Electrochemical fabrication of electroactive ordered mesoporous electrode

Mohammad Rafiee,[*a] Babak Karimi,[a] Yousef Abdossalami Asl[a] and Hojatollah Vali[b]

[a] Department of Chemistry, Institute for Advanced Studies in Basic Sciences (IASBS), P.O.Box 45195-1159, Gava Zang, Zanjan, Iran

[b] Earth & Planetary Sciences, 3450 University St., Montreal, Quebec, H3A 2A7 Canada

* E-mail: rafiee@iasbs.ac.ir

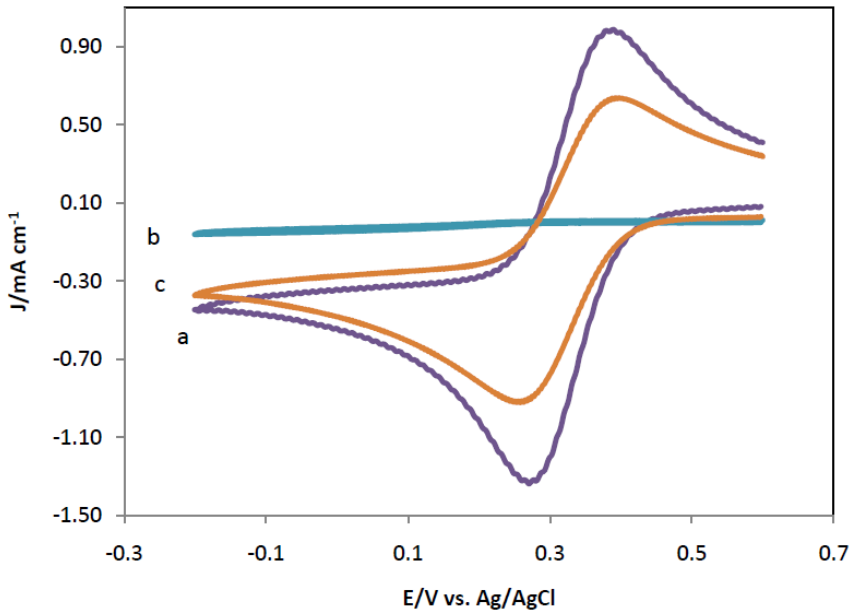

Figure 1S. Cyclic voltammograms of $Fe(CN)_6^{3-}$ (5 mM) on (a) bare GC electrode (b) covered by silica film before and (c) after surfactant extraction. Phosphate buffer solution pH 6, Scan rate: 100 mVs^{-1}.

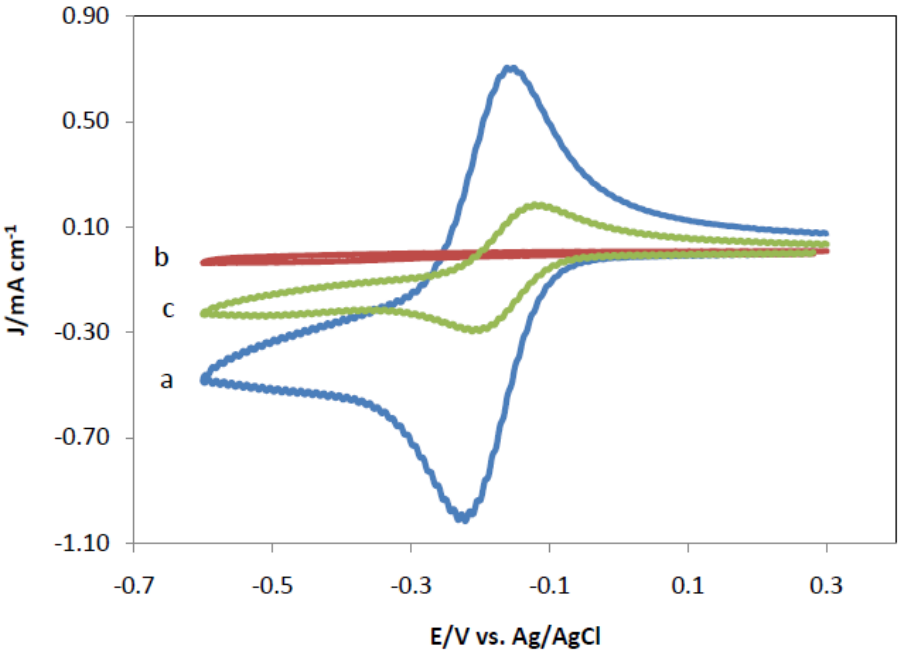

Figure 2S. Cyclic voltammograms of $Ru(NH_3)_6^{3+}$ (5 mM) on (a) bare GC electrode (b) covered by silica film before and (c) after surfactant extraction. Phosphate buffer solution pH 6, Scan rate: 100 mVs^{-1}.

