B126

基于功能化石墨烯一步法制备固态电化学发光传感器

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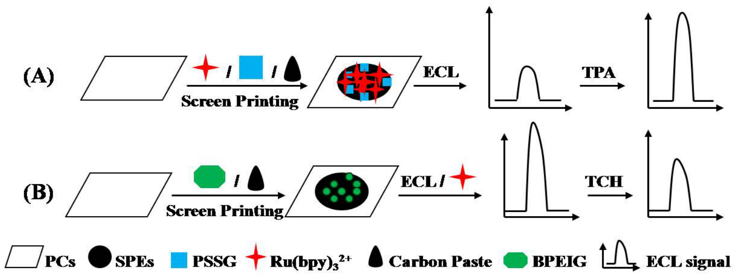
摘 要：鉴于丝网印刷电极易操作性，辅助于不同的功能化石墨烯材料，实现了在纸芯片上通过一步法制得固态的电化学发光传感器。将碳糊、功能化石墨烯及 Ru(bpy)$_3^{2+}$或者共反应物掺杂混合后直接印刷到纸芯片上，优化混合组分的原料组成及配比，便可制得稳定重现的纸芯片固态电化学发光传感器，以此简化传感器的制作步骤。

关键词：纸芯片；一步法；功能化石墨烯；电化学发光；

1 引言

纸芯片因其具有成本低，便携，制作简单等优点而被广泛使用，同时丝网印刷技术具有易于操作的特性，可以有效的将碳糊，或者其他可印刷材料印刷到纸芯片上来制得各种图案，比如电极，也使得纸芯片在电化学以及电化学发光的平台上具有应用潜力。

在这里，我们结合纸芯片以及丝网印刷技术通过便捷，快速的一步法实现了制得固态 Ru(bpy)$_3^{2+}$和共反应物电化学发光传感器，其原理图为图 1。



PCs:纸芯片；SPEs：丝网印刷电极；TCH:盐酸四环素；TPA:三丙胺

PSSG:聚苯乙烯磺酸钠功能化的石墨烯；BPEIG:聚乙烯亚胺功能化的石墨烯

图1：固态Ru(bpy)$_3^{2+}$（A）和共反应物(B)电化学发光传感器的制作原理及应用

2 实验部分

通过光刻技术制得亲水区域为 8mm 的纸芯片（用于集成三电极体系），然后将碳糊、功能化石墨烯及 Ru(bpy)$_3^{2+}$或者共反应物掺杂混合后通过丝网印刷到纸芯片上，作为工作电极（直径为 4mm）,对电极（碳糊，宽度为 1mm）以及参比电极（银，直径为 4mm）印刷到纸芯片另一面，便可制得固态的 Ru(bpy)$_3^{2+}$或者共反应物电化学发光传感器。

3 结果与讨论

用 TPA 验证固态的 Ru(bpy)$_3^{2+}$ 传感器的电化学发光反应，发现 Ru(bpy)$_3^{2+}$ 传感器能够实现 TPA 的检测，TPA 浓度从 10 nM to 200 μM 具有线性关系（如图 2），检测线达到了 5.0 nM，通过具有很好的重现性（如图 3）. 另外，对于制得的共反应物传感器我们采用了淬灭的机理进行了验证，同时实现了盐酸四环素的检测，检测限达到了 2.22 nM（如图 4）.

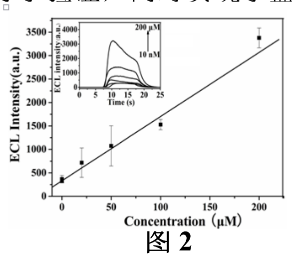


图 2

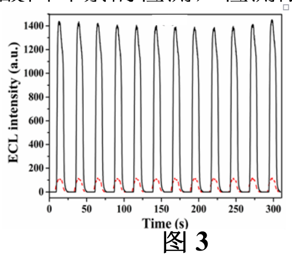


图 3

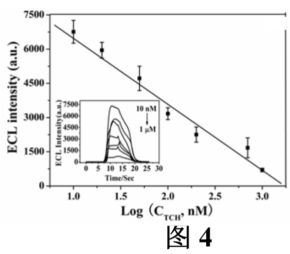


图 4

图2：电化学发光强度和不同浓度（10 nM 到200 μM）三丙胺的关系图；**图3**：存在(实线)和不存在（虚线）100 μM 三丙胺下电化学发光强度和时间的关系图；**图4**：电化学发光强度相对于不同浓度（10 nM 到 1 μM）盐酸四环素的关系图，插图为相应浓度的电化学发光行为

4 结论

通过一步法制得 $Ru(bpy)_3^{2+}$传感器和共反应物传感器从制作上简单易行，节约时间,并具有较好的重现性与灵敏性，用于实际检测也具有可行性。

致谢

感谢吉林省科技发展计划项目(No. 201201006)

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One-step Process for Fabricating Paper-based Solid-state Electrochemiluminescence Sensor Based on Functionalized Graphene

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Abstract

Taking advantage of simple manipulation of the screen printed electrodes, with the assistance of different functionalized graphene materials, a simple and time-saving one-step process was developed for fabricating solid-state electrochemiluminescence (ECL) sensors on paper-based chips (PCs). The solid-state $Ru(bpy)_3^{2+}$ or co-reactant ECL sensors could be facilely obtained by screen-printing the mixture of $Ru(bpy)_3^{2+}$/poly(sodium 4-styrenesulfonate) functionalized graphene nanosheets (PSSG)/carbon paste or branch poly(ethylenimine) (BPEI)-functionalized graphene nanosheets (BPEIG)/carbon paste through one-step process on the PCs, respectively. The ECL behavior of $Ru(bpy)_3^{2+}$ ECL sensor was investigated using tripropylamine (TPA) and detection limit (S/N=3) of 5.0 nM was obtained. It also exhibited excellent reproducibility and linear relationship with the concentration of TPA (R=0.991). In addition, the ECL behaviors of the coreactant sensor were measured for tetracycline hydrochloride (TCH) by inhibition method. A linear relationship between the ECL intensity versus logarithm of the concentration of TCH was gained in a range of 1×10^{-8} to 1×10^{-6} M and the detection limit was as low as 2.22 nM. Therefore the one-step process for fabricating paper-based ECL sensor was confirmed with the advantages of simplicity, high efficiency and potential applicability.

Keywords: Paper-based chips; One-step process; Functionalized graphene; Electrochemiluminescence sensor