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导电高聚物/溶液界面SERS 效应的诱导产生

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摘要 导电高聚物是发展迅速且应用广泛的重要电极材料, 由于大多数电化学反应发生在导电高聚物/金属和导电高聚物/溶液界面, 如果能获得其界面结构的信息, 将对导电高聚物表面所发生的电化学反应以及导电高聚物的聚合、降解的机理研究有极大的帮助, 但无论是常规电化学技术还是一般光谱电化学技术都难于得到有关界面结构的信息, 因为通常情况下较强的导电高聚物膜本体的信号(图1(a))将“淹没”来自界面的信号. 所幸的是表面增强拉曼散射(SERS)效应能极大地增强来自紧邻金属和溶液的聚合物单层的信号, 因而适合于导电高聚物/金属和导电高聚物/溶液的界面结构的特殊要求. 只要导电高聚物膜的厚度不致影响到来自于高聚物/金属界面的SERS信号, 就可以利用其研究高聚物/金属界面的结构, 见图1(b). 例如, 人们已现场研究了经SERS活化的金电极上吡咯和苯胺的电化学初聚过程^[1,2]. 但据我们所知, 由于难于在导电高聚物/溶液界面诱导出SERS效应, 目前还没有关于其界面结构SERS研究的正式报导. Gui和Devine^[3]通过在铁电极上沉积一层不连续的银岛膜的方法成功地获得了极薄的铁钝化膜(1~3 nm)的SERS谱图. 本文简要报道利用类似的方法, 尝试在诸如聚吡咯(PPY)和聚苯胺(PAN)等导电高聚物膜表面上电沉积一些银微粒, 从而诱导其靠近溶液侧的表面层产生SERS效应.

图2为纯PPY膜和沉积了银微岛的PPY膜的Raman谱图.通过比较可以发现它们几乎相同,但沉积了银微岛后的PPY膜的Raman谱图信号略变弱.即使改变沉积条件,例如沉积电位和电量以及膜厚,情况仍然如此.这说明未能诱导出PPY表面层的SERS谱图,沉积银微岛后谱图强度减弱则主要是由于入射光被银微岛削弱的缘故.然而PAN体系则大不相同,沉积了银微岛的PAN膜和纯PAN膜的Raman谱图虽也十分相似(见图3),但前者(图3(a))却要比后者(图3(b))强得多,这表明聚苯胺膜上沉积的银微岛使其表面层的信号得到了很大的增强,所以有理由认为图3(a)主要为PAN膜表面层的SERS信号. PAN膜表面层的SERS谱图与PAN膜体相的Raman谱图非常相似说明具有相同的分子结构和构象.但从以往有关PPY初聚的SERS研究中可知在基底电极上形成的最初几层聚合物膜的SERS谱图与所得聚合物膜体的谱图存在较明显区别^[1],这是由于导电高聚物的诱发聚合一般是首先以齐聚物在基底上聚集和沉积,在此基础上形成聚合物进而形成膜本体,因而聚合物表面层的结构与膜本体的相似而它们都不同于紧靠基底的最初形成的几层的结构,用同样的方法却不能在PPY膜表面诱导出SERS效应的原因尚不清楚,可能与诸如紧密的瘤结状或疏松的枝状的不同聚合物表面对银微岛的成核和成长的影响有关,这将可能使所得银微岛的不适合于SERS效应的诱导产生.这一结果表明导电高聚物/溶液界面SERS效应的诱导产生要比导电性较好的金属钝化膜/溶液界面的复杂和困难.还需要进一步开展更系统的研究工作以便得到明确的结论,并将SERS研究扩展到更多的非金属电极体系.

关键词 导电高聚物,表面增强拉曼散射效应,聚吡咯,聚苯胺

SERS Effect Induced from Conducting Polymer/Solution Interfaces^①

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In order to study the mechanisms of electropolymerization, electrochemical reactions and degradation of conducting polymer electrodes, it is of special importance to obtain the structural information of conducting polymer/metal and polymer/solution interfaces in which most electrochemical reactions take place. However because the interfacial signal is generally submerged by a stronger signal from the bulk film, it is very difficult to extract them using either conventional electrochemical or spectroelectrochemical techniques, see Fig. 1 (a). Fortunately, the surface enhanced Raman spectroscopy (SERS) can meet such special requirement for the study of conducting polymer/metal and polymer/solution interfaces since it can significantly enhance the signal of the first monolayer of polymer adjacent to the metal or to the solution. It makes possible to examine the interfacial region between metal and the conducting polymer films as long as the later are not so thick that block the SERS signal from the interfaces, see Fig. 1 (b). For example, Au electrodes treated by the SERS activation have been employed in our laboratory to in-situ study at a very early stage of electropolymerization