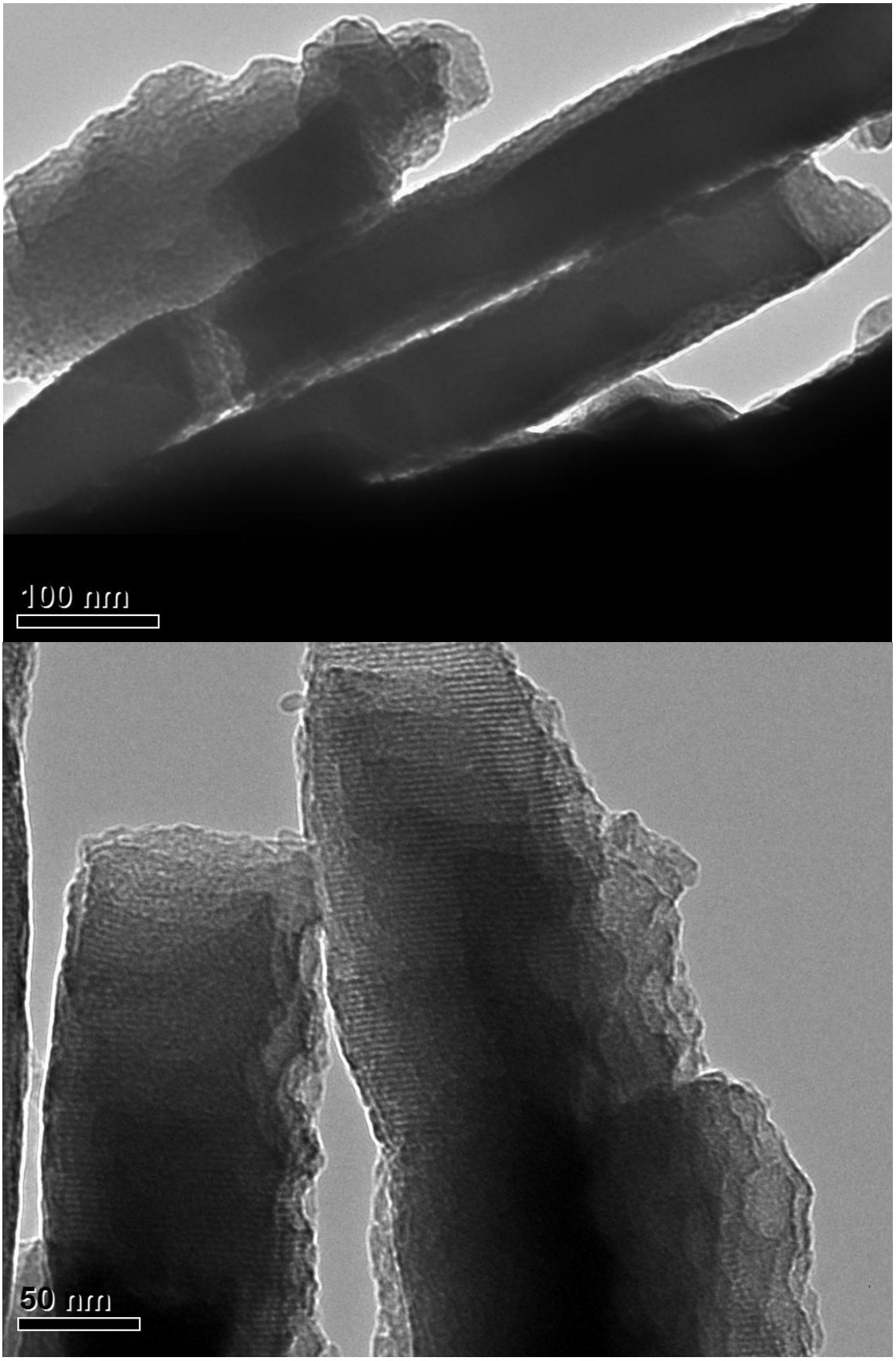

Figure 3S. Side-view TEM images of silica film correspond to a film deposited on GC at -2.2 V for 20 s from a sol containing the molar ratio for APTES to TEOS 0.1.

