuNPs/PANI- and CuNPs/PANI/graphene-modified electrodes, the current increased with the concentration of injected glucose. It is noticeable that both CuNPs/PANI and CuNPs/PANI/graphene achieve 95% of the steady-state current within 3 s after the injection of glucose, suggesting their good electrocatalytic performances with fast mass transport and electron transfer properties. Within the low concentration range (1 to 54 μ M as shown in inset of Figure 4a), the response times of CuNPs/PANI and CuNPs/PANI/0.5% graphene were 2 s, while the composite of higher graphene content displayed slightly longer response time of 3 s. This is due to the slower mass transport process of glucose from solution to the CuNPs/PANI within graphene layers as shown in Figure 1d. Figure 4a indicates that CuNPs/PANI has large response currents toward glucose, and the currents get even larger with the graphene incorporated. Moreover, the response current of CuNPs/PANI/graphene remained stable at relatively high glucose concentrations, (for example, 3.66 mM from 1550 to 1660 s) compared to that of CuNPs/PANI which was rising slowly. This can be attributed to the fast electron transfer between CuNPs/PANI and

graphene. Among the three CuNPs/PANI/graphene composites of different graphene contents, the highest response current was achieved with 1 % graphene. A higher response current was obtained when the graphene content was increased from 0.5 to 1 % as a result of faster electron transfer rate facilitated by more graphene. With 2 % graphene in the composite, however, more graphene was exposed to the surface (as shown by TEM) resulting in a reduction of the number of active sites of CuNP available for glucose detection, thus the response current.

Electrodes	Detection limit (µM)	Applied potential (V vs SCE)*	Response time (s)	Linear range (mM)	Ref.
CuNPs/PANI/1% graphene	0.27	0.5	3	0.001-3.7	this work
CuO nanorods	4	0.6		0.004-8.0	[46]
CuNPs/MWCNTs	0.5	0.35		0.01-0.3	[47]
Cu@Chit-CNT	0.05	0.5		0.005-1	[30]
Cu/Graphene	0.5	0.5	<2	0.05-4.5	[17]
CuNPs/Meso-PANI	2.83	0.6	<5	0.01-24	[16]
Cu/PANI	9.36	0.6	10	0.02-10	[16]

Table 1 Comparison of analytical performances of non-enzymatic glucose sensors based on metal(oxide) NPs.

*Potential applied on electrode can alter the response current, thus sensitivity.

The corresponding current-concentration calibration curve of CuNPs/PANI/1% graphene-modified electrode was plotted in **Figure 4b**. The response of the CuNPs/PANI/1% graphene-modified electrode can be represented approximately by two linear ranges[48]: (1) a low concentration range from 1.0 μ M to 0.96 mM and (2) a high concentration range from 0.96 to 3.7 mM. The linear regression equations are shown with correlation coefficient R² = 0.9983 and 0.9939, respectively, suggesting an excellent current-concentration response. At an applied potential of 0.5 V, the sensitivity of the CuNPs/PANI/1% graphene-electrode determined by the slope of the linear fitting is 149.6 μ A cm⁻² M⁻¹, which is higher than that of Cu/PANI (51.4 μ A cm⁻² M⁻¹) and most of other reported systems. This remarkable high sensitivity of CuNPs/PANI/1% graphene composite is the combined effect of the high conductivity of graphene and the large surface area of CuNPs. The calculated detection limit of CuNPs/PANI/1% graphene is 0.27 μ M (S/N=3). A comparison of the CuNPs/PANI/1% graphene with some of the reported non-enzymatic glucose sensors based on metal NPs are summarized in **Table 1**.

It is well known that dopamine, ascorbic acid, lactose, sucrose, and uric acid are present in biological samples and they can interfere the detection of glucose. In order to test the potential of CuNPs/PANI/graphene composite in real life glucose detection, interference experiments were carried out. **Figure 5a** shows the results of current response measurement with the interferences using a CuNPs/PANI/1%

graphene-modified GCE, where 100 µM glucose, 10 µM dopamine, 10 µM ascorbic acid, 10 µM uric acid, 10 µM lactose, and 10 µM sucrose were injected sequentially. Compared to the oxidation current of glucose, those from all the interferents were minimal, demonstrating superior selectivity of CuNPs/PANI/1% graphene composite toward glucose oxidation and good resistance to surface poisoning. Moreover, we used mice serum as a practical sample to evaluate the performance of CuNPs/PANI/1% graphene composite. By using High Performance Liquid Chromatography (HPLC), the glucose concentration in the serum was 7.7 mM, which was comparable to the value of 8.4 mM determined by our glucose sensor. The small difference could be attributed to the impurities, such as ascorbic acid.



Figure 5 (a) Interference experiment of CuNPs/PANI/1% graphene composite in 0.1 M NaOH solution with glucose concentration of 100 μ M and interference (dopamine, ascorbic acid, uric acid, lactose, and sucrose) concentration of 10 μ M; (b) Amperometric response of CuNPs/PANI/1% graphene composite with different storage time under room temperature and open-air conditions.

The long-term stability of as-prepared CuNPs/PANI/1% graphene composite was also studied. A freshlyprepared sensor was first tested for its sensitivity and stored under open-air conditions at room temperature up to one month. **Figure 5b** compares the amperimetric responses from a freshly-prepared, one week-old, and one month-old sensor, which shows the sensitivity of 149.6 μ A cm⁻² M⁻¹, 145.2 μ A cm⁻² M⁻¹, and 152.7 μ A cm⁻² M⁻¹, respectively. The sensitivity towards glucose detection has not significantly changed even after one month, suggesting that the composite sensor has a highly stable structure.

4 Conclusion

We have introduced CuNPs into PANI nanofibers by *in-situ* reduction method under mild conditions, and CuNPs/PANI/graphene composite was successfully prepared. The morphology of both CuNPs/PANI and CuNPs/PANI/graphene studied by SEM and TEM showed monodispersed CuNPs with a diameter of 2-4 nm. XPS and UV-Vis spectra showed that CuNPs have electronic interaction with PANI *via* the N atoms and donate electrons to the PANI backbone. The CuNPs/PANI/graphene composite was demonstrated as an excellent glucose sensor with high sensitivity and short response time, which can be attributed to the high activity of CuNPs and good conductivity of graphene. Further development of the CuNPs/PANI/graphene composite into a practical electrocatalyst for glucose oxidation is ongoing in our laboratory.

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