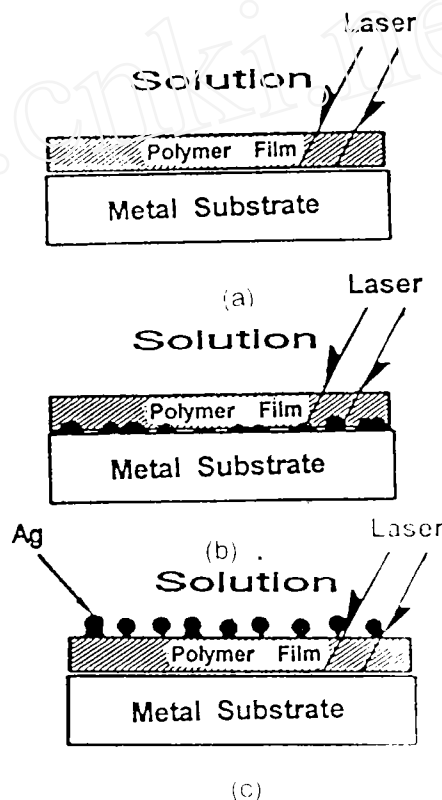


Fig. 1 Schemes of (a) normal Raman studies on thin polymer films and SERS on (b) polymer/metal interface and (c) polymer/solution interface.

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of pyrrole^[1] and aniline^[2]. Gui and Devine have successfully obtained SERS signals from thin passive films (1~3 nm or less) of iron by the deposition of a discontinuous layer of Ag on iron electrodes^[3]. But to our knowledge, there is no report about the SERS study of conducting polymer/solution interface, indicating that it is much more difficult to induce the SERS effect. In this communication, an attempt to find a way to induce the SERS effect on the top layers of polymer films adjacent to the solution, Fig. 1(c), is briefly described.

A thin PPY film (about 0.1 μm) was potentiostatically polymerized on an Au electrode in an aqueous solution of 0.02 mol/L pyrrole+0.1 mol/L HNO_3 at +0.7 V vs. SCE. A PAN film (0.1~0.2 μm) was formed on an Au electrode by sweeping the potential between -0.1 V and +0.9 V vs. SCE in aqueous solutions of 0.2 mol/L aniline+0.5 mol/L HClO_4 . After the polymerization, a deposition procedure of Ag similar to that of Gui and Devine was carried out, some microislands of Ag were deposited on the conducting polymer films, such as polyaniline (PAN) and polypyrrole (PPY), by holding the potential at -0.1 V in 1.0 mmol/L AgNO_3 + 1.0 mmol/L HNO_3 . Raman measurement of PPY and PAN were carried out respectively by Ramanor U1000 (Jobin-Yvon) using 514.5 nm radiation and by Ramascop 2000 (Renishaw) using 632.8 nm^[4] radiation.

Comparing the spectrum of bare PPY film with that of the PPY covered by microislands of Ag, one can see from Fig. 2 that the two Raman spectra were almost identical except that the signal intensity became slightly weaker after the deposition of microislands of Ag. The result indicates that the SERS effect was not induced on the top layers of PPY. The weakening of the signal is mainly due to the discontinuous Ag layer blocked partially the incident laser beam. This was true even when many different deposition conditions were employed, such as varying the deposition potential and charge and varying the film thickness of PPY as well.