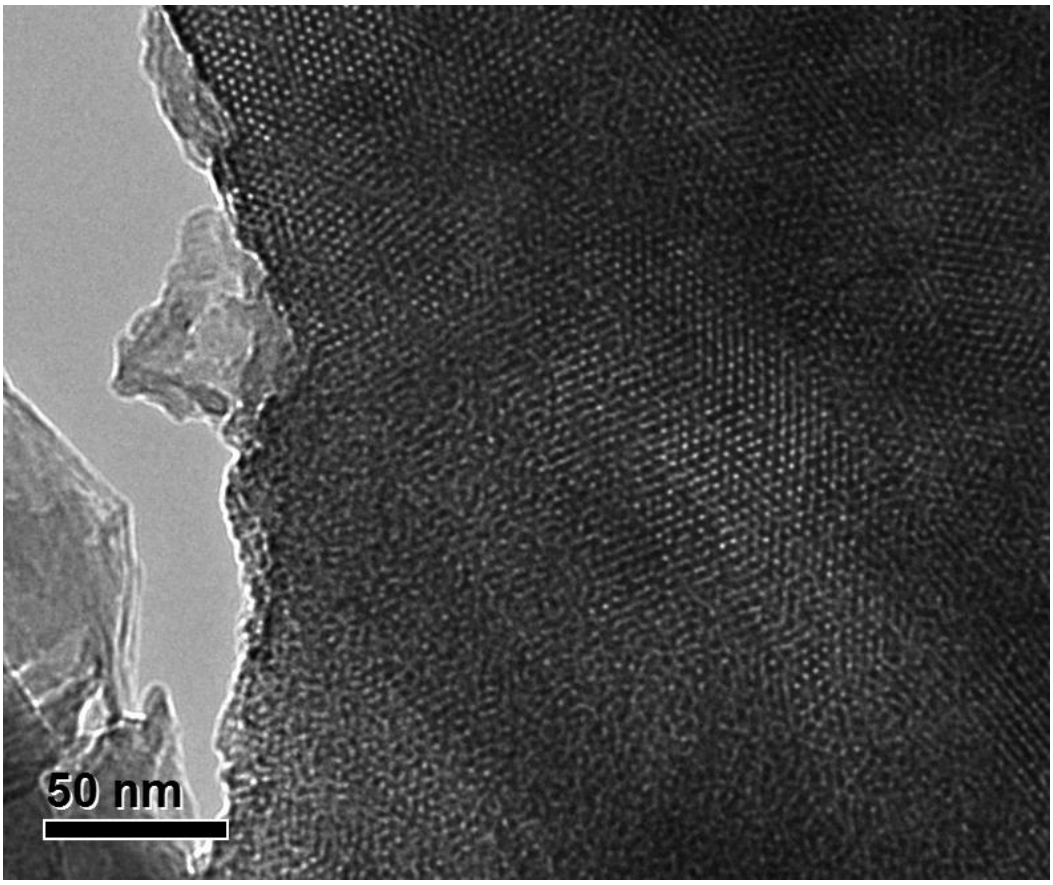

Figure 4S. Top-view TEM images of silica film correspond to a film deposited on GC at -2.2 V for 20 s from a sol containing the molar ratio for APTES to TEOS 0.1.

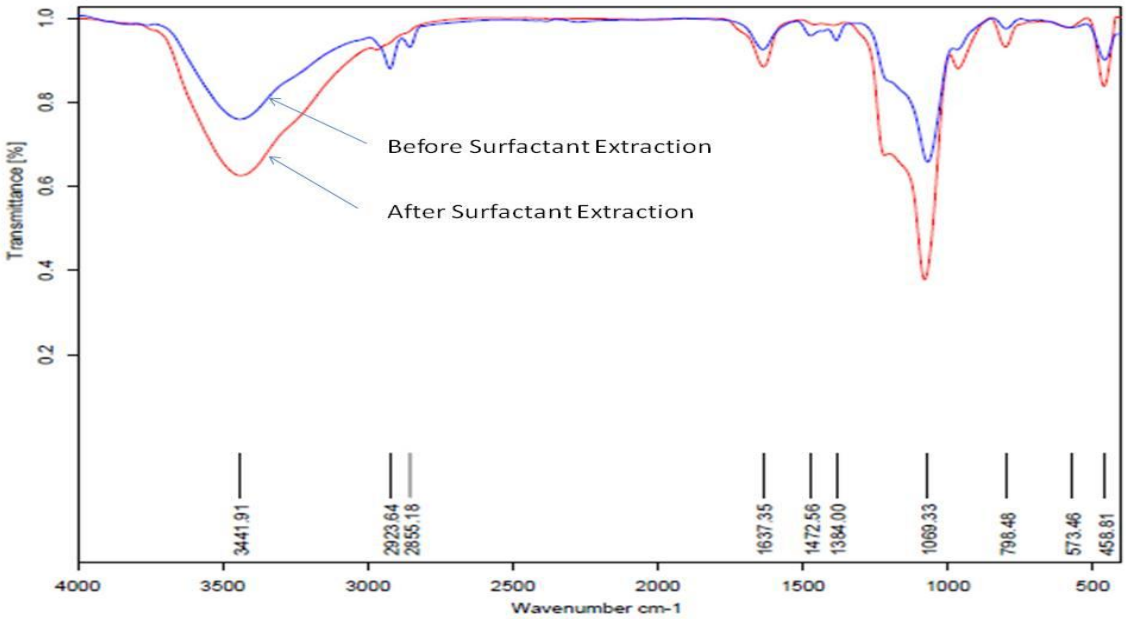

Figure 5S. IR spectrum of scratched aminopropyl functionalized film before and after extraction of CTAB.

