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The influence of ionic liquids on the fabrication of nonenzymatic glucose electrochemical sensor

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ABSTRACT

Gold nanoparticles (GNPs) embedded in a Bucky gel consisting of carbon nanotubes (CNTs) and ionic liquid (IL) show an excellent electrocatalytic activity to glucose oxidation owing to some synergistic effects among GNPs, CNTs and IL. Each component in such a composite has its specific function while there are complicate interactions among them. Based on this strategy, the use of composite as the modified coating allows the fabrication of a novel nonenzymatic glucose electrochemical sensor, which shows a substantial enhancement in detection sensitivity. This paper centers on the influence of several ILs with various anions and cations as well as alkyl branch lengths on the function of sensor. Based on our results, the performance of the sensor is strongly influenced by ILs. A few conclusions can be drawn. Firstly, an imidazolium cation facilitates both the stability of sensor and the efficiencies of GNPs and CNTs, while the alkyl branch lengths have few effects on the performance of sensor. Secondly, a hydrophilic anion is beneficial to the formation of environment where the direct oxidation of glucose takes place. Thirdly, other anions such as BF_4^- and PF_6^- do not matter for imidazolium-based IL. Fourthly, non-imidazolium-based IL militates against the dispersion of CNTs and GNPs in Bucky gel, reducing the detection sensitivity to glucose. Of the ILs studied, the best performance for glucose determination is obtained with an IL mainly benefitted by the combination of imidazole and sulfonate.

1. Introduction

On one hand, of all the nanomaterials, GNPs and CNTs may be of the greatest interests for nonenzymatic glucose sensing because of their extraordinary physicochemical characteristics in the past decade [1–6]. On the other hand, the interest in ILs has grown dramatically as their unique properties such as high thermal stability, wide potential windows, high conductivity and negligible vapor pressure, make them especially promising toward the sensor application [7–11]. A so-called Bucky gel has showed improvements in direct electrochemistry of glucose [12]. Not like ordinary organogels or hydrogels, this gel discovered by Fukushima in 2003 [13] is a kind of mixture of CNTs and IL. Our previous work indicates that the dispersion of GNPs in a Bucky gel highly increase the rate of electron transfer between glucose and electrode [14]. Briefly, the relationship among GNPs, CNTs and IL is as follows: GNPs are regarded as cores of composite, CNTs as support for GNPs, IL as bridges connecting GNPs/CNTs one another and Bucky gel as a platform for the whole composite. Basically, the most remarkable characteristic for IL is that it can be designed by choosing specific cations and anions to meet specific requirements, so the motivation for this study is derived primarily from the anticipation of the improvement of the sensor performance for sensitive and selective detection of glucose, by using different GNPs/CNTs/IL composites on glassy carbon electrode (GCE). The sensors were constructed by incorporating GNPs to different Bucky gel made of various ILs. The sensing mechanism was investigated in the presence and absence of glucose. In this paper, 11 ILs including 5 imidazolium-based, 2 tetrabutyl ammonium-based and 2 pyrrolidinium-based as well as 2 piperdinium-based, were tested for comparison purposes with obvious difference in the response of sensor to glucose. This work maybe paves the way for the fabrication of novel sensor with a versatile IL combined with various nanoparticles.

2. Experimental

D-Glucose and hydrogen tetrachloroaurate (III) trihydrate ($HAuCl_4 \cdot 3H_2O$, 99.9%) were purchased from Sigma–Aldrich. The multi-walled CNTs with mean diameter of about 30 nm were obtained from the Tsinghua University of China as gifts. They were produced by catalytic chemical vapor deposition (CCVD) method, and the details of synthesis were reported elsewhere [15,16]. The ILs were purchased from Lanzhou Institute of Chemical Physics of China. The purities of CNTs and IL are both more than 99%. Triply

