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1 Amino-grafting of montmorillonite improved by acid activation and application 2 to the electroanalysis of catechol

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9

10

11 Abstract

12 In this work, a natural sodium-montmorillonite clay mineral (Mt-Na) was functionalized
13 with amine groups, either by direct grafting (Mt-NH₂) or via acid activation followed by
14 grafting (MtH-NH₂) of [3(2-aminoethyl)amino]propyltrimethoxysilane (AEP-TMS). The
15 morphology and structure of the resulting composite materials were characterized by scanning
16 electron microscopy, X-ray diffraction, N₂ adsorption-desorption isotherms (BET method)
17 infrared spectroscopy, CHN elemental analysis and thermogravimetric analyses (TGA). The
18 obtained organoclays were then used to modify the surface of a glassy carbon electrode
19 (GCE), and the permselectivity and accumulation properties of the resulting films were
20 investigated by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS).
21 The results indicated that MtH-NH₂ modified GCE (GCE/MtH-NH₂) exhibited some charge
22 selectivity features and can be applied to the electrochemical oxidation of catechol (CT). By
23 plotting the double logarithmic variation of anodic peak currents (*I*_{pa}) *versus* potential scan
24 rate, the obtained slope value of 0.49 revealed a diffusion-controlled electron-transfer
25 mechanisms for the redox process. The electrochemical behavior of CT on the modified
26 electrode was also studied using differential pulse voltammetry (DPV). The sensitivities of
27 GCE/MtH-NH₂ for CT were 1.71, 3.87 and 1.35-fold greater than signals obtained on the bare
28 GCE, GCE/Mt-Na and GCE/Mt-NH₂ respectively, due to the ability of the aminated materials
29 to strongly accumulate CT. After optimization, GCE/MtH-NH₂ was used for CT
30 determination by differential pulse voltammetry that gave rise to a linear response in the
31 concentration range from 5 μM to 80 μM (*R*² = 0.999), and to a detection limit of 0.65 μM.
32 The proposed method was applied to CT detection in water samples and in a tea sample.

33 **Keywords:** Montmorillonite, Acid activation, Grafting, Organoclays, Electroanalysis,
34 Catechol

35 1. Introduction

36 Phenolic compounds are present at low levels in subterranean and drinking waters, as a result
37 of their wide use in textiles, plastics, dyes, paper, herbicides and pesticides (Shan et al., 2009;
38 Lu et al., 2010, Zhao et al., 2012). As environmental pollutants, dihydroxybenzene isomers
39 have been the subject of many studies due to their presence and difficult degradation (Wang et
40 al., 2012). Catechol (CT, 1,2-dihydroxybenzene) is one of the most important phenolic
41 compounds found in teas, vegetables, fruits and tobaccos. Considered as one of the key
42 fragments of tea catechins, CT is contained in tea at various concentrations ranging from 0.1
43 mg.g⁻¹ to 0.1 g.g⁻¹ (Montserrat et al., 2010; Li et al., 2009). Tea also contains proteins, amino
44 acids, alkaloids, carbohydrates, lipoids, organic acids and inorganic elements. CT is of great
45 biological importance with respect to anti-oxidant properties, antiviral and enzyme activities;
46 however, an excessive intake may cause some health problems (Chambers, 1988; Yue et al.,
47 2013). CT is considered as an environmental pollutant by the European Union (EU) (Xie et
48 al., 2006). It is responsible for renal tube degeneration and liver function decrease (Aziz et al.,
49 2007). At low concentration in foods and cigarettes, it can cause mutagenesis and cancerous
50 alterations (Hirakawa et al., 2002). Thus, it is critical to establish highly sensitive and
51 selective analytical tools to identify and quantify traces of catechol in environmental samples.
52 Up to now, the most commonly used analytical methods include spectrophotometry (Nagaraja
53 et al., 2001), gas chromatography (Moldoveanu & Kiser, 2007) and high-performance liquid
54 chromatography (HPLC) (Marrubini et al., 2005). These techniques have some disadvantages,
55 such as complicated operation, poor selectivity and high cost and require highly skilled
56 manpower. Electroanalytical methods may be of interest owing to their sensitivity, rapidity,
57 simplicity and low cost (Fekadu et al., 2013). Thus, some electrochemical methods have been
58 developed for the sensitive detection of CT (Wang et al., 2007; Lin et al., 2009; Zhao et al.,
59 2009, 2012; Yue et al., 2013; Yuan et al., 2013). They are mostly based on the use of
60 chemically modified electrodes, such as anthraquinone modified carbon paste electrode
61 (Fekadu et al., 2013), multi-walled carbon nanotube modified carbon paste electrode
62 (Yongqing et al., 2017) and mesoporous Al-doped silica modified electrode (Lin et al., 2009).
63 The modification of the electrode surface is intended to enhance both sensitivity and
64 selectivity of the detection, but the above examples are based on the use of rather costly
65 modifiers. The development of new composite materials, cheap and easy to prepare, likely to
66 be used as effective electrode modifiers for the sensitive detection of CT is still needed.

67 Clay minerals are considered nowadays as interesting adsorbent materials due their low cost,
68 abundance, their morphology ensuring a high surface-to-volume ratio and thus developing
69 large active surface areas. In that context, for instance, [Kong et al. \(2011\)](#) reported a
70 palygorskite modified carbon paste electrode for the determination of CT. However the
71 adsorption capacities and the intrinsic selectivity of natural clays towards organic and
72 inorganic pollutants can be low, restricting the extensive use of these materials ([Guggenheim
73 and Martin, 1995](#)). In the aim to get more efficient adsorbents, the elaboration of organic-
74 inorganic hybrid materials based on the chemical modification of surface properties of natural
75 clays with organo-functional moieties has become a promising way during the past decades
76 ([Tonle et al., 2003, 2005](#)). The so-called organoclays can be obtained by modifying clays and
77 clay minerals with organic groups through several processes: intercalation (or insertion), ion
78 exchange, pillaring or surface grafting ([Park et al., 2004; Piscitelli et al., 2010](#)). On the other
79 hand, organoclay modified electrodes have been largely exploited in electroanalysis ([Tonle et
80 al., 2015](#)), and most studies reported to date have been focused on layered clay minerals
81 (smectite and kaolinite being the most investigated ones), which can be grafted via the
82 hydroxyl groups localized at the outer surfaces or on the edges of clay particles (for smectite-
83 type clays) or along the unshared plane of the alumina sheets in kaolinite.
84 In this study, amino-functionalized montmorillonites (Mt-NH₂ and MtH-NH₂) have been
85 prepared by grafting [3(2-aminoethyl)propyltrimethoxysilane (AEP-TMS) on purified clay
86 mineral sample (Mt-Na), then on the same clay sample chemically activated in acid medium
87 (MtH). For MtH-NH₂ material, the acid activation was performed before the grafting process
88 to increase its surface area and enrich its structure with –OH binding sites ([Gonzalez et al.,
89 1984; Rodriguez et al., 1994, Angela de Mello et al. 2009](#)). This may further result in an
90 enhancement of the amount of grafted organosilanes. After characterization of the starting and
91 modified clay materials, it was demonstrated that MtH-NH₂ can be used as prominent
92 modifier for a GCE, and exploited for the preconcentration and sensitive detection of CT in
93 water and tea samples.

94

95 **2. Experimental**

96 *2.1. Clay mineral, materials and chemicals*

97 The Na-montmorillonite clay mineral used in this work was obtained from the Source
98 Clays Repository, University of Missouri-Columbia (Columbia, MO 65211, USA). The Na-
99 montmorillonite has the chemical formula NaSi₁₆(Al₆FeMg)O₂₀(OH)₄ ([Van Olphen &](#)

100 [Fritpiat, 1979](#)). All chemicals were obtained commercially and used without further
101 purification. Catechol ($C_6H_6O_2$, 99%, Sigma-Aldrich), H_3BO_3 (98%, Fisher Scientific
102 International), HCl (36%, Phillip Harris), CH_3COOH (Prolabo), KCl (99.5%, Fisher Scientific
103 International), H_3PO_4 (63%, Prolabo), K_2HPO_4 (99% Prolabo), KH_2PO_4 (99% Prolabo),
104 (CH_3COONa) (99% Prolabo), Hexaammineruthenium(III) chloride ($Ru(NH_3)_6Cl_3$, 98%,
105 Sigma-Aldrich), and potassium hexacyanoferrate(III) ($K_3Fe(CN)_6$, Fluka) served as redox
106 probes for permeability characterization of the film modified electrodes. Various electrolytes
107 such as acetate buffer solution (0.1 M AB), phosphate buffer solution (0.1 M PB), and
108 Britton-Robinson buffer solution (0.1 M BRB) were prepared from the appropriate chemicals
109 mentioned above. The grafting agent ([3-(2-Aminoethylamino)propyl]trimethoxysilane, AEP-
110 TMS, $\geq 98\%$) used for clay modification was obtained from Sigma-Aldrich. A tea sample was
111 purchased from local market and treated as follow. Briefly, the tea sample was powdered with
112 a mortar and a weighed portion (0.055 g) was used for catechol extraction with 50 mL of 90%
113 ethanol/water solution for 24 h shaking at $80^\circ C$. The mixture was filtered and the volume
114 made up to 25.0 mL for further measurement. All solutions were prepared with distilled water
115 and experiments were carried out at room temperature.

116 *2.2. Preparation of grafted materials*

117 Before the grafting process, 1.5 g of sodium montmorillonite (Mt-Na) was activated
118 with 150 mL of a 0.1 M HCl solution. This suspension was stirred for 4 h. Acid activation
119 was used to remove sodium ions from the interlayer region. Then, 1 g of acid-activated
120 montmorillonite, previously dried at $130^\circ C$ for 4 h, was dispersed in 50 mL of 0.1 M AEP-
121 TMS in dry toluene. The resulting mixture was heated and allowed to reflux under stirring for
122 72 h in an inert N_2 atmosphere. The solid obtained was washed successively with toluene,
123 ethyl alcohol and then filtered. The product MtH-NH₂ was finally dried for 2 h at $120^\circ C$ in an
124 inert nitrogen atmosphere and stored in a flask. The same procedure was applied to get Mt-
125 NH₂, using the purified clay without the acid activation step.

126 *2.3. Preparation of the working electrodes*

127 The elaboration of sensors involved the deposition of each organoclay films onto glassy
128 carbon electrode (GCE) surfaces by "drop coating". The GCE was first polished with alumina
129 pastes and then rinsed for 5 min in a 1:1 water-ethanol mixture under sonication in order to
130 remove any remaining alumina particles. Subsequently, aqueous dispersions of either raw Mt-
131 Na, Mt-NH₂ or MtH-NH₂ (at $5\text{ mg}\cdot\text{mL}^{-1}$) were prepared and 6 μL (30 μg of clay) were drop-

132 coated onto the top of the GCE (surface area: 0.071 cm²), which was dried at 110°C for 4 min
133 in an oven prior to use. Throughout the text, the modified electrodes are referred to as
134 GCE/Mt-Na, GCE/Mt-NH₂ and GCE/MtH-NH₂ for the GCE modified by raw Mt-Na, Mt-
135 NH₂ and MtH-NH₂, respectively.

