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New synthesis of poly ortho-methoxyaniline nanostructures and its application to construct modified multi-wall carbon nanotube/graphite paste electrode for simultaneous determination of uric acid and folic acid

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ABSTRACT

Uric acid (UA) and folic acid (FA) are compounds of biomedical interest. In humans, about 70% of daily uric acid disposal occurs via the kidneys, and in 5–25% of humans, impaired renal (kidney) excretion leads to hyperuricemia. Folate is another form folic acid of which is known as, is one of the B vitamins. It is used as a supplement by women to prevent neural tube defects developing during pregnancy. Polyortho-methoxyaniline nanostructures (POMANS) was synthesized with a new two phase (organic-water) synthesis method. The POMANS was characterized using transmission electron microscopy (TEM) and Fourier transform IR (FTIR). This polymer was used to construct a modified multi-wall carbon nanotube, graphite paste electrode (POMANS-MWCNT/GPE). Linear sweep voltammograms (LSV), cyclic voltammetry (CV) and chronoamperometry were used to investigate the suitability of polyortho-methoxyaniline with multi-wall carbon nanotubes paste electrode as a modifier for the electrocatalytic oxidation of UA and FA in aqueous solutions with various pHs. The results showed that POMANS-MWCNT/GPE had high anodic peak currents for the electrooxidation of UA and FA in pH 6.0.Under the optimized conditions, The catalytic peak currents obtained, was linearly dependent on the UA and FA concentrations in the range of 0.6–52 and 0.5–68 μM with two segments and the detection limits 0.157 and 0.113 μM for UA and FA were, respectively. Finally, the proposed method was also examined as a sensitive, simple and inexpensive electrochemical sensor for the simultaneous determination of UA and FA in real samples such as urine and serum.

1. Introduction

Conducting polymers (CPs) such as polyaniline, polypyrrole, polythiophene and their derivatives, has been used as modifier in electrochemical sensors, catalysts and electro chromic materials and many more, etc. [1–5]. Among different CPs, poly ortho-methoxyaniline (POMA)has been one of the most extensively studied polymers in fabrication of the sensor devices, because POMA has useful features including high electrical conductivity, good environmental stability, electrochemical redox activity even in neutral pH solutions [6–9].To increase the surface area of catalysis, enhance catalytic activity and sensitivity due to the increase of surface, POMA has been supported by different material [10,11].

Uric acid (2,6,8-trihydroxypurine) (UA) the end metabolic product of purine through the liver, is present in blood and urine. Abnormal UA level in a human body could be caused

by several diseases such as gout, hyperuricemia, Lesch–Nyan syndrome, as well as cardiovascular and chronic renal diseases. Hence, monitoring of the concentration of UA in biological fluids may be used as an early warning of the presence of these diseases. Electrochemical sensors for the determination of UA are simple, rapid, inexpensive and easy to use [12–16]. Folic acid, ((2*S*)-2-[(4-{[(2-amino-4-hydroxypteridin-6yl)methyl]amino}phenyl) formamido] pentanedioic acid), also known as vitamin B_c, vitamin M and folacin, is a form of the water-soluble vitamin B_9. FA deficiency causes failure to make the purines and thymine required for DNA synthesis. FA is necessary for cell development, for metabolism of specific biochemical reactions in the body and the metabolism of specific anticonvulsant drugs [17–19]. Since, UA and FA always co-exist in the human body fluids. So, it has essential for the simultaneous determination of UA and FA.

Carbon nanotubes (CNTs, includes multi-wall carbon nanotubes and single-wall carbon nanotubes), the new forms of elementary carbon, are composed of graphitic sheets rolled into closed concentric cylinders with diameter of nanometers and length of micrometers. Because of the special tube structure, CNTs possess several unique properties such as good electrical conductivity, high chemical stability, and extremely high mechanical strength [20]. The better performance of the CNTs electrode compared to other electrodes may be due to the carbon nanotube dimensions, the electronic structure, and the topologic