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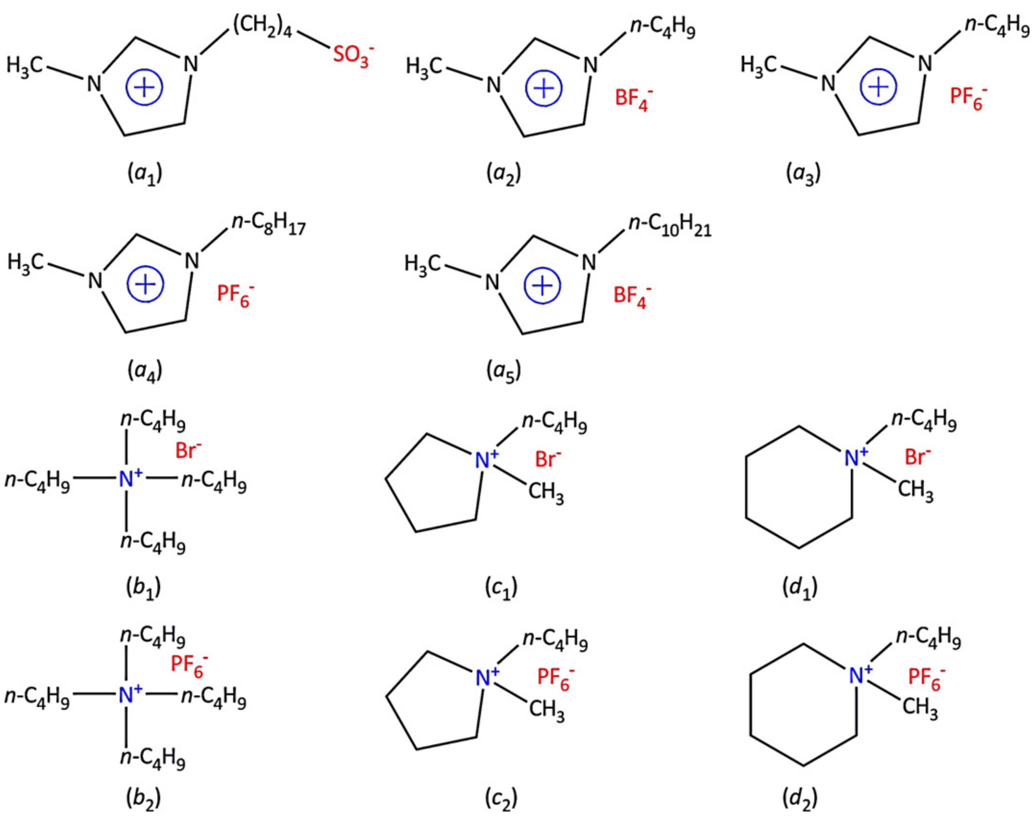


Fig. 1. The structures and abbreviations of 11 ILs in this work. (a_1) 1-(4-sulfonylbutyl)-3-methyl imidazolium, [C_4mim]SO_3; (a_2) 1-butyl-3-methyl-imidazolium tetrafluoroborate, [Bmim]BF_4; (a_3) 1-butyl-3-methyl-imidazolium hexafluorophosphate, [Bmim]PF_6; (a_4) 1-octyl-3-methyl-imidazolium hexafluorophosphate, [Omim]PF_6; (a_5) 1-decyl-3-methyl-imidazolium tetrafluoroborate, [C_{10}mim]BF_4; (b_1) tetrabutyl-ammonium bromide, [TBA]Br; (b_2) tetrabutyl-ammonium hexafluorophosphate, [TBA]PF_6; (c_1) *N*-butyl-*N*′-methyl-pyrrolidinium bromide, [bmPYR]Br; (c_2) *N*-butyl-*N*′-methyl-pyrrolidinium hexafluorophosphate, [bmPYR]PF_6; (d_1) *N*-butyl-*N*′-methyl-piperdinium bromide, [bmPIP]Br; (d_2) *N*-butyl-*N*′-methyl-piperdinium hexafluorophosphate, [bmPIP]PF_6.

distilled water was used throughout the experiments. Highly purity nitrogen was used for deaeration. All other chemicals were of analytical reagent grade and used without further purification.