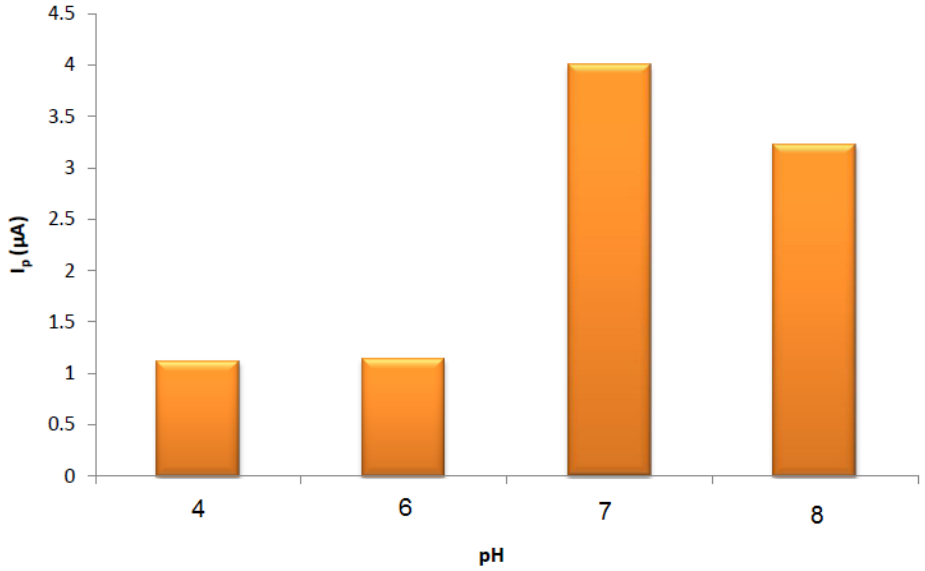

Figure 6S. The peak currents of aminocatechol functionalized electrode (A_2 or C_2) for the electrochemical functionalization of electrodes at various pHs; The numbers on horizontal axis refer to the solution pHs: pH=4 acetate buffer solution 0.1 M, pH=6-8 phosphate buffer solutions with various NaH2PO4/Na2HPO4 and ionic strength 0.1 M.

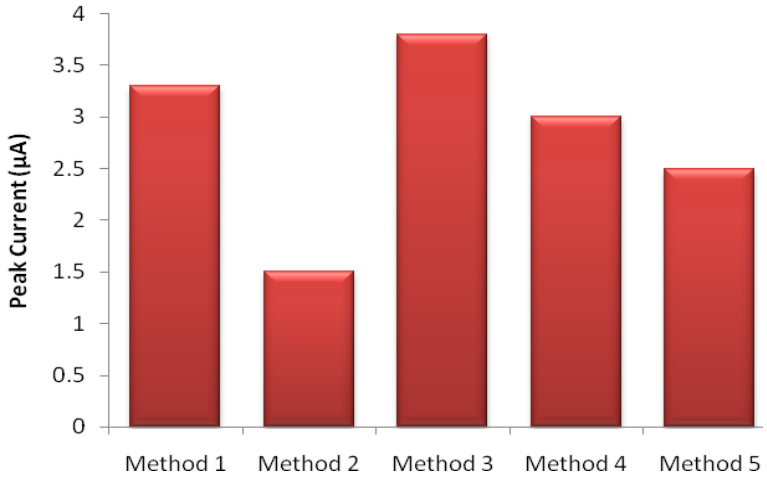

Figure 7S. The peak currents (A_2 or C_2) for various methods of extraction. The methods refer to the method of surfactant extraction: Method 1: extraction in ethanol, Method 2: extraction in acidic ethanol, Method 3 extraction in acidic ethanol and 10 minutes remaining in pH 7 phosphate buffer solution, Method 4: extraction in aqueous phosphate buffer, Method 5, extraction in aqueous acetate solution.

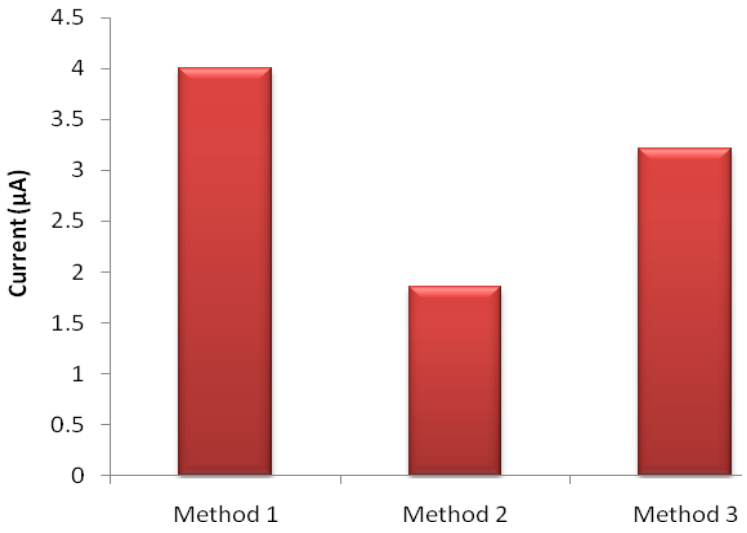

Figure 8S. The peak currents (A_2 or C_2) for various methods of electrochemical functionalization. The methods refer to the method of applying potential to the electrode in 0.1 M phosphate buffer and 5.0 mM catechol solution: Method 1: 50 potentiodynamic cycle method in potential range of -0.2 V to 0.7 V vs. Ag/AgCl; Method 3: double steps potentiostatic: 20 minutes potentiostatic at 0.5 followed by 10 minutes potentiostatic at -0.2 V.