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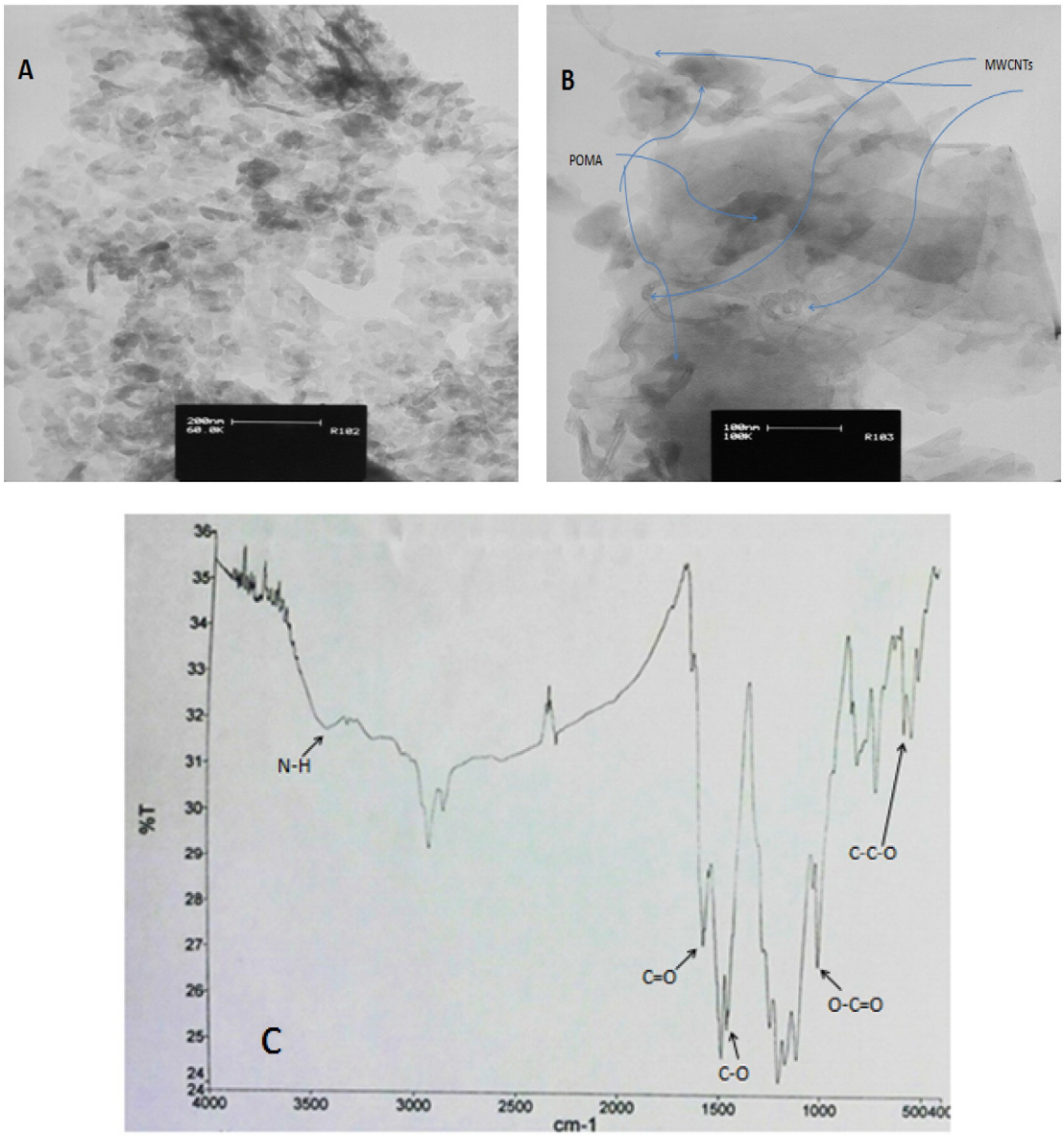

Fig. 1. TEM images of (A) POMANS(B)POMANS-MWCNT/GPE, and (C) FTIR spectrum of POMANS.

defects present on the tube surface [21,22]. Problems of low catalytic performance for analysis of toxic and biologic compounds with CNTs, nano composites and its hybrids are improved [23,24]. It has been reported that carbon nanotube-modified electrodes were successfully applied to study and determine many biological compounds, drugs and toxic materials [25–28].

To our knowledge, there are no similar studies on the polymerization of poly ortho-methoxyaniline nanostructures (POMANS) and its application as novel modifier in modified graphite paste electrode including MWCNTs for the simultaneous determination of uric acid and folic acid in aqueous solution. The present work describes the synthesis of POMA with a new two phase (organic-water) method. The electrochemistry behavior of POMANS-MWCNTs/GPE and investigation of its electrocatalytic effect on simultaneous determination of UA and FA was studied in details. It was found that the POMANS-MWCNTs/GPE showed an electrocatalytic activity towards the oxidation of UA and FA by enhancing its oxidation currents when compared to bare GPE and MWCNTs/GPE. Finally, in order to demonstrate the catalytic ability of the modified electrode in the determination of UA and FA in real samples, we examined this method for the voltammetric simultaneous determination of UA and FA in samples of serum and urine.

2. Experimental

2.1. Chemicals

Isobutyl methyl ketone (4-methyl-2-pentanone), potassium persulfate ($K_2S_2O_8$), phosphoric acid, hydrochloric acid and sodium hydroxide with analytical grade were obtained from Merck company. Uric acid, folic acid, multi-wall carbon nanotubes, with nanotube diameters, OD = 20–30 nm, wall thickness = 1–2 nm, length = 0.5–2 μm and purity >95%, graphite powder and high-viscosity paraffin oil were purchased from Aldrich. Ortho-methoxyaniline (OMA)was prepared from Aldrich and was purified immediately prior to use by passing small aliquots through an activated alumina column. All solutions were freshly prepared by doubly distilled water (DDW), purged with pure nitrogen gas (99.999%) before investigations.

2.2. Instrumentation

All electrochemical experiments were performed using a SAMA 500 Electroanalyser (SAMA Research Center, Iran)controlled by a personal computer. A platinum wire was used as the auxiliary electrode. A saturated calomel electrode (SCE) and POMANS-MWCNTs/GPE were used