The XPS were recorded on a AXIS Ultra X-ray photoelectron spectrometer, using monochromatized Al Kα X-ray as the excitation source and choosing C 1s (284.6 eV) as the reference (Kratos, UK). The TEM images were obtained using Tecnai F30 transmission electron microscope (Phlips-FEI, Holland). The three-electrode electrochemical cell contained a GCE modified with GNPs/CNTs/IL composite, a platinum wire as counter electrode and an Ag/AgCl (3 M KCl) reference. Cyclic voltammetry (CV) measurements were performed using a CHI 660C electrochemical workstation (Shanghai, China). All solutions were deoxygenated by highly purified nitrogen bubbling for 10 min, and nitrogen was passed over the top of the solution during the experiments. All measurements were conducted at room temperature (25 ± 2 °C).

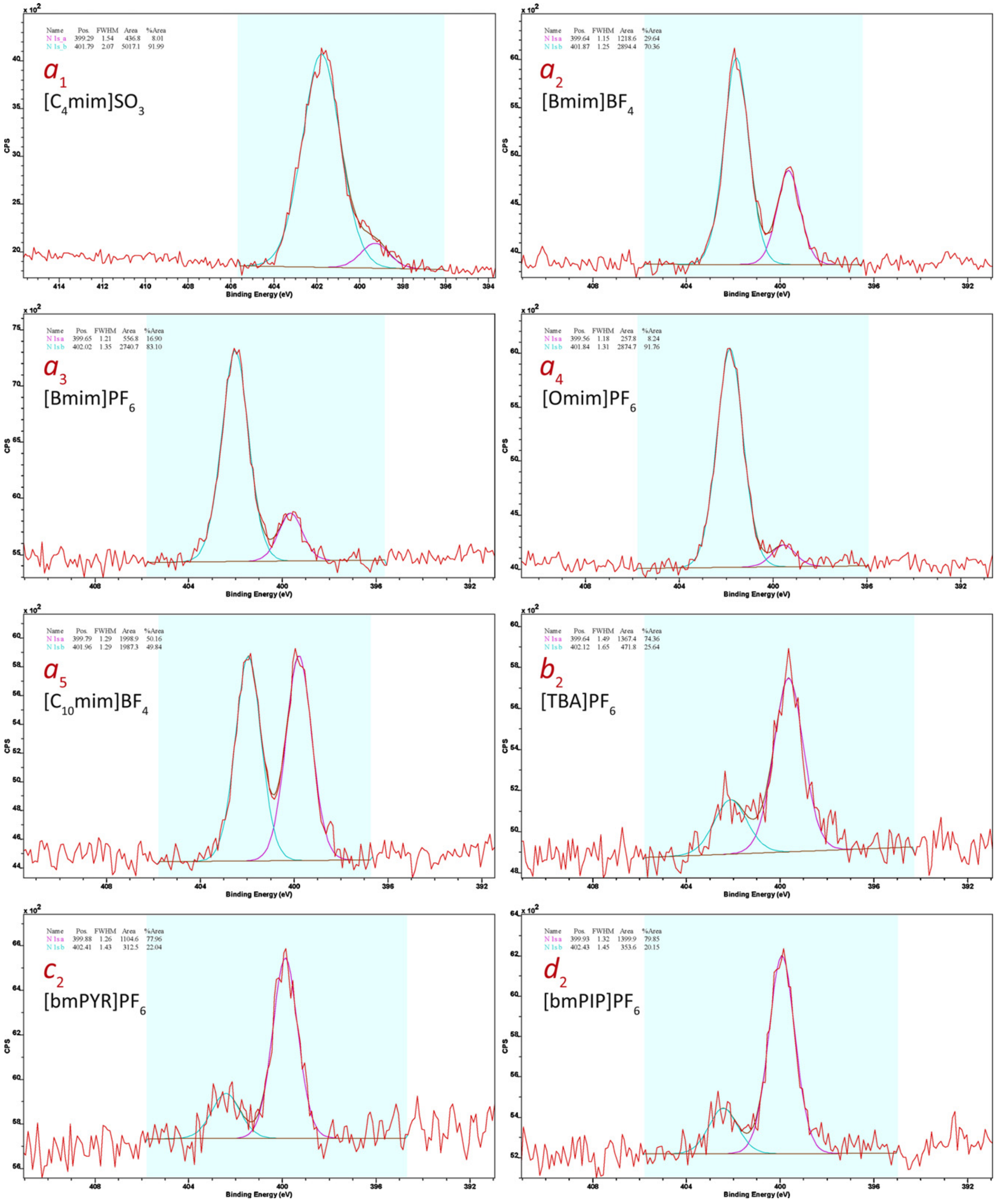
GNPs and carboxylated multi-walled CNTs were prepared according to Frens [17] and Tan [18], respectively. Fig. 1 shows the structures and abbreviations of 11 ILs in this work. They are roughly divided into 4 groups by cation, and the codes are denominated for the sake of convenience in discussion. As to composites, depending on the water-solubility of IL, there are two preparation methods as follows. The composites containing soluble ILs (a_1, b_1, c_1 and d_1) were prepared by adding 4.0 ml of GNPs solution and 10 mg of CNTs into 100 mg of IL with ultrasonic agitation for 10 min. For the composites containing insoluble ILs (a_{2-5}, b_2, c_2 and d_2), the preparation method is a bit different. First, 10 mg of CNTs with 4.0 ml of GNPs solution were sonicated for 10 min. Then, the mixture was centrifuged at 3000 rpm for 10 min and the supernate was removed. Last, the black precipitate mixed with 100 mg of IL was sonicated in 4 ml of dimethyl formamide (DMF) for 5 min. All the as-prepared composites were diluted 20 times by DMF so as to deposit a thin layer on the electrode surface.