136 *2.4. Electrochemical procedures and apparatus*

137 Cyclic voltammetry, electrochemical impedance spectroscopy (EIS) and differential
138 pulse voltammetry (DPV) measurements were performed using the palmsens³ potentiostat,
139 equipped with the PS Trace 4.2 electrochemical analysis system and connected to a computer.
140 The voltammograms were recorded under quiescent conditions immediately after the
141 immersion of the working electrode in a conventional single compartment cell containing the
142 “analyte + electrolyte” solution, a pseudo reference electrode (Ag/Ag⁺) and a platinum wire
143 auxiliary electrode. Differential pulse voltammetry (DPV) measurements were performed in a
144 25 mL electrochemical cell containing 0.1 M Britton-Robinson buffer (BRB) solution (pH 4)
145 and catechol at appropriate concentrations, in the potential range from -0.2 V to 0.8 V. All
146 experiments were conducted at room temperature (25°C). EIS were carried out in 5 mM
147 [Fe(CN)₆]^{3-/4-} (1:1) solution containing 0.1 M KCl over the frequency range of 0.1 Hz-10
148 kHz. The morphology of modified GCEs was analyzed by scanning electron microscopy
149 (SEM) using a JEOL JCM-6000 apparatus (acceleration voltage of 15 kV). Fourier transform
150 infrared spectroscopy (FTIR) was applied to assess the presence of organic groups in the final
151 materials, using a Nicolet 8700 apparatus equipped with a specular reflectance accessory
152 (Smart Collector). The crystallinity of raw and modified clay materials was determined by X-
153 ray diffraction analysis using a Stoe Stadi-p X-ray powder diffractometer (Stoe & Cie GmbH,
154 Darmstadt, Germany), with Cu K α 1 radiation (40 kV, 30 mA and $\lambda_{\text{Cu}}=1.54056 \text{ \AA}$). The
155 Brunauer-Emmett-Teller (BET) surface areas of the samples were determined by means of
156 N₂ adsorption at 77.13 K using a micromeritics model sorptometer (Thermo Electron
157 Corporation, Sorptomatic Advanced Data Processing). Before N₂ adsorption, the samples
158 were degassed at 307.13 K under vacuum. The surface area was defined from linear part of
159 the BET equation. CHN elemental analysis was performed using CHNS Analyzer Euro EA
160 3000. The thermal behavior of the clay mineral before and after its modification was
161 investigated by the thermogravimetric analysis (STA 409 C equipment Netzsch Geratebau
162 GmbH, Germany). Approximately 10 mg of each dried sample were heated from 25 to 1000
163 °C under nitrogen atmosphere with a heating rate of 10 °C/min. The pH of solutions was
164 monitored using an Inolab pH-meter.

165 3. Results and discussion

166 3.1. Physico-chemical characterization of composite materials

167 FTIR spectroscopy was used to identify and compare the functional groups present in natural
168 montmorillonite (Mt-Na), acid treated Mt (MtH) and modified montmorillonite (Mt-NH₂ and
169 MtH-NH₂) as shown in Fig. 1. On the spectrum of raw clay mineral (Fig. 1a), one can observe
170 a stretching vibration band at 3620 cm⁻¹, which is characteristic of Al-OH stretching of the
171 octahedral sites of natural montmorillonite (Biernacka, 2005), while the bending mode of
172 such hydroxyl groups appears at 916 cm⁻¹ (Qin et al., 2010). The peaks observed at 3404 and 1640
173 cm⁻¹ are attributed to the -OH stretching and bending vibrations of physisorbed water in the
174 interlamellar space of montmorillonite, respectively. Others observed bands, appearing on all
175 investigated materials between 700 and 450 cm⁻¹ correspond to Si-O-Si stretching (690 cm⁻¹)
176 and deformation (516 and 468 cm⁻¹) of tetrahedral sites (Mendelovici, 1973). The signals at
177 885, 843 and 777 cm⁻¹ are due to Al-OH deformation, Fe-OH deformation and Mg-OH
178 deformation respectively (Amarasinghe et al., 2008; Katti et al., 2006). After acid activation,
179 some changes in the FTIR spectra (Fig. 1b) can be observed. The band intensity at 3620 and
180 1640 cm⁻¹ increased slightly, thus suggesting that the MtH sample is more hydrophilic than
181 the Mt-Na. The appearance of a shoulder around 3150 cm⁻¹ traduces the presence of Si-OH
182 groups arising upon Si-O-Al bonds breaking during the acid pretreatment. The OH stretching
183 region of Mt is sensitive to the effects of interlayer modification, and the intercalation
184 followed by the grafting of the organosilane on the internal surface -OH groups of MtH
185 should have a major influence on the OH stretching pattern of the grafted organoclays. As a
186 matter of fact, upon grafting of AEP-TMS, some pronounced changes occurred in the spectra
187 of amino-montmorillonite clays samples (Mt-NH₂ and MtH-NH₂) (Fig. 1c and 1d): the new
188 absorption band at 2928 cm⁻¹ is due to the antisymmetric stretching of -CH₂ bonds (Qin et al.,
189 2010, Xue et al., 2011,) while the bands appearing at 1473 cm⁻¹ and 1316 cm⁻¹ are assigned to
190 -CH₂- scissoring deformation (symmetric and asymmetric respectively), both from the silane
191 coupling agent. The symmetric stretching of -CH₂ bonds are also visible at 2840 cm⁻¹ (Qin et
192 al., 2010). Comparing curves (c) & (d) of Figure 1 enables to point out qualitatively the
193 interest of the acidic treatment on the efficiency of the functionalization (slightly more intense
194 C-H bond for the MtH-NH₂ sample). The grafting process leads to a decrease in the intensity
195 of the bands characteristics of OH stretching and bending vibrations of adsorbed water and
196 the hydroxyl groups (respectively at 3404 and 1640 cm⁻¹) and a very small deviation of the
197 positions of these bands. This is due in one hand to the involvement of the hydroxyl groups in

198 the grafting process, and in another hand to the removal of cations from the octahedral layer
199 which causes some loss of water molecules.

200

201

(Figure 1 near here)

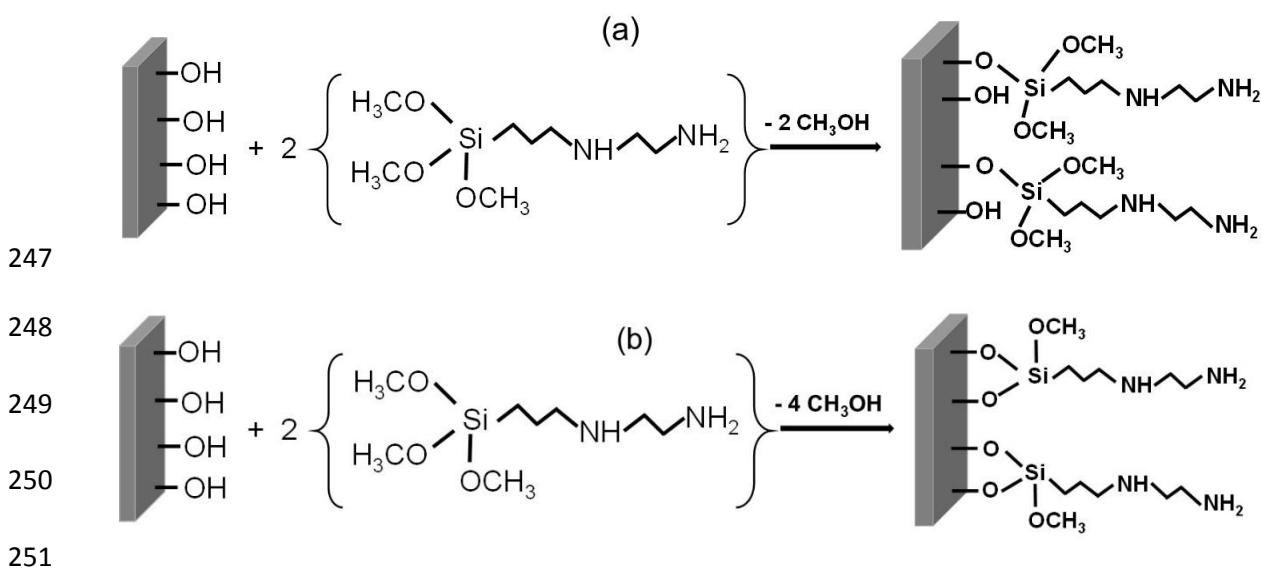
202 XRD patterns of raw Mt-Na, acid treated Mt (MtH), Mt-NH₂ and MtH-NH₂ are shown in Fig.
203 2. A comparison of the results obtained indicates that the original structure has been retained
204 after modification. An approximate value of 1.21 nm ($2\theta = 7.3^\circ$) was estimated for the basal
205 spacing d_{001} of the Mt-Na sample (Fig. 2A, curve a). The acid activation led to an increase in
206 the basal spacing (1.21 to 1.30 nm), most likely due to water adsorption. The increased
207 hydrophilic feature of the MtH (Fig. 2A, curve b) with respect to the starting Mt was
208 previously indicated by the IR results. Direct grafting of AEP-TMS onto Mt-Na showed a
209 minimal difference in basal spacing between the Mt-Na and Mt-NH₂ samples (1.21 nm to 1.36
210 nm at $2\theta = 6.5^\circ$) (Fig. 2A, curve c). This slight difference is probably due to a small amount
211 of AEP-TMS in the interlamellar space of the clay mineral. Usually, the intercalation of guest
212 species in montmorillonite layers induces significant changes in the basal spacing (Mercier &
213 Detellier, 1995). The acid activation used in MtH-NH₂ synthesis resulted in a much bigger
214 increase in the basal spacing of the MtH and MtH-NH₂ samples (1.30 nm to 1.80 nm) (Fig.
215 2A, curve c), probably due to AEP-TMS incorporated in basal spacing. It may indicate that
216 the silane molecules were mainly hydrolyzed and condensed with the hydroxyl groups on the
217 external surface of Mt. Another explanation could be that the interlayer organosilane
218 molecules were hydrolyzed and condensed to form a cross-linked structure, causing small
219 increase on the basal spacing and influencing the grafting of AEP-TMS on MtH. The TGA
220 curves (Fig. 2B) revealed a significant increase in the loss of adsorbed water mass on the MtH
221 (Fig. 2B, curve b) compared to raw Mt (Fig. 2B, curve a). Usually, the increase in water
222 content leads to an increase in the basal spacing. This increase in water molecules is explained
223 by the replacement of sodium ions in the interlayer space by water molecules. On the
224 materials Mt-NH₂ (Fig. 2B, curve c) and MtH-NH₂ (Fig. 2B, curve d), the mass losses of
225 absorbed water are comparable to that of the raw clay. Our hypothesis is that for the Mt-NH₂
226 sample, the organosilane was grafted on the surface without replacement of sodium ions while
227 for the MtH-NH₂, there was replacement of water molecules in the interlayer space of MtH
228 and grafting on the surface.