Fig. 3(a) was a Raman spectrum of PAN film covered by microislands of Ag in 0.5 mol/L HClO_4 . Six strong bands were appeared at 1 174 cm^{-1} , 1 236 cm^{-1} , 1 338 cm^{-1} , 1 500 cm^{-1} , 1 590 cm^{-1} and 1 622 cm^{-1} respectively, which could be assigned to the in-plane bending vibration of CH groups, the mixed mode of the stretching vibration of CC and CN groups, the stretching vibration of -C-N- groups, the stretching vibration of C=N groups, the stretching vibration of quinoid rings and the stretching vibration of benzenoid ring^[5]. By comparing this spectrum with a spectrum of the bare PAN film, as shown in Fig. 3(b), one can find that these two spectra were quite similar but the intensity of the former (Fig. 3(a)) was much higher than that of the later. It reveals that the Raman signal was enhanced significantly by the microislands of Ag deposited on the surface, which is in contrast to the PPY system shown in Fig. 2. It is therefore reasonable to consider that the spectrum of Fig. 3(a) is mainly contributed by the SERS signal from the top layers of PAN film. The slight difference between the SERS and Raman spectra in Fig. 3 is that the ratio of the stretching vibration of quinoid rings to that of benzenoid rings. In the former the stretching vibration intensity is higher than that in the later. This indicates that the amount of quinoid rings in the repeat units, which contain four rings are differentiated by the quinoid and benzenoid rings^[6] in the top layers of PAN, is greater

compared to the amount of quinoid rings in the repeat units in the bulk. The very good similarity between the SERS and Raman spectra in Fig. 3 indicates that molecular structure and the conformation of the top layers and the bulk of the PAN film are essentially the same. However, in our previous SERS study of the initial stage of electropolymerization of PPY films^[1], it was found that the SERS spectrum of the first several layers formed at the substrate were considerably more different from the Raman spectrum of the bulk film. This is because the electropolymerization was initiated by the formation of the oligomers that were aggregated and precipitated at the substrate^[7]. After that, further polymerization occurred at the polymers to form the bulk film. Consequently, the structure of the top layer is similar to that of the bulk, but it is different from that of the first layer adjacent to the substrate. The reason for the negative result of the PPY system is not clear by now. It might relate to the nucleation and formation of the Ag microislands at the various polymer surfaces such as compact nodules and branching dendrites, this may result in the unsuitability of the morphology of microislands of Ag to inducing of SERS effect. Nevertheless, our results show the complexity and difficulties that arise to inducing SERS from conducting polymer film rather than from that of smooth passive metal film. More systematic work is required to make a definite conclusion and to extend the SERS study to more electrode systems.

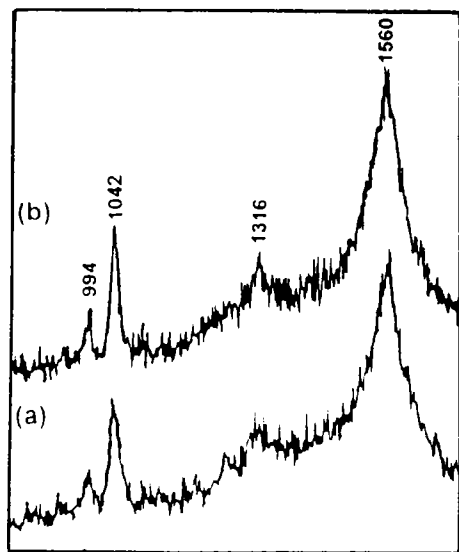


Fig. 2 Raman spectra of polypyrrole in 0.5 mol/L NaF. (a) Covered by microislands of Ag; (b) Bare PPY film. Excitation line: 514.5 nm; applied potential: -0.6 V vs. SCE

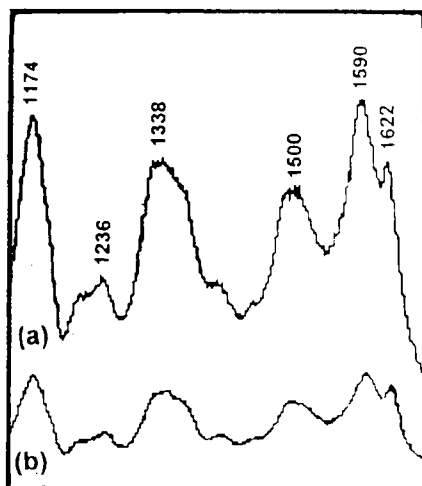


Fig. 3 Raman spectra of polyaniline in 0.5 mol/L HClO_4 . (a) Covered by microislands of Ag; (b) Bare PPY film. Excitation line: 632.8 nm; applied potential: 0.3 V vs. SCE

Key words Conducting polymer, Surface enhanced Raman effect, Polypyrrole, Polyaniline

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