Prior to use, a GCE with a diameter of 3 mm was polished with 0.05 μm alumina slurry, and then washed ultrasonically in distilled water and ethanol for a few minutes, respectively. After that, the sensor was fabricated by casting 2.0 μl of the composite solution on the well-polished GCE and being dried under an infrared lamp.

3. Results and discussion

3.1. Influences of anion and alkyl branch lengths

The anion in IL affects the stability of the sensor. For example, not like BF_4^- or PF_6^-, the use of bromide-based IL makes the sensor very unstable. We suppose that this might be related to the water-solubility of ILs. The composite containing soluble IL such as b_1, c_1 or d_1 has poor adhesion to GCE and thus results in an instable response of sensor. To our surprise, the composite containing soluble sulfonate-based IL a_1 shows a stable and good response. This should be the consequence of specific π–π conjugation interaction between CNTs and imidazole ring locating at the other end of IL a_1. This conjugation facilitates the N conversion from amine to imine [13], as can be observed in the XPS patterns (Fig. 2) where imine N and amine N fraction in total N of IL a_1 are about 8% and 92%, corresponding to the XPS binding energy located at 399 and 402 eV, respectively. Similar phenomena are evident in the composite containing IL a_3 or a_4. In the cases of ILs a_2 or a_5 containing BF_4^-, the



a_1 $[C_4mim]SO_3$

Name	Pos.	FWHM	Area	%Area
N 1s_a	399.29	1.54	436.8	8.01
N 1s_b	401.79	2.07	5017.1	91.99

a_2 $[Bmim]BF_4$

Name	Pos.	FWHM	Area	%Area
N 1sa	399.64	1.15	1218.6	29.64
N 1sb	401.87	1.25	2894.4	70.36

a_3 $[Bmim]PF_6$

Name	Pos.	FWHM	Area	%Area
N 1sa	399.65	1.21	556.8	16.90
N 1sb	402.02	1.35	2740.7	83.10

