

**Ultrasensitive Voltammetric Determination of Catechol at Gold Atomic Cluster/Poly(3,4-ethylenedioxythiophene) Nanocomposite Electrode**

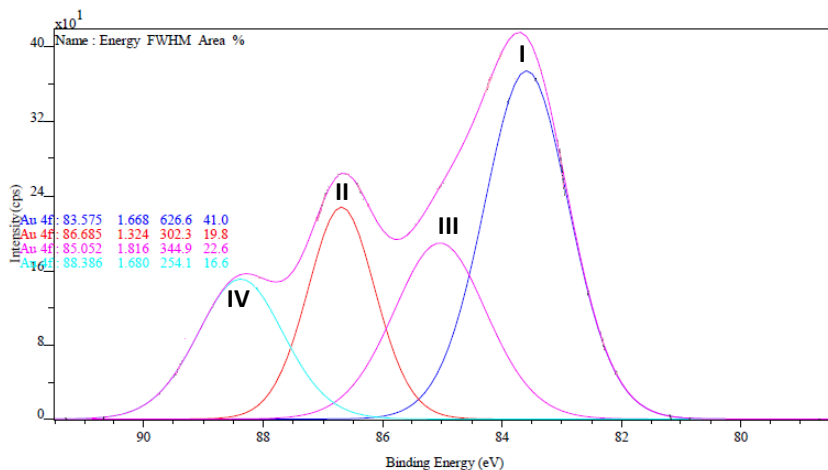
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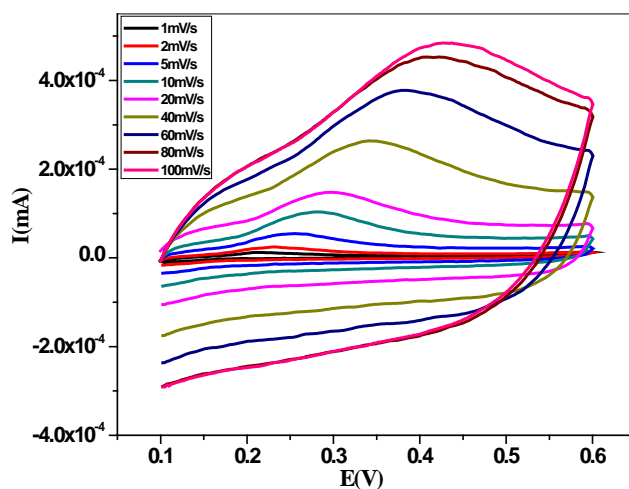
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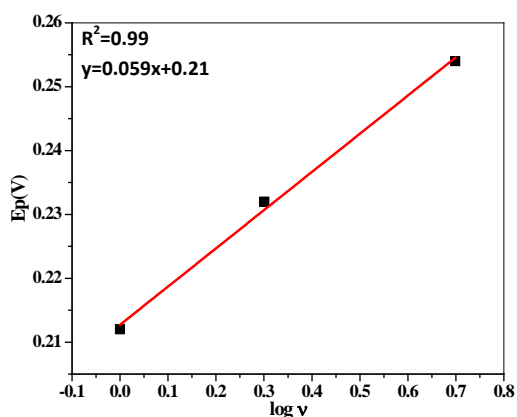
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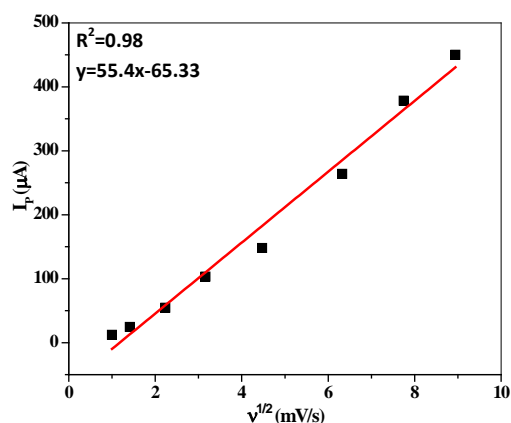
**Figure S1:** XPS spectra of electrochemically synthesized Au clusters in presence of 50mM CTAB



