Stabilization of 4-phenylurazole by electrografting on a nano-fibrillated mesoporous carbon modified electrode. Reactivity of anchored triazolinedione groups against Michael-type addition at electrode/electrolyte interface

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Abstrtact:

Fabricartion of a redox-active electrode by modification of a glassy carbon electrode (GCE) with a unique ionic liquid derived fibrillated mesoporous carbon (IFMC) following the electrografting of 4-phenylurazole *via* electrochemical reduction of 4-(4-nitrophenyl)urazole in the presence of sodium nitrite has been described. The resulted electrode shows the prominent electrochemical performance. The efficieny of the electrode has been evaluated over the entire range of pHs. The oxidized form of ungrafted 4-phenyluazole, 4-phenyl-1,2,4-triazoline-3,5-dione, is highly unstable due to fast ring cleavage. In contrast to oxidation of the ungrafted 4-phenylurazole, the electrografted 4-phenyl-1,2,4-triazoline-3,5-dione exhibits a high stability in a wide range of pHs. The anchored 4-phenyl-1,2,4-triazoline-3,5-dione groups are reactive against Michael-type addition. Further modification of the electrode can be achieved by the Michael-type addition reaction of the triazolinedione groups with nucleophiles at the solid/liquid interface.

Keywords:

Ionic liquid derived fibrillated mesoporous carbon, 4-Phenylurazole**,** Electrografting, Diazonium ion, Michael-type addition reaction, Oxidative ring cleavage

1. Introduction:

Ordered mesoporous carbons (OMC) have been widespread used in electrochemistry in recent years. This great deal of attention originates from the unique features of high accessible surface development, tunable ordered pore channels, good conductivity, facilitated diffusion and chemical and thermal stability [1-3]. These prominent capabilities convert them to potential candidates for electrode modification [4-6]. Karimi et al. previously presented a protocol to fabricate a novel ionic liquid derived fibrillated mesoporous carbon (IFMC) with superior electrochemical operation using ionic liquid as the carbon source in the presence of ordered mesoporous silica SBA-15 as a structural guide [7-9]. An effective electrode can be fabricated by deposition a thin film of IFMC on a electrode surface. The resulted electrode with high electrochemical performance can be utilized to modify the electrode with redox-active organic materials. Redox-active compounds improve the surface performance for conveniently use in electroanalytical [10-11], electrocatalysis [12-13], capacitors [14-15] and sensing functions. Considerable amounts of reports in the literatures are devoted to fabricate of electroactive organic electrodes [16-19]. There are many routes to graft redox-active and other organic groups to the surface of electrodes. One of the convenient methods consists of covalent attachment of aryl radicals to electrode prepared from electroreduction of aryl diazonium salts. Intensive studies have underlined the efficiency electrochemical reduction of diazonium salts to graft organic groups on the electrode surface [20-28].

The current work studies electrografting of the redox-active urazole groups with electrochemical reduction of 4-(4-nitrophenyl)urazole in the presence of sodium nitrite to in situ generation of the corresponding diazonium salt on the glassy carbon electrode modified with IFMC. Since the diazonium salts suffer from instability, in situ generation of the diazonium salt starting from 4-(4-nitrophenyl)urazole led to immediate reducing of the unstable diazonium for grafting of 4-phenylurazole as a typical urazole. Urazoles and triazolinediones (TADs), the oxidized form of urazoles, are promising groups in a broad range of applications in various scientific fields. A recent published review in 2015 was addressed a detailed discussion of the use of triazolinediones at different synthetic routes [29]. TADs as electron-deficient groups are reactive in Michael addition, Diels-Alder, click chemistry and Ene reactions. In the recent three years, the number of published papers focused on conjugation reaction of TADs with peptides [30], amino acids [31-33] and proteins [34] has been increased. In addition, in recent years we developed investigation on the electrochemical behavior of these derivatives [35-37]. In this direction, following of our research works, we anticipate that stabilization of TAD at electrode surface will expand biological and chemical applications of urazole to the surface of electrodes. However, the results of the previous studies revealed that the oxidized form of urazoles are unstable in mild acidic, natural and basic aqueous solutions resulted from fast oxidative ring cleavage [37-38]. It is more critical for the case of 4-PU and derivatives with electron withdrawing groups so that these compounds undergo fast oxidative ring cleavage even in aqueous acidic solutions [37]. Interestingly, green electrografting of 4-PU to the IFMC with electron-donating properties of the electron rich carbon and nitrogen centers results high stability of oxidative form of 4-PU (4-PUox) in a broad range of pHs. In contrast to the high stability, 4-PUox at the electrode surface is reactive against Michael-type addition reactions. So post-immobilizing of a large range of molecules can be successfully occurred at the redox-activated surface by applying oxidative potential of 4-PU in the presence of various nucleophiles. Post-functionalization of the electrode would be applicable in sensor fabrication, separation fields and biological immobilizations. Feasibility of the post-immobilization of the electrode was stablished by introducing of glutathione as a peptide [39] and 4-clorosulfinic acid as a typical nucleophile.