229

230

(Figure 2 near here)

231 Elemental analysis was performed on the amino-grafted materials (Mt-NH₂ and MtH-NH₂)
 232 for C, H and N. The results obtained were 11.07 % C, 2.60 % H, 4.66 % N for Mt-NH₂ and
 233 9.73 % C, 2.44 % H, 3.89 % N for MtH-NH₂. This was evidence of the presence of nitrogen-
 234 containing moieties. To determine the structural formula of the grafted clay using the the
 235 chemical formula of Mt, NaSi₁₆(Al₆FeMg)O₂₀(OH)₄, we assumed grafting via one, two, three
 236 or four methoxy groups on one clay mineral structural unit as usually obtained during
 237 silylation of montmorillonite surfaces (Su et al., 2012). The theoretical content of C: 11.34%,
 238 H: 2.72%, N: 3.78% for Mt-NH₂ and 10.04 % C, 2.46 % H, 3.90 % N for MtH-NH₂ is in
 239 accordance with the mechanism proposed in Scheme 1, supporting the idea that the chemical
 240 bonding of AEP-TMS on the clay material was effective as revealed by infrared results. The
 241 proposed structural formulas of Mt-NH₂ and MtH-NH₂ were
 242 NaSi₁₆(Al₆FeMg)O₂₀(OH)₂[OSi(OCH₃)₂(CH₂)₃NH(CH₂)₂NH₂]₂ and
 243 Si₁₆(Al₅FeMg)O₂₁(OH)₃[O₂Si(OCH₃)(CH₂)₃NH(CH₂)₂NH₂]₂ respectively. An increase in Si-
 244 OHs bonds and a decrease in the number of Al can be observed in the MtH-NH₂ formula
 245 compared to Mt-NH₂ formula. These increase and decrease occurred during the acid
 246 pretreatment by Si-O-Al bonds breaking during the removal of Al.



252 **Scheme 1.** Proposed mechanism for the grafting of AEP-TMS on (a) Mt and (b) MtH.

253 The sodium montmorillonite clay sample is mesoporous with a specific surface area of 31.48
 254 m²/g. After direct grafting, the specific surface area of the synthesized material (Mt-NH₂)
 255 decreased to 8.49 m²/g, suggesting that the organosilane is covalently bound to the individual

256 -OH groups at the edge of clay platelets, as shown by a previous work (Celis et al., 2000). It is
257 known that the low silanol surface density of montmorillonite clay mineral is a main factor
258 limiting the covalent grafting of organic ligands and that better performance can be obtained
259 by grafting organic functions in the interlayer region of montmorillonite (Celis et al., 2000;
260 Mercier and Detellier, 1995). Another sample of sodium montmorillonite was activated in
261 acid medium (MtH) and then functionalized (MtH-NH₂). A specific surface area of 19.66
262 m²/g obtained for the MtH-NH₂ material suggests a low graft rate on the surface of the
263 material but the increase in basal spacing obtained in XRD analysis from 1.36 nm (Mt-NH₂)
264 to 1.80 nm (MtH-NH₂) confirms the intercalation followed by the concomitant coupling of the
265 organosilane moieties on the -OH groups found the internal surface of on the clay layers, and
266 on the borders of the clay platelets.

267 SEM micrographs of the GCE modified in turn by Mt-Na, acid treated Mt (MtH), Mt-NH₂
268 and MtH-NH₂ respectively are shown in Fig. 3. On the micrographs of GCE/Mt-Na and
269 GCE/MtH (Fig. 3a & 3b), one can observe the strong tendency toward aggregation and the
270 compact aspect of the material, with particles arranged in the form of agglomerates of
271 irregular shape and flat surface. For the Mt-NH₂ and MtH-NH₂ modified GCEs (Fig. 3c & 3d),
272 the particles are even more agglomerated and present onto the electrode surface as big
273 aggregates, suggesting that the functionalization of clay may have contributed to enhance the
274 edge-to-edge and face-to face interactions between organoclay platelets.

275

276 **(Figure 3 near here)**

277

278 *3.2. Permeability properties of various modified electrodes*

279 The electrochemical behavior of redox species at clay modified electrodes is expected to be
280 affected by three main parameters: the concentration of the analyte, the accessible area of the
281 working electrode and the speed of mass transfer for the probe within the film (Fitch, 1990).
282 Cyclic voltammetry (CV) was applied to the modified electrodes to evaluate their
283 preconcentration/rejection properties or permselective behavior towards [Fe(CN)₆]³⁻ and
284 [Ru(NH₃)₆]³⁺ electroactive probes. CV experiments were performed using the bare GCE,
285 GCE/Mt-Na, GCE/Mt-NH₂ and GCE/MtH-NH₂ in 0.1 M KCl/HCl solution at pH 1. Both
286 probes gave rise to well defined reversible CV responses at on the bare GCE (curves (a) in
287 Figure 4(A) & (B)). The peak current values obtained are I_{pa} 3.06 μA (anodic), I_{pc} 2.9 μA

288 (cathodic) and I_{pa} 1.46 μA (anodic), I_{pc} 1.95 μA (cathodic), respectively for $[\text{Fe}(\text{CN})_6]^{3-}$ and
289 $[\text{Ru}(\text{NH}_3)_6]^{3+}$ probes, and they did not change upon multiple potential scanning. This was not
290 the case when recording multisweep CV curves at the clay-modified electrodes. Typical
291 results obtained for 0.5 mM $[\text{Fe}(\text{CN})_6]^{3-}$ probe (in the potential range of 0.0 V to 0.6 V) are
292 illustrated in Fig. S1 (Supplementary data). On Fig. S1a, one can see that the voltammetric
293 signal on the GCE/Mt-Na is constant over multiple potential scans, the peak currents values
294 (I_{pa} 1.30 μA , I_{pc} 1.27 μA) lower than those obtained at the bare. Such behavior is explained
295 by the electrostatic repulsions between the negative surfaces of Mt-Na and the anionic probe
296 $[\text{Fe}(\text{CN})_6]^{3-}$ (Tonle et al., 2004). On the opposite, CV signals were found to grow dramatically
297 upon multisweep scan when using the amino-montmorillonite modified GCE (Fig. S1 b & c),
298 indicating the progressive accumulation of $[\text{Fe}(\text{CN})_6]^{3-}$ that leveled off after about 50 scans,
299 with steady-state peak current values larger by one order of magnitude than on bare GCE
300 (Fig. 4A). Such accumulation is due to the electrostatic attraction between the negative redox
301 probe $[\text{Fe}(\text{CN})_6]^{3-}$ and the positively charged amino groups present in the AEP-TMS chain
302 grafted onto the montmorillonite surface (which are protonated in the acidic analysis medium
303 used here, in the form of $-\text{NH}_3^+$ groups). As also shown in Fig. 4A, the electrochemical signal
304 after 50 scans on GCE/MtH-NH₂ (I_{pa} 22.22 μA , I_{pc} 23.66 μA) is significantly higher than
305 those obtained on GCE/Mt-NH₂ (I_{pa} 14.79 μA , I_{pc} 17.74 μA). This difference is due to a
306 larger content of AEP-TMS groups grafted onto the acid-treated montmorillonite.

307 Cyclic voltammetry of cationic probe $[\text{Ru}(\text{NH}_3)_6]^{3+}$ (Fig. S2 in Supplementary data) was also
308 carried out in the potential range of -0.5 V to 0.0 V in the same electrolyte solution as above
309 (0.1 M KCl/HCl, pH 1). For GCE coated with Mt-Na, a progressive accumulation was
310 observed, reaching steady-state current values after about 50 scans (Fig. S2a). The peak
311 currents at saturation (I_{pa} 19.33 μA , I_{pc} 18.06 μA) were much larger than those obtained at
312 the bare GCE (I_{pa} 1.46 μA , I_{pc} 1.95 μA), as explained by favorable electrostatic attraction
313 between the cationic redox probe and the negatively charged montmorillonite platelets. This
314 behavior results from both true physical diffusion of the analyte upon ion exchange in the
315 coating, and mass-charge transfer phenomena arising from potential scanning (Tonle et al.,
316 2004). On the opposite, when using GCE/Mt-NH₂ and GCE/MtH-NH₂ in the same conditions
317 (Fig. S2 b & c), the protonated organoclay films acted as electrostatic barrier preventing the
318 uptake of the cationic $[\text{Ru}(\text{NH}_3)_6]^{3+}$ species. This resulted in much lower redox peak currents
319 on GCE/Mt-NH₂ (I_{pa} 3.81 μA , I_{pc} 4.81 μA) and GCE/MtH-NH₂ (I_{pa} 2.21 μA , I_{pc} 3.62 μA)
320 than for the non-grafted clay film electrode GCE/Mt-Na (Fig. 4B), as explained by the
321 electrostatic repulsions between the positively charged redox probe and the $-\text{NH}_3^+$ groups of

322 the organoclays. Again, the permselective effect was more intense for GCE/MtH-NH₂
323 electrode, supporting the idea that acid activation prior to AEP-TMS grafting resulted in more
324 effective montmorillonite modification.

325 **(Figure 4 near here)**

326 *3.3. EIS results*

327 Electrochemical impedance spectroscopy (EIS) was used to evaluate the electrochemical
328 properties of the various electrodes. In EIS, the semicircle portion at higher frequencies
329 corresponds to the electron-transfer limited process (equals the charge-transfer resistance,
330 R_{ct}), and the linear part at lower frequencies corresponds to the diffusion process. Fig. 5
331 shows the Nyquist plots of EIS for the bare GCE, GCE/Mt-Na, GCE/Mt-NH₂ and GCE/MtH-
332 NH₂ electrodes, as recorded in 0.1 M KCl containing 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ (1:1) solution over
333 the frequency range of 0.1 Hz-10 kHz. At the bare GCE (curve (a) in Fig. 5), the probe is easy
334 to transfer electron on the electrode surface, yet with a non-negligible R_{ct} value of 4736 Ω .
335 The charge-transfer resistance was even larger ($R_{ct} = 5263 \Omega$) when using GCE/Mt-Na (curve
336 (b) in Fig. 5), which is explained by some shielding behavior of the positively charged Mt
337 clay particles on the anionic $[\text{Fe}(\text{CN})_6]^{3-/4-}$ species. With the grafting of AEP-TMS on Mt-Na,
338 the resistance decreased (see curves (c) and (d) of Fig. 5), implying that Mt-NH₂ and MtH-
339 NH₂ promote the transport properties of the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ probes. This resulted in lower R_{ct}
340 values ($R_{ct} = 114.35 \Omega$ with GCE/MtH-NH₂ and $R_{ct} = 167.84 \Omega$ with GCE/Mt-NH₂), the small
341 difference between them being again due to the fact that acid activation allowed the binding
342 of a greater amount of AEP-TMS moieties on the Mt clay.