a_4 $[Omim]PF_6$

Name	Pos.	FWHM	Area	%Area
N 1sa	399.56	1.18	257.8	8.24
N 1sb	401.84	1.31	2874.7	91.76

a_5 $[C_{10}mim]BF_4$

Name	Pos.	FWHM	Area	%Area
N 1sa	399.79	1.29	1998.9	50.16
N 1sb	401.96	1.29	1987.3	49.84

b_2 $[TBA]PF_6$

Name	Pos.	FWHM	Area	%Area
N 1sa	399.64	1.49	1367.4	74.36
N 1sb	402.12	1.65	471.8	25.64

c_2 $[bmPYR]PF_6$

Name	Pos.	FWHM	Area	%Area
N 1sa	399.88	1.26	1104.6	77.96
N 1sb	402.41	1.43	312.5	22.04

d_2 $[bmPIP]PF_6$

Name	Pos.	FWHM	Area	%Area
N 1sa	399.93	1.32	1399.9	79.85
N 1sb	402.43	1.45	353.6	20.15

Fig. 2. N $1s_{a-b}$ XPS patterns of GNPs/CNTs/IL composite with different ILs.

above conjugation interaction may be weaken by electron-deficient boron. That is why we choose PF_6^- as anion in non-imidazolium-based IL for studying. Nevertheless, the N conversion from amine to imine in ILs b_2, c_2 and d_2 is very low.

Basically, only those composites GNPs/CNTs/IL being well immobilized on the electrode surface may the detection of glucose become true. Therefore, our study focused on the cases of ILs a_{1-5}, b_2, c_2 and d_2.

As known, GNPs play a critical role in the good electrocatalysis toward glucose because they can selectively enhance the faradic current of a sluggish reaction. It is understandable that the surrounding microenvironment of GNPs should also contribute to such