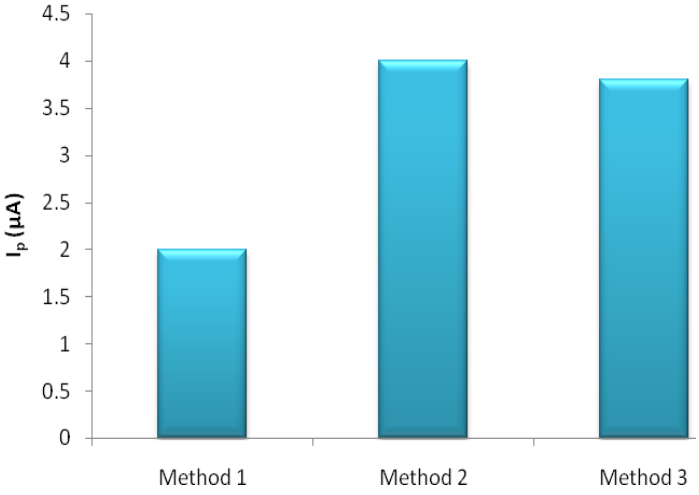

Figure 9S. The peak currents of modified electrode (A_2 or C_2) for various conditions of potentiodynamic functionalization. The methods refer to the number of cycles and scan rates of modification step in 0.1 M phosphate buffer and 5.0 mM catechol solution: Method 1: 20 potentiodynamic cycle method in potential range of -0.2 V to 0.7 V vs. Ag/AgCl with scan rate 25 mVs^{-1}; Method 2: 100 cycles with scan rate 100 mVs^{-1}; Method 3: 500 cycles with scan rate 500 mVs^{-1};

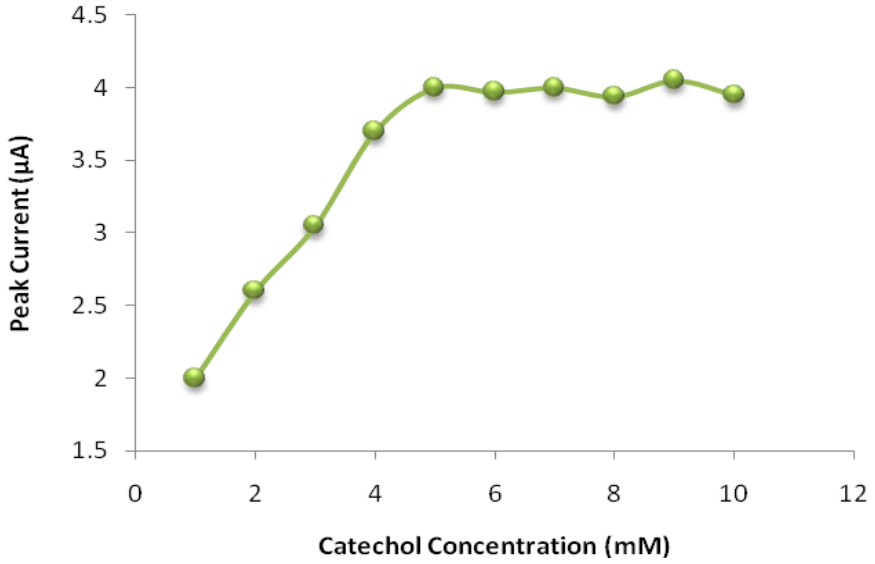

Figure 10S. The plot of anodic peak currents of electrochemically functionalized electrode versus concentration of catechol in phosphate buffer solution, pH =7 (solution of electrochemical modification step)