343 **(Figure 5 near here)**

344

345 *3.4. Preliminary studies on the electrochemical behavior of catechol*

346 *3.4.1. Direct electrochemistry of catechol*

347 The electrochemical behaviour of catechol on various electrodes was carried out in 0.1 M
348 Britton-Robinson buffer (BRB) solution at pH 4 in the potential range from -0.2 V to 0.8 V,
349 and the results are shown in Fig. 6. A pair of quasi-reversible redox peaks are observed on all
350 CV curves, indicating that the electroactive substance can reach and be detected on all
351 electrode surfaces. Nevertheless, significant variations in peak intensity were observed

352 depending on the electrode type. Peak currents were almost 2-fold lower on GCE/Mt-Nathan
353 on bare GCE (curves(a) & (b) on Fig. 6), whereas significantly more intense signals were
354 observed when passing to GCE modified by amino-grafted materials (curves(c) & (d) on Fig.
355 6). This indicates the interest of the amino-grafted materials for enhancing the CT oxidation
356 signal, suggesting the existence of accumulation effects originating from the grafted material,
357 which are likely to improve the detection of CT, yet with slightly better response for
358 GCE/MtH-NH₂ than for GCE/Mt-NH₂ (compare curves (c) & (d) on Fig. 6). This
359 demonstrates the interest of the acid activation used during the grafted process to prepare
360 MtH-NH₂ material, and also for CT detection. Such improvement is similar to that observed
361 for the negatively charged redox probe discussed above (Fig. 4A), but in the present case
362 “simple” electrostatic considerations cannot explain the phenomenon as catechol is neutral at
363 pH values below its pKa (9.14) (Nurchi et al., 2009), and deprotonated at pH above that pKa.
364 The CV results indicate a clear positive effect of the ethylenediamino groups grafted on the
365 clay material, and this was also confirmed for CT detection by DPV (see section 3.5.1). A
366 possible explanation could be a favoured incorporation of CT in the organoclay as a result of
367 larger interlayer distance between the clay sheets upon grafting (see section 3.1 and Fig. 2)
368 and also a more hydrophobic environment generated by the acidic treatment (in comparison
369 to the hydrophilic Mt-Na material). The O and N groups of Mt-NH₂ and MtH-NH₂ acted as
370 electron transfer mediators by possibly forming hydrogen bonding interactions with hydroxyl
371 groups of CT. They have contributed to weakening the hydroxyl bond energies and facilitated
372 the electron transfer through O- -HO and N- -HO (Ding et al., 2005).
373 The Mt-NH₂ and MtH-NH₂ modifiers might also contribute to accelerate the electron transfer
374 rates for catechol oxidation, as suggested from slightly lower overpotentials with respect to
375 bare GCE (compare peak potentials of curves c & d to curve a in Fig. 6), also in agreement
376 with the much lower charge transfer resistance values observed by EIS for the modified
377 electrodes (see section 3.3). Due to its better performance with respect to CT detection, the
378 GCE/MtH-NH₂ electrode was used for further experiments.

379

380

(Figure6 near here)

381

382 *3.4.2. Effect of scan rate on the electrochemical response of catechol at GCE/MtH-NH₂*

383 The influence of potential scan rate on the electrochemical response of catechol was studied
384 by cyclic voltammetry and the results obtained are shown in Fig. 7. The peak currents
385 increased with the scan rate in the studied range (Fig. 7a), remaining linear with the square
386 root of the scan rate ($v^{1/2}$) (Fig. 7b). This indicates a diffusion-controlled process,
387 phenomenon that was also confirmed by plotting the double logarithmic of I_{pa} vs scan rate
388 (Fig. 7c), giving a slope ($\partial \log(I_{pa})/\partial \log(v)$) equal to 0.49, close to 0.5, the characteristic value
389 for a diffusion-controlled electron-transfer mechanism (Shih et al., 2004).

390

391

(Figure 7 near here)

392

393 3.5. Differential pulse voltammetry study

394 3.5.1. Importance of the modification of Mt and effect of the detection medium

395 In order to evaluate the ability of AEP-TMS grafted Mt to accumulate quantitatively CT and
396 the interest of the acid activation step before grafting, DPVs of 0.1 mM CT were recorded in
397 0.1 M BRB solution (pH 4) on bare GCE, GCE/Mt-Na, GCE/Mt-NH₂ and GCE/MtH-NH₂
398 (Fig. 8). Peak currents were found to decrease from the bare GCE (1.7 μ A) to GCE/Mt-Na
399 (0.75 μ A), and increase when passing from GCE/Mt-Na (0.75 μ A) to GCE/Mt-NH₂ (2.15 μ A)
400 and to GCE/MtH-NH₂ (2.9 μ A). Meanwhile, the peak potentials shifted towards less anodic
401 values: from +0.358 V on bare GCE to +0.271 V on GCE/Mt-Na, to +0.270 V on GCE/Mt-
402 NH₂ and to +0.260 V on GCE/MtH-NH₂. This indicates an the ability of Mt-NH₂ and MtH-
403 NH₂ to induce effective enhancement of CT oxidation signal and improve the electron transfer
404 rates, confirming the existence of both accumulation and electrocatalytic effects as suggested
405 above, originating from the organoclay materials with respect to the detection of CT. Note
406 that acid activation improved somewhat further the electrochemical detection of CT by
407 increasing the current peak signal.

408

409

(Figure 8 near here)

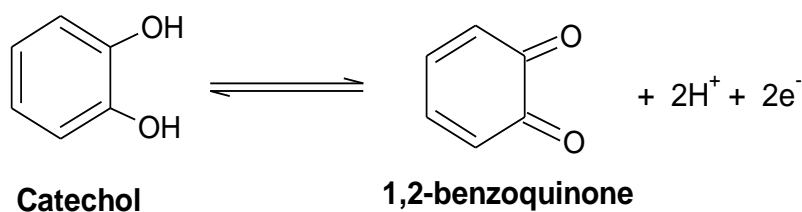
410

411 Some optimization studies were also performed. Although the composition of the detection
412 medium was not really critical (on the basis of three different buffer solutions), the BRB
413 solution (pH 4) was found to be more sensitive to CT detection (see Fig. S3, Supplementary

414 data). It will be thus used for further experiments. Fig. S4 (Supplementary data) shows the
415 dependence of DPV peak currents on the accumulation time for the analysis of 0.1 mM CT at
416 GCE/MtH-NH₂ electrode. The response was very fast, and the electrode was saturated after
417 30 s, reaching a plateau up to 140 s preconcentration. Fast adsorptive equilibrium is probably
418 due to low resistance to mass transport in such highly porous film electrode. A duration of 30
419 s was used afterwards for the accumulation of CT.

420 3.5.2. Influence of pH on the peak current and potential

421 The influence of the pH of the detection medium on the electrochemical response of CT was
422 studied in the range from 2 to 8 in BRB solution. Fig. 9a and curve (2) on Fig. 9b show that
423 the oxidation peak potentials of CT on GCE/MtH-NH₂ shifted negatively with an increase in
424 the solution pH, indicating that protons are involved in the reaction process at the electrode
425 surface. The linear regression equation was $E_p(\text{V}) = -0.0521 \text{ pH} + 0.4819$ ($R^2 = 0.998$),
426 demonstrating that equal number of electrons and protons are involved in the oxidation of CT.
427 This is in agreement with the previously reported mechanism for CT, that is oxidized to 1,2-
428 benzoquinone (Scheme 2) (Temerk et al., 2006; Unnikrishnan et al., 2012; Yue et al., 2013).
429 Curve (1) on Fig. 9b shows the variation of the peak current of CT with pH. The peak
430 intensity was high in acidic media, for pH values below 5, with a maximum at pH 2. The
431 electrode response became less pronounced in basic media. The preconcentration of CT was
432 more effective in acidic media on GCE/MtH-NH₂, a BRB solution at pH 2 was used in further
433 experiments.



434
435 **Scheme 2.** Mechanism of catechol oxidation

436
437 **(Figure 9 near here)**

438
439

440 3.5.3. Calibration

441 The calibration graph for CT detection was plotted from DPV analyses performed under the
442 optimal conditions obtained above, in the concentration range from 5 μM to 80 μM , using the
443 GCE/MtH-NH₂ electrode. As shown by the inset in Fig. 10, a linear variation of peak current
444 (I_p) vs CT concentration was obtained in the explored range, with a sensitivity of 0.0468
445 $\mu\text{A}\cdot\mu\text{M}^{-1}$ and a correlation coefficient of 0.999. The detection limit, defined by the relation
446 $3S_b/m$ (where S_b represents the standard deviation on the blank and m the slope on the
447 calibration graph) as the analyte concentration yielding such smallest detectable signal
448 (Ghoneim et al., 2000) was estimated to 0.65 μM . This demonstrates that GCE/MtH-NH₂ can
449 be exploited for the electroanalysis of CT in aqueous media in the μM range. The analytical
450 performance of GCE/MtH-NH₂ electrode is comparable or better than some data reported in
451 previous literature as shown in Table 1. A relative standard deviation (RSD) of 3.1 % for
452 parallel detections of 0.1 mM CT using five distinct electrodes (see Fig. S5 in Supplementary
453 data) was obtained, indicating a good reproducibility and repeatability of the modified
454 electrode. The anodic peak current of CT lost 4.6 % of its initial value, after 5 consecutive
455 DPV measurements on the same electrode and in the same conditions. This result shows that
456 the proposed electrode is mechanical stable and reliable for the determination of CT. The
457 performance of the method proposed herein is comparable, and even better than some data
458 already reported on the quantification of CT using other modified electrodes (Figueiredo et
459 al., 2007; Sun et al., 2008; Li et al., 2009; Zhu et al., 2009).

460

461 **(Figure 10 near here)**

462 **(Table 1 near here)**

463 *3.6. Interference of some organic molecules and real samples analysis*

464 The effect of potential interfering molecules including hydroquinone, ascorbic acid,
465 dopamine, citric acid, uric acid, D-glucose and quercetin on the DPVs response of CT has
466 been studied. The results obtained are presented in Table 2. The tolerance limit was defined as
467 the concentration ratio of the additive over CT causing less than 5.0 % relative error. Each
468 interfering species was added in the supporting electrolyte in a concentration 5-fold higher
469 than CT concentration. The results obtained showed that the oxidation peak of CT is greatly
470 affected by the presence of hydroquinone, ascorbic acid and quercetin. Catechol and
471 hydroquinone are two isomers of phenolic compounds. The broad DPV response obtained at
472 the GCE/MtH-NH₂ indicated a very tiny sign of multiple components that were not easily

473 separated. However, the selectivity of the proposed sensor was evidenced by the neglected
474 responses toward interfering species, by considering the tolerance limit defined earlier.

475

476

(Table 2 near here)

477

478 The proposed method was applied to the determination of CT in one tea sample. In this
479 experiment, the concentration of CT was calculated using the standard addition method. The
480 concentration of CT in tea sample was 0.851 mg.g^{-1} . The detection of CT was also evaluated
481 for the analysis of tap and lake water samples after filtering with a Whatman paper (diameter:
482 125mm). In DPV, no signal of CT was detected in the natural (non-spiked) water samples
483 when using GCE/MtH-NH₂, indicating that their CT contents were below the detection limit
484 ($0.65 \text{ }\mu\text{M}$). Therefore, recovery experiments were performed by measuring the DPV
485 responses from samples to which known concentrations of CT were added. The quantitative
486 results are summarized in Table 3. Recovery percentages of more than 110% obtained in the
487 case of lake water are due to intensive agricultural activities around the lake where other
488 organic compounds are found upon leaching. Yet, the amino groups on the organoclay has
489 high affinity with many biomolecules, a fact that could explain such a result.