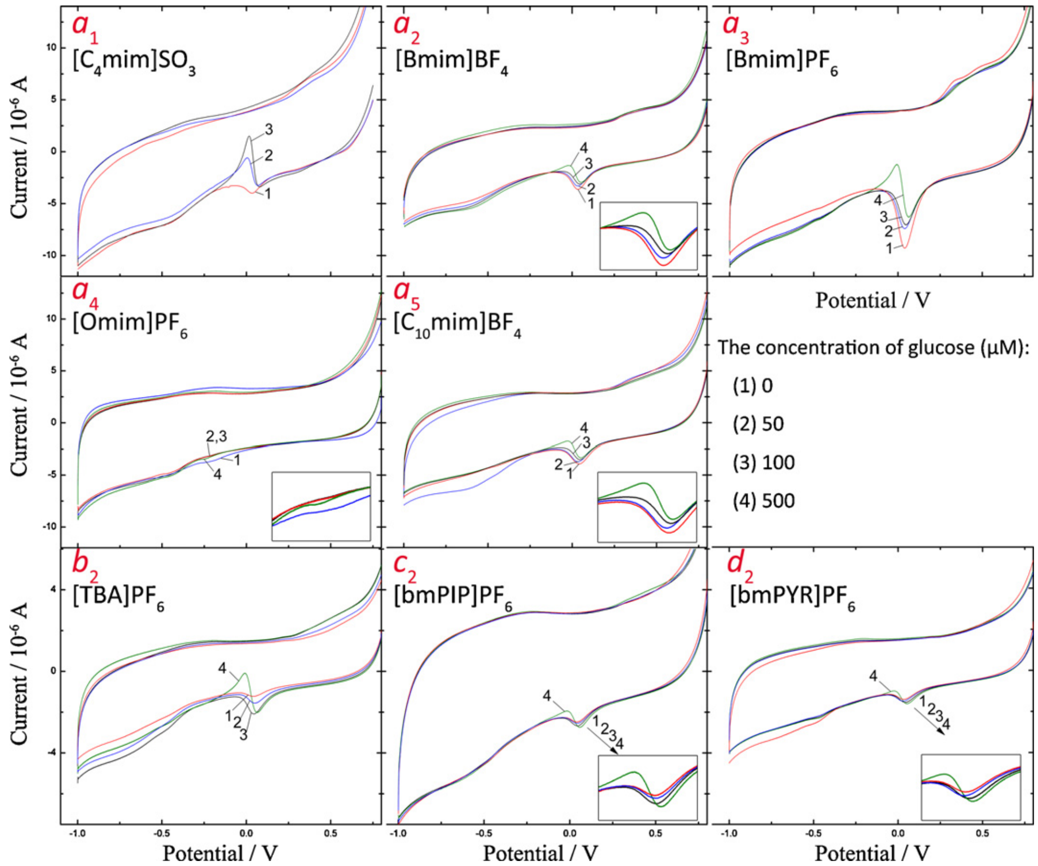


Fig. 3. CVs in the absence or the presence of glucose at GNPs/CNTs/IL GCE with different ILs. Scan rate: 100 mV/s. Supporting electrolyte: 0.1 M NaOH.

an electrocatalysis in a way. Based on our previous results, GNPs embedded in a Bucky gel lead to higher electrocatalytic activity because that may take advantage of high surface area and good electrocatalytic activity of both GNPs and CNTs [14]. In fact, the presence of IL that acts as bridges also strongly influences the activity of GNPs. More accurately, it has great impacts on the number of active GNPs. Fig. 3 shows the CVs of various IL-based sensors in 0.1 M NaOH solution in the absence or the presence of glucose. All curves 1 correspond to the case without glucose. Except IL a_4, namely [Omin]PF_6, a pronounced reduction peak appears at about 0.05 V, which is associated with the reduction of gold oxide. It is because a great deal of free and active GNPs are formed in an instant that the direct oxidation of glucose is dramatically facilitated to result in a sharp oxidation peak at about 0.00 V (curves 2–4) during the potential sweep in the cathodic direction. Though such an oxidation peak is partially overlapped with the reduction peak of gold oxide, it has no proven effect on the detection of glucose after correction because the reduction peak of gold oxide is stable and irrelevant to glucose. Actually, the detection sensitivity is obviously dominated by IL in composite if the amount of other component (GNPs and CNTs) is fixed. As shown in Fig. 3, even if similar imidazolium-based IL is applied, the response to glucose electro-oxidation differs in thousands ways. Comparing ILs a_2 and a_3, the only difference between them is the anion. IL a_3 with PF_6^- seems a bit better than BF_4^- in the aspect of peak shape. Meanwhile, comparing ILs a_2 and a_5 with the same BF_4^- but different alkyl branch lengths, the former is a bit better than the latter in the aspect of detection sensitivity while the sensitivities are 30 μM and 50 μM, respectively. A conclusion seems to be drawn that either the counterion PF_6^- or the shorter alkyl branch facilitates the improvement of sensor. However, when IL a_4 that meets the above conditions is used, there is still no response to glucose even upon addition of 500 μM glucose. Obviously, the result is entirely alien from what have been intended. It is easy to explain this phenomenon in a viewpoint of the production of free and active GNPs. Differing from other ILs, in the case of IL a_4, not only the gold oxide does not start to be reduced until at about −0.1 V, but also the production rate of free GNPs is very slow as being observed from low peak current. This potential is at least 0.3 V more negative than other ILs, which is too negative for glucose to be electro-oxidized.