2. Experimental

2.1. Apparatus and reagents

Synthesis of IFMC and urazole derivatives was performed according to our published procedures [7-9, 40]. Sodium nitrite, phosphate and acetate salts and other reagents and solvents were purchased from commercial companies at high possible purity. Cyclic voltammograms were recorded using PGSTAT 30 with the common three-electrode cell configuration involving of either GCE (1.8 diameter) or IFMC/GCE as working electrode and platinum wire and Ag/AgCl as counter and reference electrodes, respectively. A Metrohm-pH meter was used to make pH measurements. The solutions with pHs of 2-3 and 6-8 were prepared using phosphate buffer. The acetate buffer was used for pHs of 4-5. Argon gas was bubbled to exclude oxygen of solution form the system during electroreduction studies. The voltammograms of the Figures 3-4 and 6-9 were plotted according to current density (current/geometrical area).

2.2. Modification of electrode with IFMC

GCE was polished with 0.3 and 0.05 μm alumina powders, respectively, rinsed with distilled water and dried in air. 1 mg IFMC was dispersed in 1 ml DMF for 40 min. Thereafter, 2 μL aliquot of the dispersion was dispensed on the GCE and exposed to air at room temperature to obtain the IFMC/GCE.

3. Results and discussion

3.1. Electrochemical reduction of 4-(4-nitrophenyl)urazole in the presence of sodium nitrite at IFMC/GCE

Cyclic voltammetry was employed to probe the difference in the features of electroreduction behavior of 4-NPU at the surfaces of GCE (Figure 1A, curve a) and