490

(Table 3 near here)

491 4. Conclusion

492 The aim of this work was to develop a voltammetric sensor based on amino-montmorillonite
493 and apply it to the detection of catechol. [3(2-aminoethyl)]propyl groups were grafted onto
494 the surface of Na-montmorillonite and acid-activated montmorillonite clays. The results of the
495 analyses by infrared spectroscopy, X-ray diffraction and EIS confirmed the effectiveness of
496 the grafting process. It was demonstrated by CV and DPV that the detection of CT is
497 improved when using the aminated montmorillonite (MtH-NH₂) obtained after acid
498 activation, in comparison to the bare glassy carbon electrode. With DPV, the peak current of
499 GCE/MtH-NH₂ was 1.71-fold greater than signal obtained on the bare GCE. After
500 optimization of the factors affecting the accumulation/detection steps, the proposed method
501 was applied to the detection of catechol in real water samples and in a commercial tea sample.

502

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509

510 **References**

- 511 Amarasinghe, P.M., Katti, K.S., Katti, D.R., 2008. Molecular hydraulic properties of montmorillonite:
512 a polarized Fourier transform infrared spectroscopic study. *Appl. Spectrosc.* 62(12), 1303-1313.
- 513 Angela de Mello F.G., Virginia S.T.C., Wander L.V., 2009. Smectite organofunctionalized with thiol
514 groups for adsorption of heavy metal ions. *Appl. Clay Sc.* 42, 410-414.
- 515 Aziz, M.A., Selvaraju, T., Yang, H., 2007. Selective determination of catechol in the presence of
516 hydroquinone at bare indium tin oxide electrodes via peak-potential separation and redox
517 cycling by hydrazine. *Electroanalysis* 19, 1543-1546.
- 518 Biernacka, K.I., Silva, A.R., Carvalho, A. P., Pires, J., Freire, C., 2005. Organo-laponites as novel
519 mesoporous supports for Manganese(III) salen catalysts. *Langmuir* 21(23), 10825-10834.
- 520 Celis, R., Hermosin, M.C., Cornejo, J., 2000. Heavy metal adsorption by functionalized clays.
521 *Environ. Sci. Technol.* 34, 4593-4599.
- 522 Chambers, J.Q., (Eds.), 1988. The Chemistry of quinonoid compounds, in: S. Patai, Z. R. (Eds.),
523 Wiley & Sons, volume 2, New York, pp 719.
- 524 Ding, Y.P., Liu, W.-L., Wu, Q.-S., Wang, X. G., 2005. Direct simultaneous determination of
525 dihydroxybenzene isomers at C-nanotube-modified electrodes by derivative voltammetry. *J.*
526 *Electroanal. Chem.* 575, 275-280.
- 527 Fekadu, M., Mesfin, R., Merid, T., Esayas, A., 2013. Electrochemical determination of catechol in tea
528 samples using anthraquinone modified carbon paste electrode. *Nat. Sci.* 5(8), 888-894.
- 529 Figueiredo, E.C., Tarley, C.R.T., Kubota, L.T., Rath, S., Arrud, M.A.Z., 2007. Online molecularly
530 imprinted solid phase extraction for the selective spectrophotometric determination of catechol.
531 *Microchem. J.* 85, 290-296.
- 532 Fitch, A., 1990. Clay-modified electrodes: a review, *Clays Clay Miner.* 38, 391-400.
- 533 Gaber, A.M.M., 2009. Electrochemical sensor for voltammetric determination of catechol based on
534 screen printed graphite electrode. *Int. J. Elechem. Sci.* 4, 1167-1177.
- 535 Ghoneim, M.M., Hassanein, A.M., Hammam, E., Beltagi, A.M., 2000. Simultaneous determination of
536 Cd, Pb Cu, Sb, Bi, Se, Zn, Mn, Ni, Co and Fe in water samples by differential pulse stripping
537 voltammetry at a hanging mercury drop electrode. *Fresenius J. Anal. Chem.* 367, 378-383.

538 Guggenheim, S., Martin, R.T., 1995. Definition of clays and clay minerals: Joint of AIPEA and CMS
539 nomenclature Committees. *Clay Miner.* 30(3), 257-259.

540 Hirakawa, K., Oikawa, S., Hiraku, Y., Hirose, I., Kawanishi, S., 2002. Catechol and hydroquinone
541 have different redox properties responsible for their differential DNA-damaging ability. *Chem.*
542 *Res. Toxicol.* 15, 76-82.

543 Katti, K.S., Katti, D.R., 2006. Relationship of swelling and swelling pressure on silica-water
544 interactions in montmorillonite. *Langmuir* 22(2), 532-537.

545 Kong, Y., Chen, X., Wang, W., Chen, Z., 2011. A novel palygorskite modified carbon paste
546 amperometric sensor for catechol determination. *Anal. Chim. Acta* 688, 203-207.

547 Li, M.G., Ni, F., Wang, Y.L., Xu, S.D., Zhang, D.D., 2009. Sensitive and facile determination of
548 catechol and hydroquinone simultaneously under coexistence of resorcinol with a Zn/Al layered
549 double hydroxide film modified glassy carbon electrode. *Electroanalysis* 21, 1521-1526.

550 Lin, H., Gan, T., Wu, K., 2009. Sensitive and rapid determination of catechol in tea samples using
551 mesoporous Al-doped silica modified electrode. *Food Chem.* 113,701-704.

552 Lu, L., Zhang, L., Zhang, X., Huan, S., Shen, G., Yu, R., 2010. A novel tyrosinase biosensor based on
553 hydroxyapatite-chitosan nanocomposite for the detection of phenolic compounds. *Anal. Chim.*
554 *Acta* 665,146-151.

555 Marrubini, G., Calleri, E., Coccini, T., Castoldi, A.F., Manzo, L., 2005. Direct analysis of phenol,
556 catechol and hydroquinone in human urine by coupled-column HPLC with fluorimetric
557 detection. *Chromatographia* 62, 25-31.

558 Mendelovici, E., 1973. Infrared study of attapulgite and HCl treated attapulgite, *Clays Clay Miner.*
559 21, 115-119.

560 Mercier, L., Detellier C., 1995. Preparation, characterization and applications as heavy metals sorbents
561 of covalently grafted thiol functionalities on the interlamellar surface of montmorillonite.
562 *Environ. Sci. Technol.* 29(5), 1318-1323.

563 Moldoveanu, S.C., Kiser, M., 2007. Gas chromatography/mass spectrometry versus liquid
564 chromatography/fluorescence detection in the analysis of phenols in mainstream cigarette
565 smoke. *J. Chromatogr. A.* 1141(1), 90-97.

566 Montserrat, C.P., Xavier, M.B., Carole, C.B., Marty, J.M., 2010. Diazonium-functionalized
567 tyrosinase-based biosensor for the detection of tea polyphenols. *Microchim. Acta* 171,187-193.

568 Nagaraja, P., Vasantha, R.A., Sunitha, K.R., 2001. A sensitive and selective spectrophotometric
569 estimation of catechol derivatives in pharmaceutical preparations. *Talanta* 55(6), 1039-1046.

570 Nurchi, V.M., Pivetta, T., Lachowicz, J.I., Crisponi, G., 2009. Effect of substituents on complex
571 stability aimed at designing new iron(III) and aluminum(III) chelators. *J. Inorg. Biochem.*
572 103(2), 227-236.

573 Ozoner, S.K., Yalvac, M., Erhan, E., 2010. Flow injection determination of catechol based on
574 polypyrrole-carbon nanotube-tyrosinase biocomposite detector. *Curr. Appl. Phys.* 10, 323-328.

575 Park, M., Shim, I.K., Jung, E.Y., Choy, J.H., 2004. Modification of external surface of laponite by
576 silanegrafting. *J. Phys. Chem. Solids* 6(2), 499-501.

577 Piscitelli, F., Posocco, P., Toth, R., Fermeglia, M., Pricl, S., Mensitieri, G., Lavorgna, M., 2010.
578 Sodium montmorillonite silylation: unexpected effect of the aminosilane chain length. *J. Colloid*
579 *Interface Sci.* 351, 108-115.

580 Qin, Z., Yuan, P., Zhu J., He H., Liu D., Yang S., 2010. Influences of thermal pretreatment
581 temperature and solvent on the organosilane modification of Al₁₃-intercalated/Al-pillared
582 montmorillonite. *Appl. Clay Sci.* 50 (4), 546-553.

583 Rodriguez, V.M.A., Gonzalez, L.J.D., Munoz, B.M.A., 1994. Acid activation of a Spanish sepiolite:
584 physicochemical characterization, free silica content and surface area of products obtained. *Clay*
585 *Miner.* 29, 361-367.

586 Shan, D., Zhang, J., Xue, H.-G., Zhang, Y.-C., Cosnier, S., Ding, S.-N., 2009. Polycrystalline bismuth
587 oxide films for development of amperometric biosensor for phenolic compounds. *Biosens.*
588 *Bioelectron.* 24, 3671-3676.

589 Shih, Y., Zen, J.M., Kumar, A.S., Chen, P.-Y., 2004. Flow injection analysis of zinc pyrithione in hair
590 care products on a cobalt phthalocyanine modified screen-printed carbon electrode. *Talanta*
591 62(5), 912-917.

592 Suarez B.M., Flores G.L.V., Vicente R.M.A., Martin J.M.P., 1995. Acid activation of a palygorskite
593 with HCl: development of physico-chemical, textural and surface properties, *Appl. Clay Sci.*
594 10, 247-258.

595 Su, L.N., Qi T., Hongping H., Jianxi Z., Peng Y., 2012. Locking effect: A novel insight in the
596 silylation of montmorillonite surfaces. *Mater. Chem. Phys.* 136(2-3), 292-295.

597 Sun, W., Li Y.Z., Yang, M.X., Li, J., Jiao, K., 2008. Application of carbon ionic liquid electrode for
598 the electrooxidative determination of catechol. *Sens. Actuator B-Chem.* 133, 387-392.

599 Temerk, Y.M., Ibrahim, H.S.M., Schuhmann, W., 2006.
600 Cathodic adsorptive stripping voltammetric determination of the antitumor drug rutin in
601 pharmaceuticals, human urine and blood serum. *Microchim. Acta* 153, 7-13.

602 Tonle, I.K., Ngameni, E., Walcarius, A., 2004. From clay to organoclay film modified electrodes:
603 tuning charge selectivity in ion exchange voltammetry. *Electrochim. Acta* 49, 3435-3443.

604 Tonle, I.K., Ngameni, E., Tchieno, F.M.M., Walcarius A., 2015. Organoclay-modified electrodes:
605 preparation, characterization and recent electroanalytical applications. *J. Solid State*
606 *Electrochem.* 19, 1949-1973.

607 Tonle, K.I., Ngameni, E., Njopwouo, D., Carteret, C., Walcarius A., 2003. Functionalization of natural
608 smectite-type clays by grafting with organosilanes: physico-chemical characterization and
609 application to mercury (II) uptake. *Phys. Chem. Chem. Phys.* 5, 4951- 496.