3.2. *Influences of imidazolium-based IL*

Of the group *a* studied, the best performance for glucose determination is obtained with a GNPs/CNTs/[C_4mim]SO_3 sensor with a detection limit of 2.0 μM. The oxidation peak currents are linearly dependent on the glucose concentration ranging from 5.0 to 120 μM with the correlation coefficient of 0.998. In comparison with other ILs in group *a*, IL a_1 has more specific structure composed of imidazolium and sulfonate. On one hand, CNTs can orient one end of IL a_1 (imidazolium ions) on their π-electronic surfaces by way of a specific π–π conjugation interaction, and such a molecular ordering may trigger clustering of the surrounding imidazolium ions and thus interconnect neighboring CNTs [12]. The originally entangled CNTs are eventually getting untangled and GNPs attaching to CNTs are well dispersed in Bucky gel. On the other hand, the water-soluble sulfonate at the other end of IL a_1 provides favorable micro-environments where hydrophilic glucose molecule moves freely inside the gel. As a direct result of this special structure, the efficiency of GNPs electocatalyzing is greatly improved. As far as the case of IL a_3 is concerned, the redox peaks

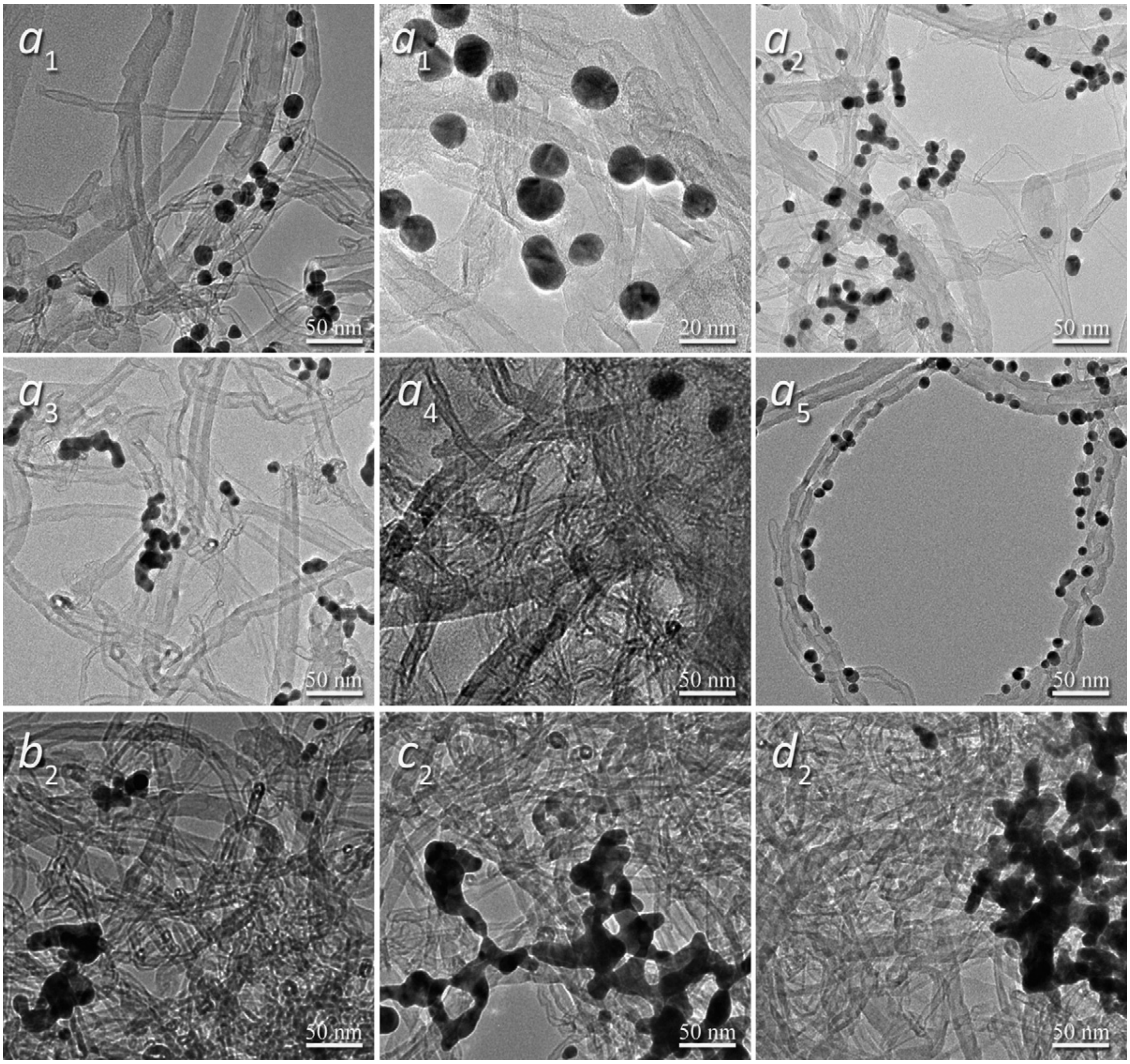


Fig. 4. TEM images of the GNPs/CNTs/IL composites with different ILs.

of GNPs at about 0.33 V and 0.05 respectively are more pronounced than IL a_1, which could enhance the oxidation of glucose. But it seems to have backfired, resulting from a lack of hydrophilic environment. In addition, it can be observed from Fig. 4 that most of GNPs have been hidden in the composite containing IL a_4, and this can be used to explain the low response to glucose from another angle.

Based on the above results, the performance of the sensor is strongly influenced by ILs, and it follows such an order as: $[C_4mim]SO_3 > [Bmim]PF_6 \approx [Bmim]BF_4 > [C_{10}mim]BF_4$. A few conclusions can be drawn for the use of IL in fabrication of glucose sensor. Firstly, an imidazolium cation facilitates both the stability of sensor and the efficiencies of GNPs and CNTs, while the alkyl branch lengths have few effects on the performance of sensor. Secondly, a hydrophilic anion is beneficial to the formation of environment where the direct oxidation of glucose takes place. Thirdly, other anions such as BF_4^- and PF_6^- do not matter for imidazolium-based IL.

3.3. Influences of non-imidazolium-based IL