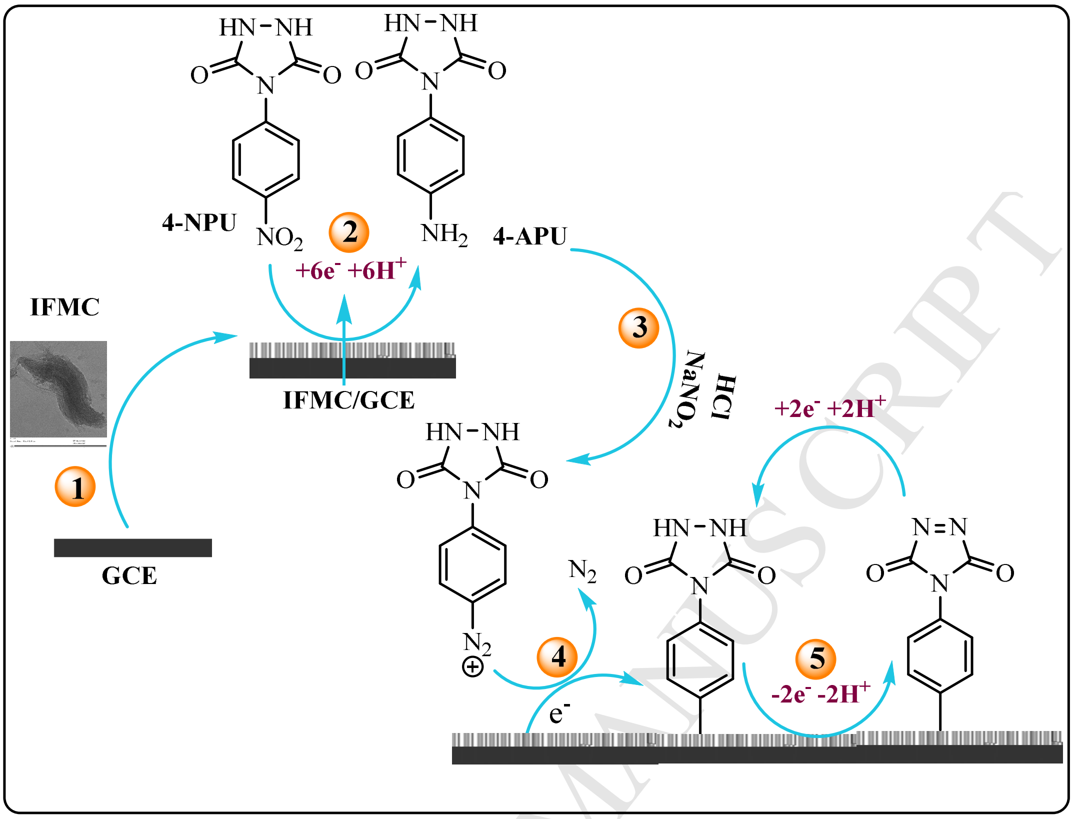
IFMC/GCE (Figure 1A, curve b). The voltammograms was plotted according to current density by dividing the current on the microscopic area. The cyclic voltammogram of 4-NPU in 0.5 M HCl at the surface of GCE exhibits three distinct peaks. The reductive C_0 peak (-0.33 V) appeared in the negative going scan arises from either electrochemical reduction of 4-NPU to 4-(4-hydroxylaminophenyl)urazole (4-HAPU) or 4-(4-aminophenyl)urazole (4-APU) during $6e^-/6H^+$ or $4e^-/4H^+$ process, respectively. A pair of redox peaks observed at +0.51 V in the reverse sweep and +0.35 V by recording the second cycle of voltammograms are connected to reversible $2e^-/2H^+$ transformation of either 4-HAPU to 4-(4-nitrosophenyl)urazole or 4-APU to 4-(4-aminophenyl)-3*H*-1,2,4-triazole-3,5(4*H*)-dione. In fact, conversion of the nitro to amine group may be incomplete in the time scale of the voltammogram. To investigate on the reduction mechanism, the electrochemical reduction of 4-NPU was performed with a long time scale technique in which the reduction of nitro to amine group is possible (experimental details in the Supporting Information). Adaptation of the potentials of the peaks in the short and long experimental time scales confirms the reduction of 4-NPU to 4-(4-aminophenyl)urazole. Curve b shows the cyclic voltammogram of 4-NPU on IFMC/GCE at the same condition of curve a. Three evident differences can be perceived: (i) even though the currents are normalized according to the microscopic surface area, the height of the peaks on IFMC/GCE is higher than those reported for GCE. This difference could be related to edge plane-like defective sites, high conductivity and ordered porous cavities of IFMC. The regular nano-fibrous carbon structure is clear in the TEM image (Figure 2); (ii) dramatically facilitation of the electron transfers is proved by shift of the reduction and oxidation peaks potentials to positive and negative directions, respectively; (iii) the reversible redox process (A_1/C_1) takes place with a small peak-to-peak separation rather than GCE with ΔEp = 160 mV at 100 mV/s. Figure 1B provides information concerning the voltammetric behavior of 1 mM 4-NPU in the absence (curve b) and presence (curve c) of 5 mM sodium nitrite in 0.5 M HCl. Clearly, the redox peaks currents (A_1/C_1) are largely decreased in the presence of sodium nitrite pointing out that 4-APU eliminates at the surface of electrode *via* chemical reaction of 4-APU with sodium nitrite (Scheme 1, step 3).

[Figure 1]

[Figure 2]

The general procedure for electrografting of 4-PU on the IFMC/GCE surface is according to Scheme 1. The modified electrode is immersed to a solution of 0.5 M HCl containing 1 mM 4-NPU and 5 mM sodium nitrite. The electrode undergoes 20 successive cycles of potential in the optimum range of 0.2 to -0.4 V vs. Ag/AgCl at 50 mV/s. Scanning the potential to the negative direction leads to electroreduction of 4-NPU to 4-APU followed by chemical reaction of 4-APU with HNO_2 to produce corresponding diazonium ion. Thereafter, reduction of the diazonium ion allows the covalent attachment of the produced aryl to the electrode surface. Figure 3 indicates the multi-cyclic voltammograms of 4-NPU obtained at IFMC/GCE in aqueous solution containing sodium nitrite (5 mM) and HCl (0.5 M). A remarkable decrease in the cathodic peak current are related to the blocking effect of the electrode.

[Figure 3]



Scheme 1: Modification of IFMC/GCE by electroreduction of 4-NPU in the presence of sodium nitrite in 0.5 M HCl.