610 Tonle, K.I., Ngameni, E., Walcarius, A., 2005. Preconcentration and voltammetric analysis of
611 mercury(II) at a carbon paste electrode modified with natural smectite-type clays grafted with
612 organic chelating groups. *Sens. Actuator B-Chem.* 110, 195-203.

613 Unnikrishnan, B., Ru, P.L., Chen, S.M., 2012. Electrochemically synthesized Pt-MnO₂ composite
614 particles for simultaneous determination of catechol and hydroquinone. *Sens. Actuator B-Chem.*
615 169, 235-242.

616 Van Olphen. H., Fritpiat. J.J., Data handbook for clay materials and other non-metallic
617 minerals. Pergamon Press. 1979.

618 Wang, G., He, X., Zhou, F., Li, Z., Fang, B., Zhang, X., Wang, L., 2012. Application of gold
619 nanoparticles/TiO₂ modified electrode for the electrooxidative determination of catechol in tea
620 samples. *Food Chem.* 135, 446-451.

621 Wang, Z., Li, S.L.Q., 2007. Simultaneous determination of dihydroxybenzene isomers at single-wall
622 carbon nanotube electrode. *Sens. Actuator B-Chem.* 127,420-425.

623 Xie, T., Liu, Q., Shi, Y., Liu, Q., 2006. Simultaneous determination of positional isomers of
624 benzenediols by capillary zone electrophoresis with square wave amperometric detection. *J.*
625 *Chromatogr. A* 1109, 317-321.

626 Xue, A., Zhou, S., Zhao, Y., Lu, X., Han P., 2011. Effective NH₂-grafting on attapulgite surfaces for
627 adsorption of reactive dyes. *J. Hazard. Mater.* 194, 7-14.

628 Yang, P., Zhu, Q.Y., Chen, Y.H., Wang, F.W., 2009. Simultaneous determination of hydroquinone
629 and catechol using poly(p-aminobenzoic acid) modified glassy carbon electrode. *J. Appl.*
630 *Polym. Sci.* 113, 2881-2886.

631 Yongqing, L., Jian, L., Yanjun, Z., 2017. Poly(sulfosalicylic acid)/multi-walled carbon nanotube
632 modified electrode for the electrochemical detection of catechol. *Int. J. Electrochem. Sci.* 12,
633 9512-9522.

634 Yuan, X., Yuan, D., Zeng, F., Zou, W., Tzorbatzoglou, F., Tsiakaras, P., Wang Y., 2013. Preparation
635 of graphitic mesoporous carbon for the simultaneous detection of hydroquinone and catechol.
636 *Appl. Catal. B Environ.* 129, 367-374.

637 Yue, X., Pang, S., Han, P., Zhang, C., Wang, J., Zhang, L., 2013. Carbon nanotubes/carbon paper
638 composite electrode for sensitive detection of catechol in the presence of hydroquinone.
639 *Electrochem. Comm.* 34, 356-359.

640 Zhao, D.-M., Zhang, X.-H., Feng, L.-J., Jia, L., Wang, S.-F., 2009. Simultaneous determination of
641 hydroquinone and catechol at PASA/MWNTs composite film modified glassy carbon electrode.
642 *Colloids Surf B: Biointerfaces* 74,317-321.

643 Zhao, Y., Song, X., Song, Q., Yin, Z., 2012. A facile route to the synthesis copper oxide/reduced
644 graphene oxide nanocomposites and electrochemical detection of catechol organic pollutant.
645 *Cryst. Eng. Comm.* 14, 6710-6719.

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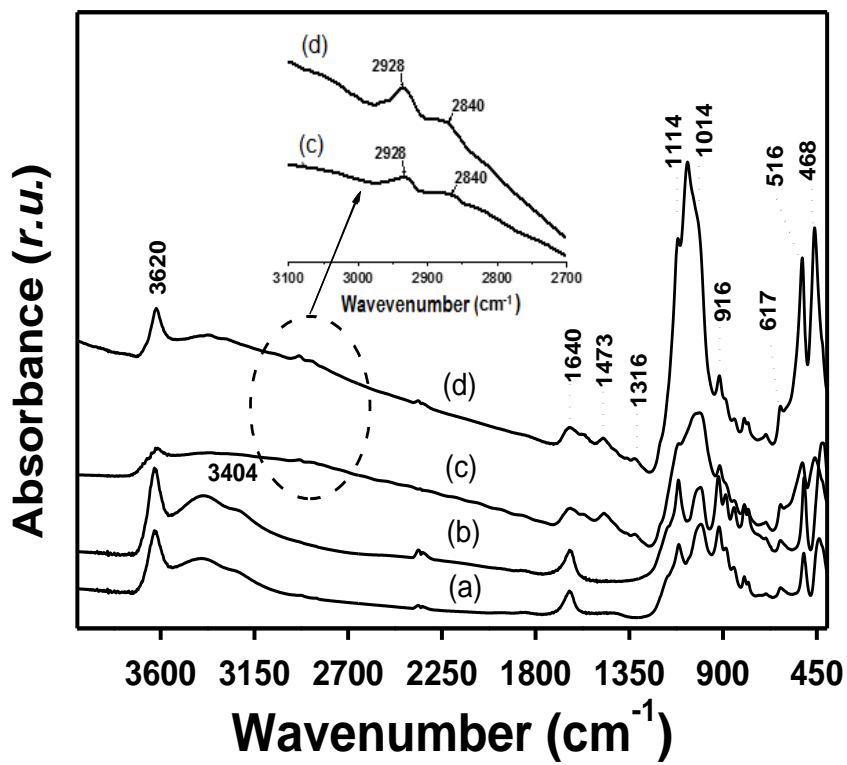


Figure 1

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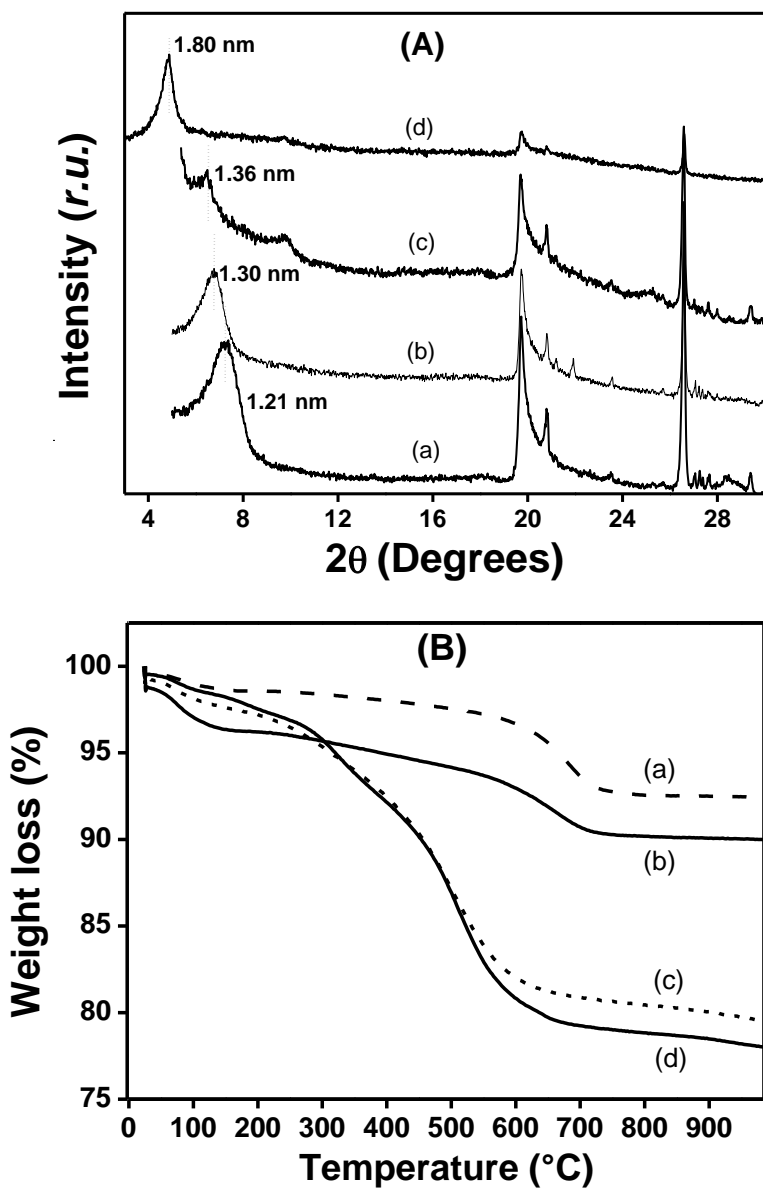


Figure 2

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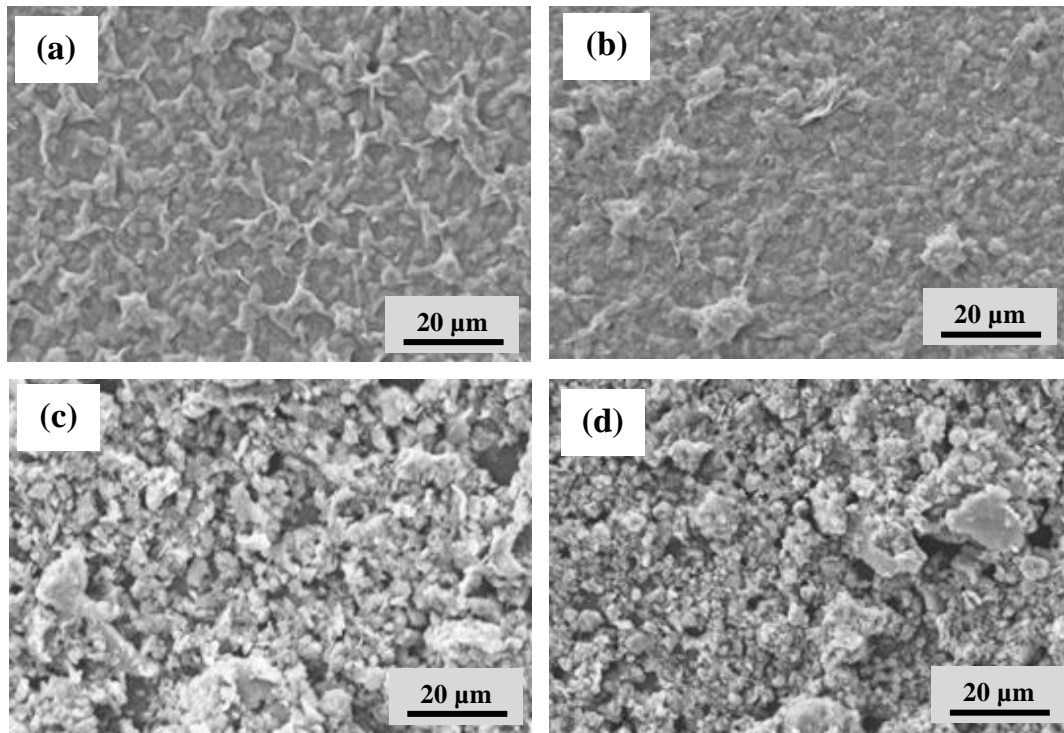