If non-imidazolium-based IL is used such as tetrabutyl ammonium-based (b_2), pyrrolidinium-based (c_2) and piperdinium-based (d_2), that would be a different story. In the case of imidazolium-based ILs, the reduction peak of gold oxide has nothing to do with the presence or absence of glucose in this system. However, as shown in Fig. 3, with the increase of glucose concentration, the gold peak current is increased, especially for IL b_2. It means that the presence of glucose can bring about some positive influences on the activity of GNPs in composite in a sense. The reason can be discovered from their TEM images shown in Fig. 4. In these composites, large quantities of GNPs clump together and thus lead to the decrease of the number of active GNPs, and a weak peak current appears (curve 1). The movement of glucose inside Bucky gel can break this aggregation more or less. As for ILs c_2 and d_2, the reduction peak current of GNPs increases with glucose concentration so long as the concentration is less than a critical value, 300 μM. In other words, low concentration of glucose has more significant impacts on GNPs peak than on the oxidation itself. The oxidation peak current increases with glucose concentration ranging from 300 to 1250 μM. In the case of IL b_2, it can be observed from Fig. 4 that some GNPs aggregate and some attach the wall of CNTs in small groups. Because of this, the GNPs peak is unstable within the glucose concentration range tested, and thus this is not suitable for glucose sensing. Based on the above results, a conclusion can be drawn that non-imidazolium-based IL militates against the dispersion of CNTs and GNPs in Bucky gel, reducing the detection sensitivity to glucose.

4. Conclusions

IL plays a key role in the fabrication of non-enzymatic glucose sensor based on GNPs/CNTs/IL composite. Not all ILs are suitable for providing a proper environment where GNPs have been taking advantage of their characteristics. Based on our results, the imidazolium-based IL is necessary compared with other kind of IL. If combined a hydrophilic group such as sulfonate on IL, the electro-oxidation of glucose would be markedly promoted. Combining the environment-friendly and designable IL with all kinds of nanomaterials having excellent electrochemical characteristics may be a new idea for developing some novel and powerful biosensors.

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