3.2. Electrochemical properties of the electrografted 4-phenylurazole

Success in the electrografting process was explored by recording the cyclic voltammogram of modified 4-PU/IFMC/GCE. Figure 4A (curve a) shows the cyclic voltammogram of 4-PU/IFMC/GCE in aqueous phosphate buffer solution (pH=2, 0.2 M). The observed voltammogram indicates a quite distinct redox signal related to 4-PU/4-PUox during $2e^-/2H^+$ process (Scheme 1, step 5). To prove the connection of the faradaic response to electrografted 4-PU, the bare IFMC/GCE underwent 20 cycles of potentials to negative direction in a solution of 0.5 M HCl only containing 1mM 4-NPU. After that, the electrode was swept in the range of -0.2 to 0.8 V at the same condition of curve a (curve b). The featureless voltammogram observed in sodium nitrite-free HCl solution confirms the role of sodium nitrite in the electrografting and rejects simple adsorption of either 4-NPU or 4-APU on the surface of electrode. The grafting of 4-PU was further confirmed by recording multi cyclic voltammograms. Figure 4B exhibits first and 100st cycles of voltammograms. No considerable decrease in the redox peaks currents approves robust coupling of 4-PU on the IFMC surface. Figure 4C compares voltammetric responses of the ungrafted (curve a) and the grafted (curve b) 4-PU on IFMC. The voltammogram of 1 mM 4-PU involves the irreversible oxidation of 4-PU to 4-PUox due to electron transfer coupled with the fast irreversible ring cleavage [37]. Comparison of the curve a and b in part C reveals that the oxidation peak potential of attached 4-PU shifts to negative direction that indicates notable facilitating in the electron transfer of anchored 4-PU. The IFMC exerts a noticeable influence on the stability of 4-PUox in aqueous solutions. In contrast to ungrafted 4-PU, the electrochemical response of 4-PU/IFMC/GCE shows a couple of redox peaks with $I_{pC2}\backslash I_{pA2}$ nearly unity. The electron-donating properties of the electron rich carbon and nitrogen centers of the unique IFMC may be the main reason for the stability. The anchored 4-PUox is stable enough to resist against ring cleavage compared to that of ungrafted 4-PUox.

[Figure 4]

3.3. The effect of pH

Figure 5 shows the oxidative voltammograms of 1 mM 4-PU (part A) and 4-cyclohexylurazole (part B) as two typical urazoles in various pHs. The voltammograms of 4-PU shows irreversible features in a wide range of pHs. However, the oxidized form of 4-cyclohexylurazole is somewhat stable in acidic media. Compared with 4-PU, cyclohexyl group by slightly electron donating properties decreases the rate of the follow up chemical reactions. The instability of the oxidized form of 4-cyclohexylurazole becomes more critical by increasing pH due to nucleophilic attack of hydroxide ion so that all urazoles exhibit irreversible voltammograms in natural and basic solutions.

[Figure 5]

Figure 6A indicates the voltammetric behavior of 4-PU/IFMC/GCE in aqueous solutions with various pHs. As is clear in this Figure the anodic and cathodic peaks shift to negative potentials as pH values increase. Interestingly, the shape waves of the cathodic part of voltammograms are prominently different whit each other in the case of free (Figure 5A) and anchored (Figure 6A) 4-phenylurazole. According to Figure 6, the grafted 4-PUox on the IFMC is protected against ring opening in acidic, natural and even in basic solutions (Scheme 2). The stability opens an opportunity to introduce different functional groups to the modified electrode.

Figure 6B displays the pH dependence of E_p for the anchored redox centers. The anodic peak potential follows the equation 1.

$$E'_{pA} = E'_{pA(pH=0)} - \left(\frac{2.303mRT}{2F}\right)pH \qquad 1$$

where m is the number of protons participating in the electron transfer, E'_{pA}(pH = 0), the anodic peak potential at pH = 0.0, R, the universal gas constant, T, temperature and F, Faraday's constant. A Nerstian behavior with a slope of 55 mV/pH over a pH range of 2 to 8 illustrates the same $2e^-/2H^+$ electrode process of the surface-confined 4-PU and ungrafted form.

[Figure 5]

3.4. The effect of scan rate

The feature of cyclic voltammograms was investigated at different potential scan rates. As is shown in Figure 7A by increasing the scan rate the anodic and cathodic peaks shift to positive and negative directions, respectively, indicating quasi-reversible electron transfer at the coated IFMC film on the GCE. The logI-logv diagram of the anchored 4-PU comprises two linear segments with slopes of 1.08 and 0.81 at 25-300 and 300-900 mV/s, respectively (Figure 7B). The slope of 1 at low scan rates confirms an adsorption-controlled process. Decreasing the slope to the value of 0.81 at higher scan rates indicates accompanying diffusion with adsorption in the electrode process. It could be related to time-consuming process of the electron transfer through the IFMC film [41].