Figure 3

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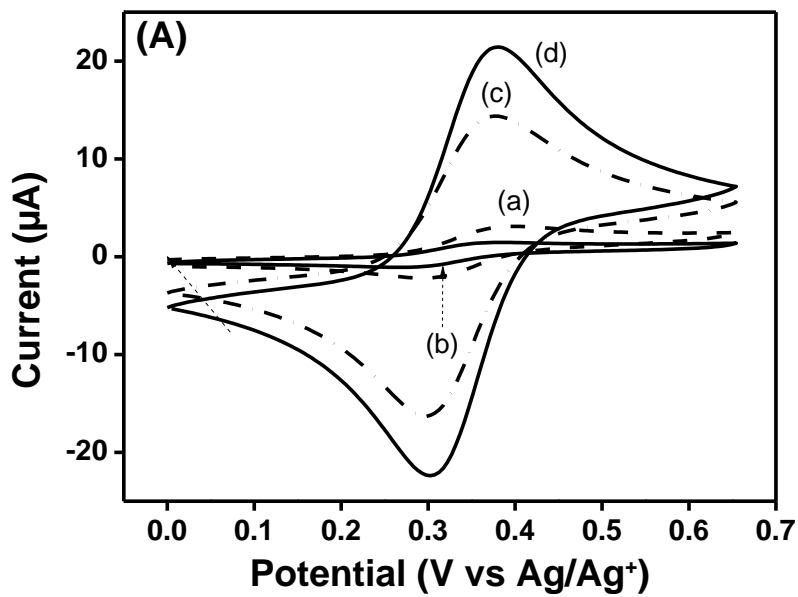
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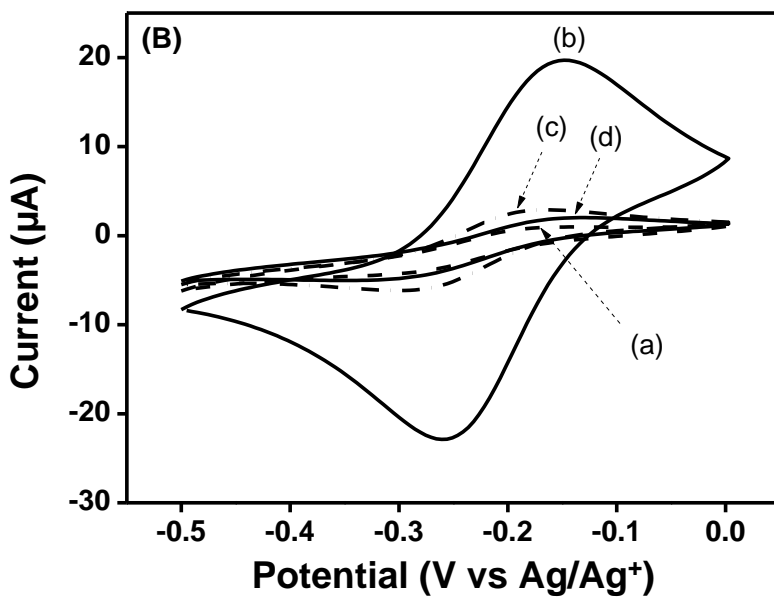
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Figure 4

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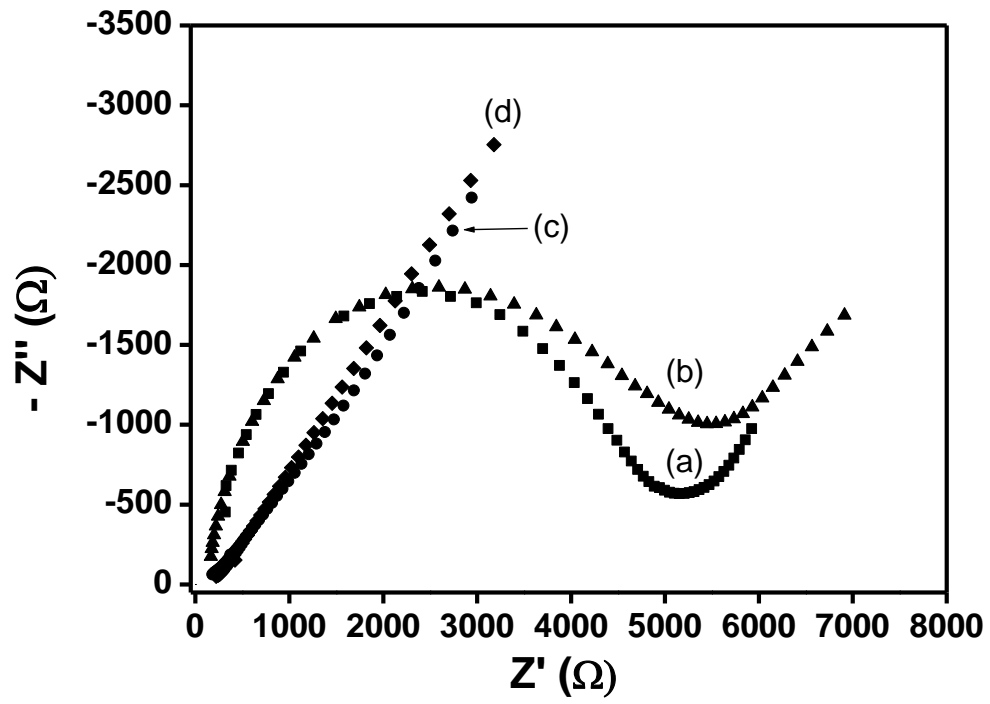
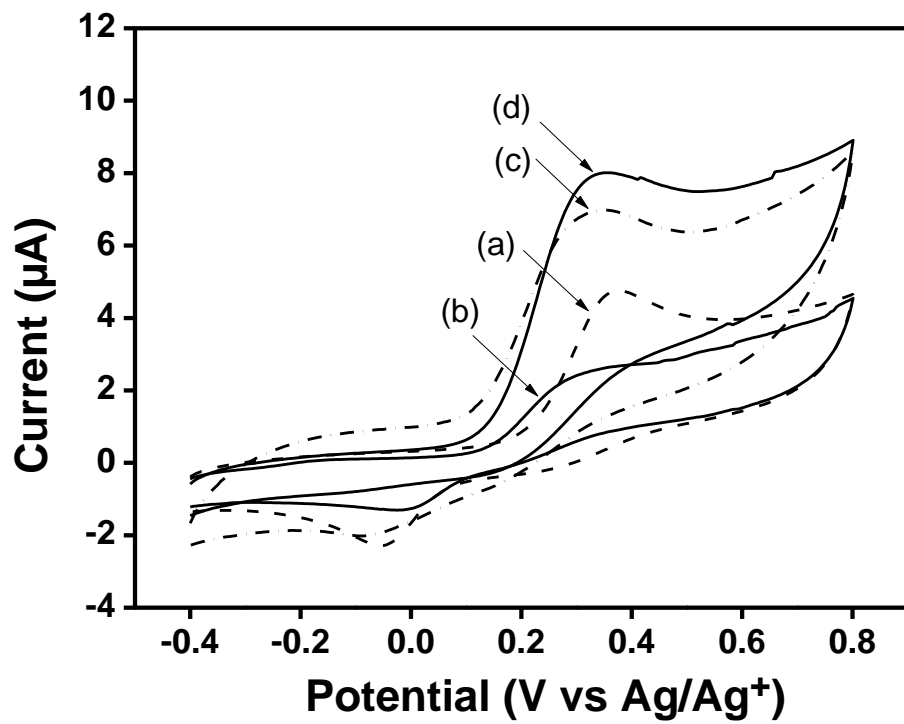


Figure 5

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Figure 6

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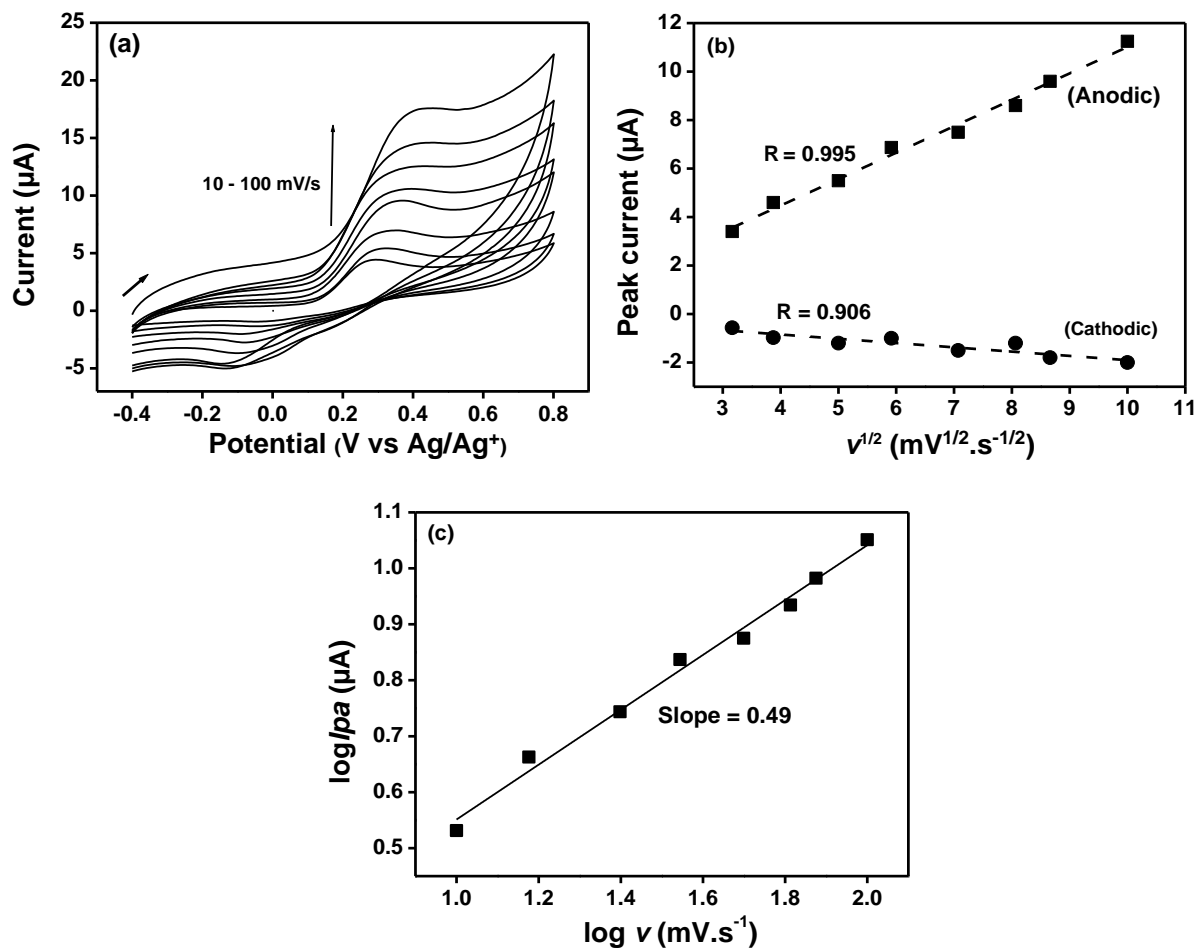