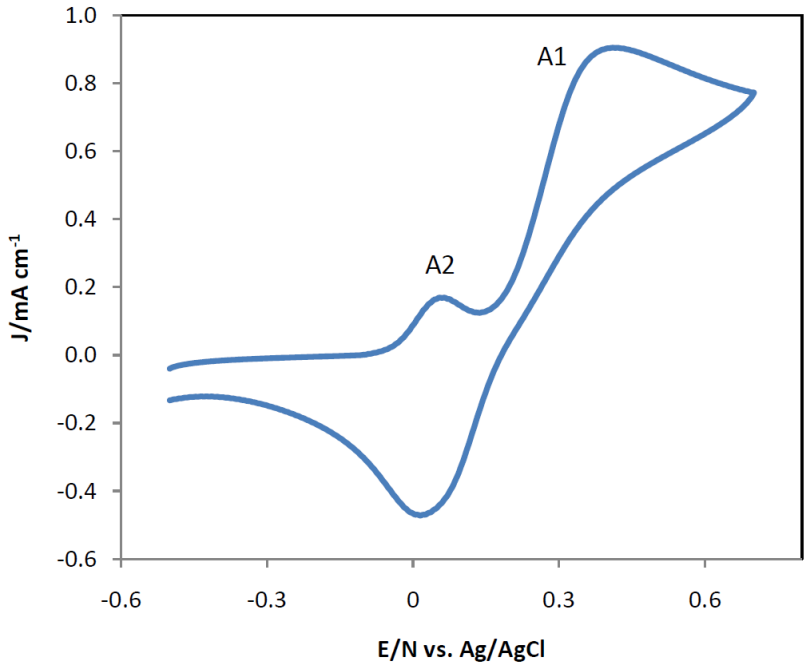

Figure 11S: Cyclic voltammogram of 5.0 mM solution of catechol on electrochemically functionalized GC-AFS.

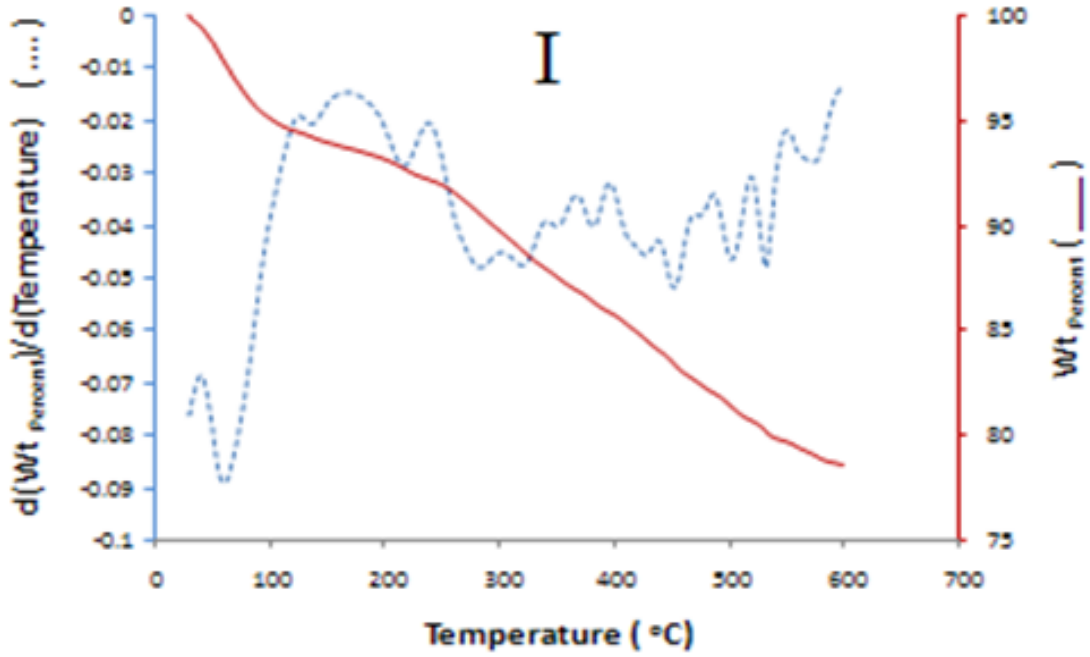

Figure 12S: Thermogravimetric analysis (TGA) of scratched amine functionalized silica thin film.

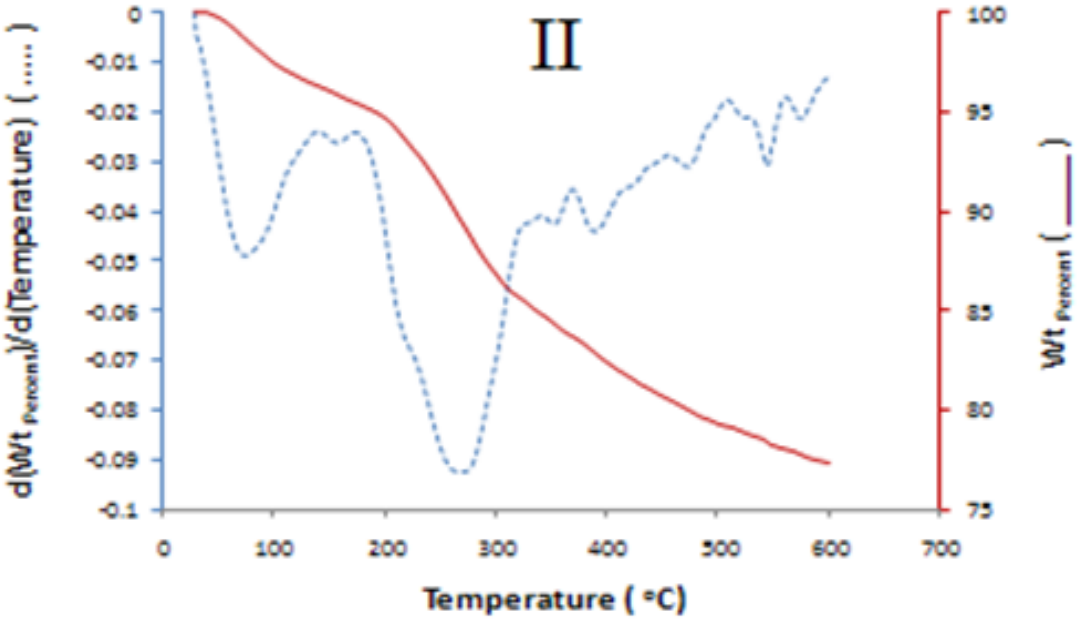

Figure 13S: Thermogravimetric analysis (TGA) of scratched aminocatechol functionalized silica thin film.