[Figure 7]

The surface coverage (Γ) of the modified electrode was estimated 2.1×10^{-9} mol/cm^2 according to Brown-Anson equation (Eq. 2) [42].

$$\Gamma = \frac{I_p 4RT}{n^2F^2Av} \qquad 2$$

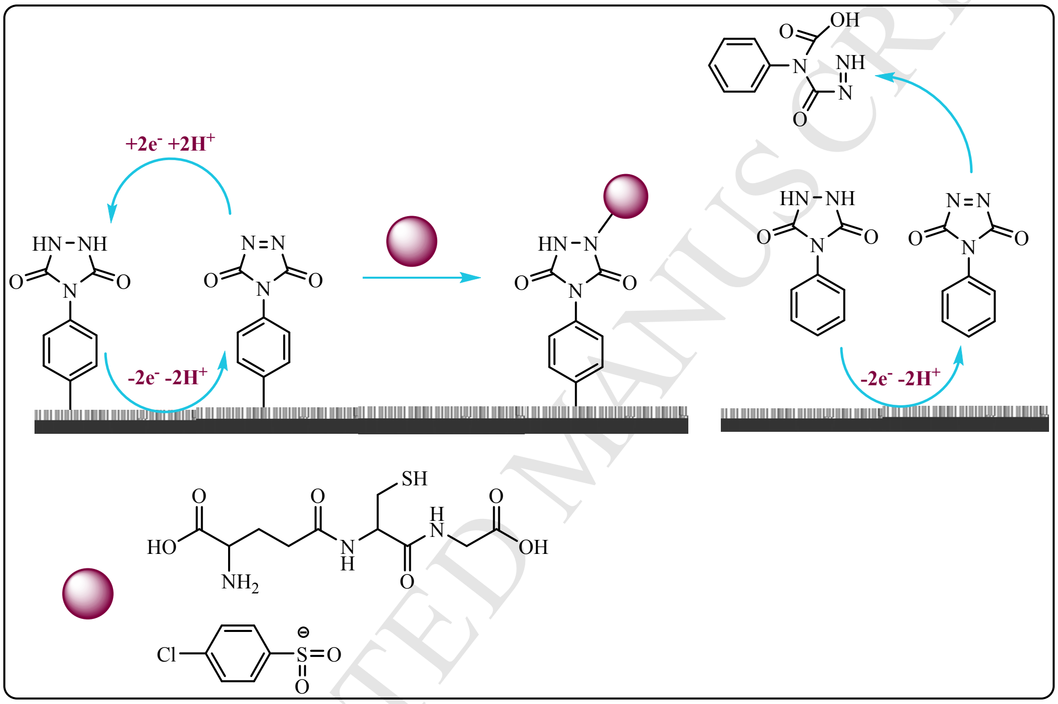
Where n is the number of electrons, I_p, the anodic peak current, A, geometrical surface area and ν, scan rate.

3.5. Electrochemical response of the anchored 4-phenylurazole to nucleophiles

Figure 8 represents the cyclic voltammograms of the fabricated electrode dipped in 5 mM and 2 mM glutathione (part A) and 4-clorosulfinic acid, SA, (part B) as typical nucleophiles, respectively. Decreasing in the cathodic current in the reverse scan displays the perturbation of the electrode process by a chemical reaction. In contrast to stability of the anchored redox centers in a wide pH range, they are reactive enough in the presence of nucleophiles. Figure 9 indicates the first and 15th cycles of voltammograms recorded in the presence of SA (2 mM). A considerable decrease in the intensity of the signal is consistent with the reactivity of the redox centers with SA. The results reflect feasibility of post-functionalization of the redox centers by simply exerting a positive potential for oxidation of the electrografted 4-PU in the presence of various nucleophiles.

[Figure 8]

[Figure 9]



Scheme 2: Difference between redox behavior of grafted and ungrafted 4-PU in the presence of nulceophiles at the surface of IFMC/GCE.

4. Conclusions

The successful application of IFMC to modify GCE was described. 4-Phenylurazole was covalently grafted on the IFMC/GCE during electroreduction of 4-NPU in the presence of sodium nitrite following in situ generation of the corresponding diazonium ion. The anchored 4-PU behaves differently from the ungrafted form on the IFMC. The attached

4-PU is oxidized at less positive potential. In contrast to instability of 4-PUox in aqueous solutions, the electrografted form on the IFMC is stable in a wide range of pHs. The grafted 4-PUox is reactive enough against nucleophilic attack. Post-functionalization of the electrode can be occurred on the urazole modified surface by applying oxidative potential of 4-PU in the presence of various nucleophiles.

Acknowledgements

The authors acknowledge to the IASBS Research Council for support this work.

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