Figure 7

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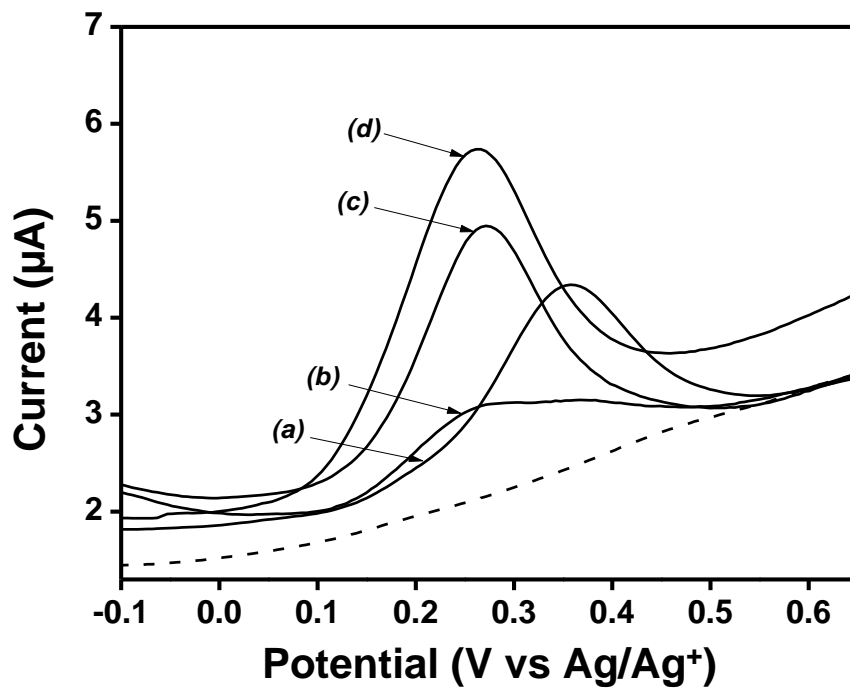


Figure 8

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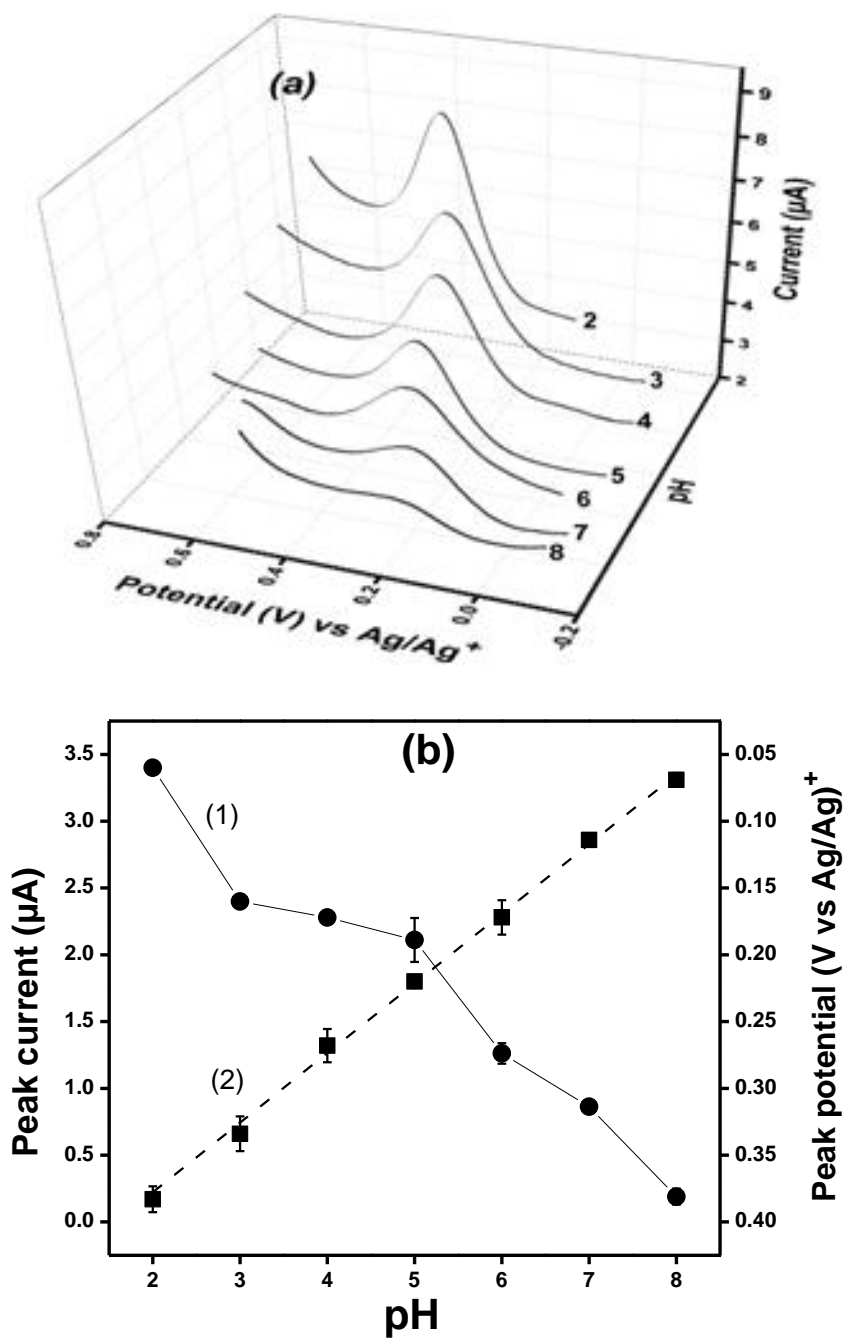
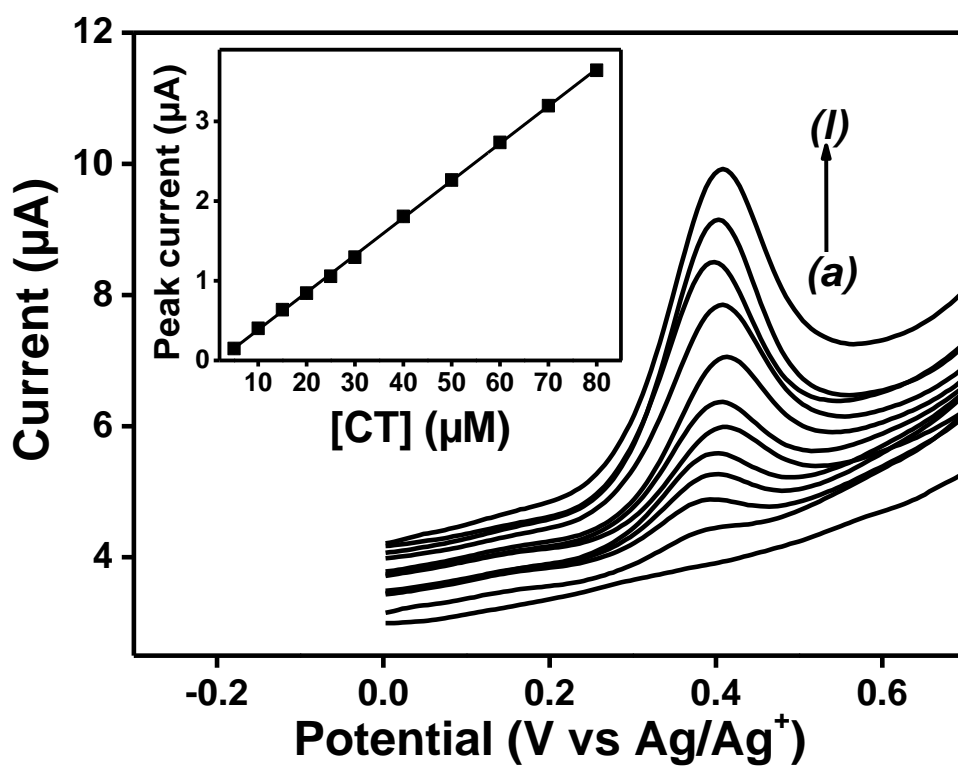


Figure 9

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Figure 10

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Figure caption

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898 **Fig. 1.** Infrared spectra of raw (a): Mt-Na, (b): MtH, (c): Mt-NH₂ and (d): MtH-NH₂.

899 **Fig. 2.** (A) Powdered X-ray diffraction patterns, and (B) TGA curves of (a): Mt-Na, (b): MtH,
900 (c): Mt-NH₂ and (4): MtH-NH₂.

901 **Fig. 3.** SEM micrographs of GCE covered with various films: (a): Mt-Na, (b): MtH, (c): Mt-
902 NH₂ and (4): MtH-NH₂.

903 **Fig. 4.** Cyclic voltammograms recorded in 0.1 M KCl/HCl (pH 1) containing (a) 0.5 mM
904 [Fe(CN)₆]³⁻ and (b) 0.5 mM [Ru(NH₃)₆]³⁺, using various electrodes: (a) Bare GCE, (b)
905 GCE/Mt-Na, (c) GCE/Mt-NH₂ and (d) GCE/MtH-NH₂. The scan rate was 20 mV.s⁻¹

906 **Fig. 5.** EIS spectra in 5 mM [Fe(CN)₆]^{3-/4-} with 0.1 M KCl at various electrodes; (a): bare
907 GCE, (b): GCE/Mt-Na, (c): GCE/Mt-NH₂ and (d): GCE/MtH-NH₂. Amplitude of the applied
908 wave potential: 5 mV.

909 **Fig. 6.** Cyclic voltammograms recorded at 50 mV.s⁻¹ for 0.2 mM CT in 0.1 M BRB solution
910 (pH 4) on (a): bare GCE, (b): GCE/Mt-Na, (c): GCE/Mt-NH₂ and (d): GCE/ MtH-NH₂.

911 **Fig. 7.** (a) Cyclic voltammograms recorded for 0.2 mM CT in 0.1 M BRB solution (pH 4) on
912 GCE/MtH-NH₂ at different scan rates (10, 15, 25, 35, 50, 65, 75 and 100 mV.s⁻¹), (b) Peak
913 current as a function of $v^{1/2}$ and (c) $\log(I_{pa})$ as a function of $\log(v)$.

914 **Fig. 8.** DPVs of 0.1 mM CT recorded in 0.1 M BRB solution (pH 4) on (a): bare GCE,
915 (b): GCE/Mt-Na, (c): GCE/Mt-NH₂ and (d): GCE/MtH-NH₂ (c). Accumulation time: 5 s. The
916 dot line represents the signal of the bare GCE in blank solution.

917 **Fig. 9.** (a) DPV curves of 0.1 mM CT (obtained in triplicate) in 0.1 M BRB solution on
918 GCE/MtH-NH₂ at various pH; (b) effect of pH, (1): on the peak current and (2): on the peak
919 potential. Accumulation time: 5 s.

920 **Fig. 10.** DPV curves recorded under optimized conditions in 0.1 M BRB solution (pH 2) on
921 GCE/MtH-NH₂ for different concentrations of CT (a-l): 5, 10, 15, 20, 25, 30, 40, 50, 60, 70
922 and 80 μ M. Accumulation time: 30 s. Inset shows the corresponding calibration graph.

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