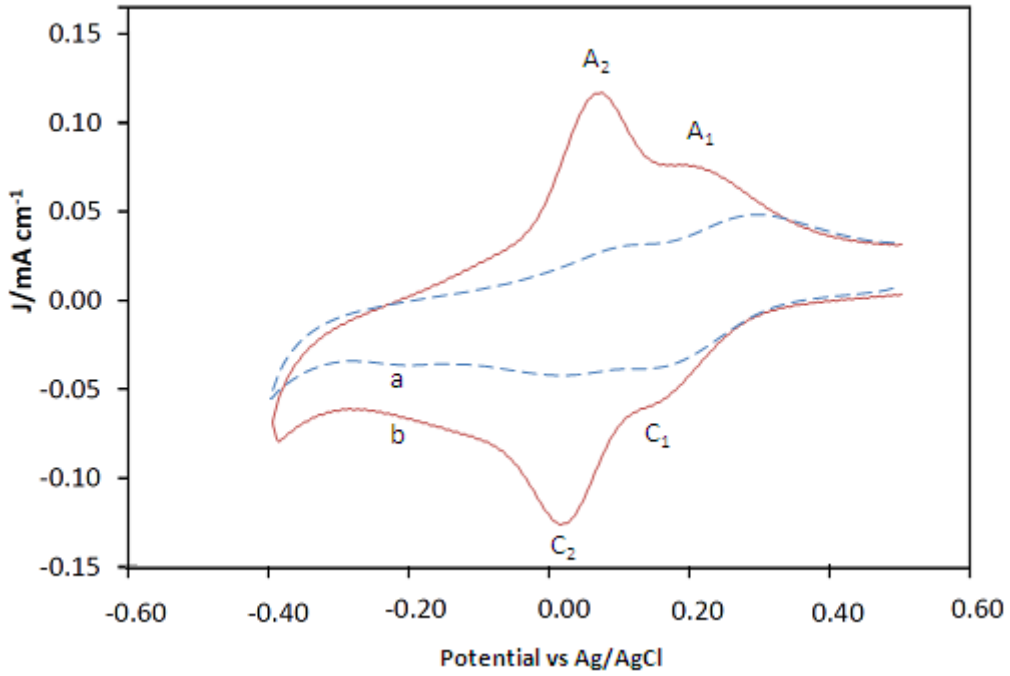

Figure 14S. The cyclic voltammograms of modified electrodes with ordered mesoporous silica film (only TEOS in sol solution) and aminopropyl functionalized silica film after electrochemical functionalization in 0.1 M phosphate buffer (pH=7.0) solution. The electrochemical functionalizations were achieved for both electrodes in obtained optimum conditions.

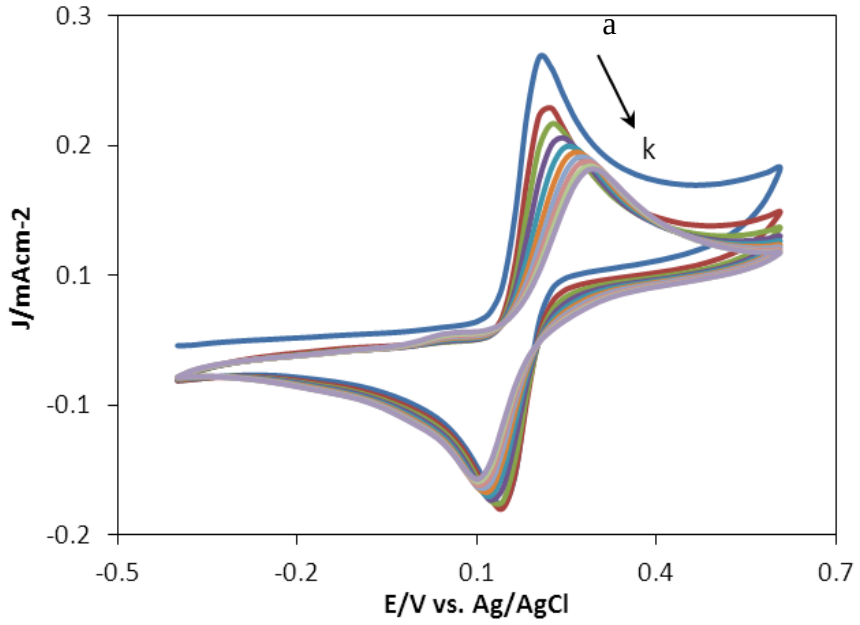

Figure 15S. Multicyclic voltammograms of 1.0 mM catechol in phosphate buffer solution, pH=7, on GC electrode. The cycles from (a) to (k) are the first to 100th cycle with 10 cycles interval. Scan rate: 100 mVs-1.

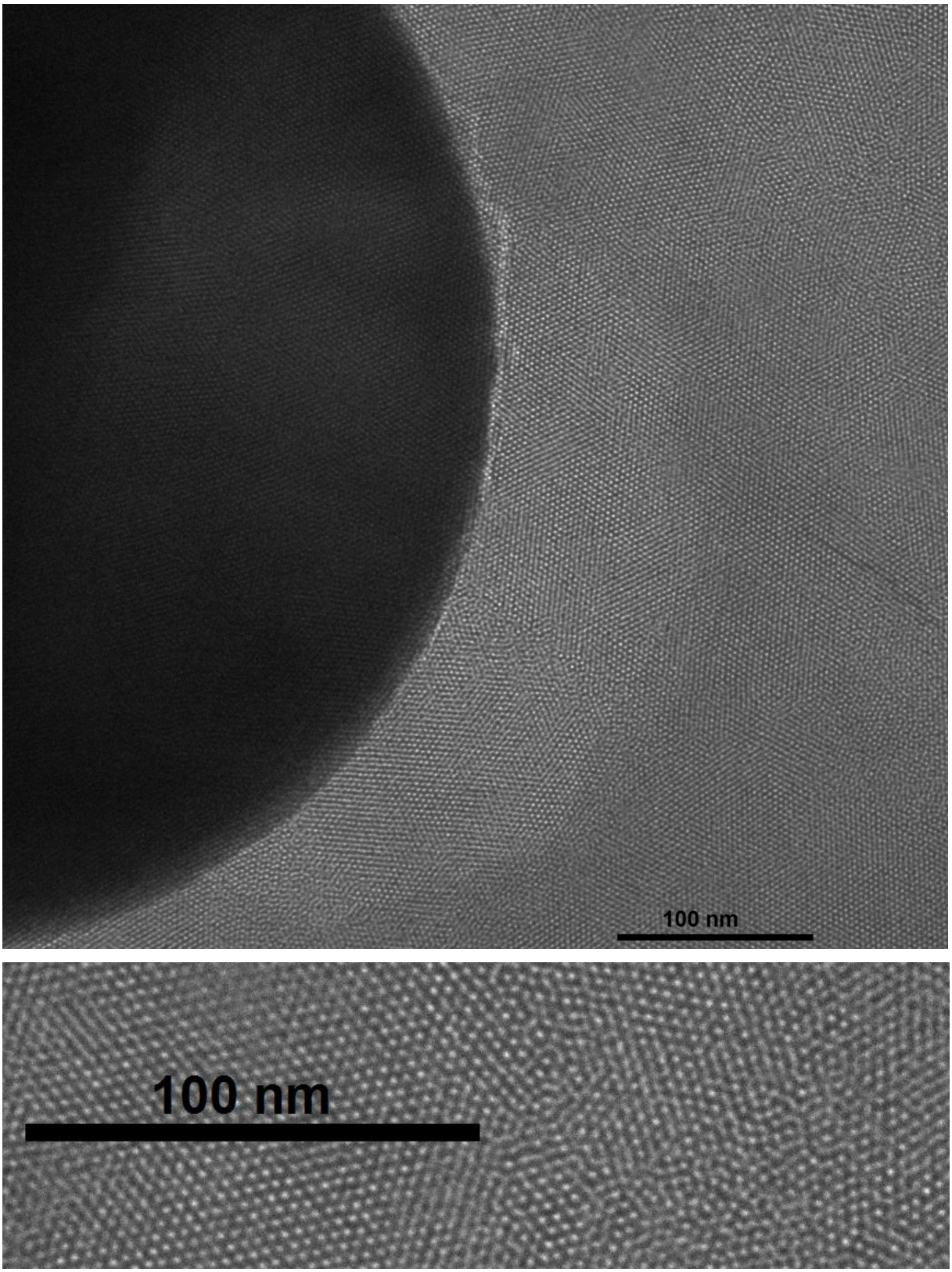

Figure 16S. Top-view TEM images of aminocatechol functionalized mesoporous silica film after surfactant extraction, activation (deptotonation of anoniumm group) and electrochemical functionalization.

Table 1S: the elemental analysis of scratched films: **sample 1** silica thin film, **Sample 2:** Amine functionalized silica thin film (obtained from sol solution containing APTS/TEOS=0.1 and **Sample 3** Aminocatechol functionalized silica thin film. All of the films obtained by EASA on the activated Glassy carbon electrode.

Sample NO.	Weight [mg]	Content [%]
1	1.8490	N:0.000 C:4.486 S:0.000 H:1.117
2	2.1730	N:1.305 C:6.985 S:0.000 H:1.772
3	4.9890	N:1.080 C:7.894 S:0.000 H:1.873