**Figure S2**

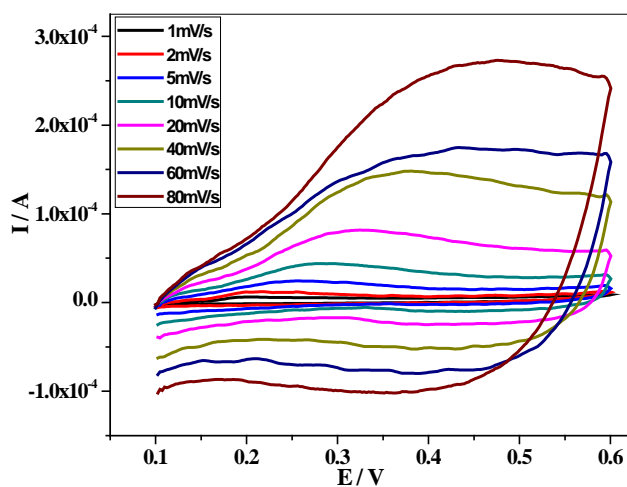


**Figure S2 (i)**

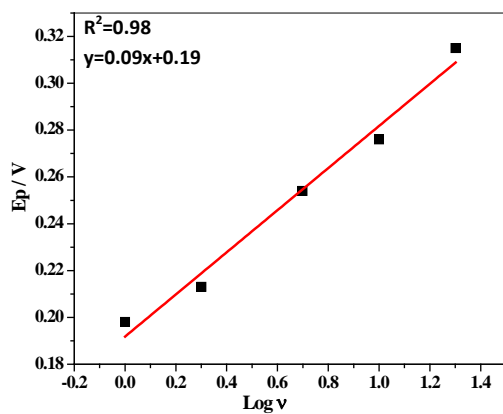


**Figure S2 (ii)**

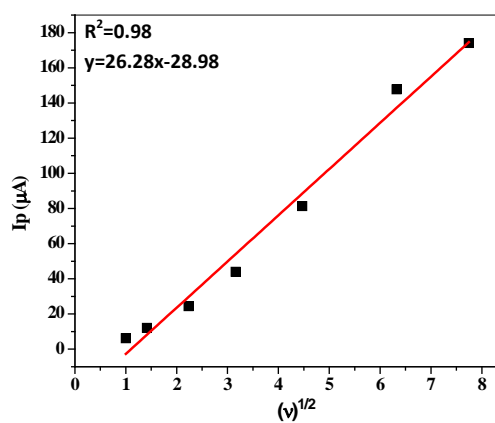
**Figure S2:** Cyclic voltammograms of oxidation of catechol ( $10^{-4}$  M) at various scan rates (1 to 100mV/s) at AuAC/PEDOT/Au nanocomposite modified gold electrode, Figure S2 (i): Plot of  $E_p$  Vs  $\log v$ , Figure S2 (ii): Plot of  $I_p$  Vs  $v^{0.5}$



**Figure S3**



**Figure S3 (i)**



**Figure S3 (ii)**

**Figure S3:** Cyclic voltammograms of oxidation of catechol ( $10^{-4}$  M) at PEDOT/Au electrode, Figure S3 (i): Plot of  $E_p$  Vs  $\log v$ , Figure S3 (ii): Plot of  $I_p$  Vs  $v^{0.5}$

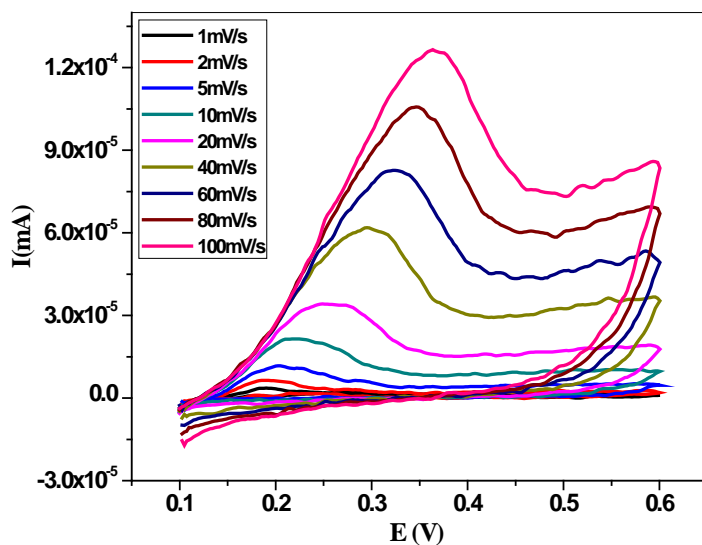


Figure S4

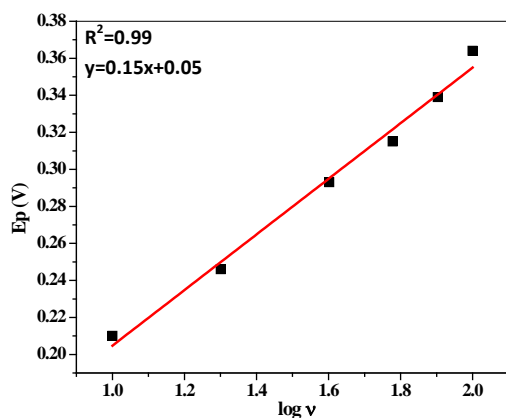


Figure S4 (i)

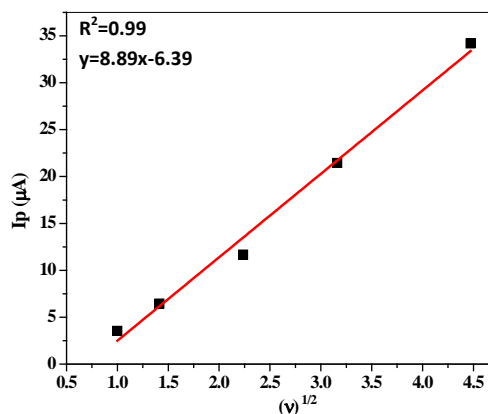
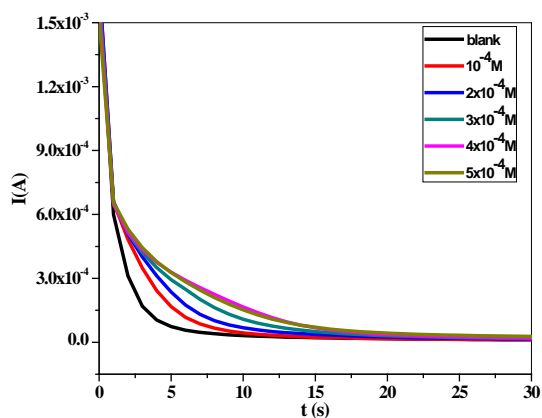


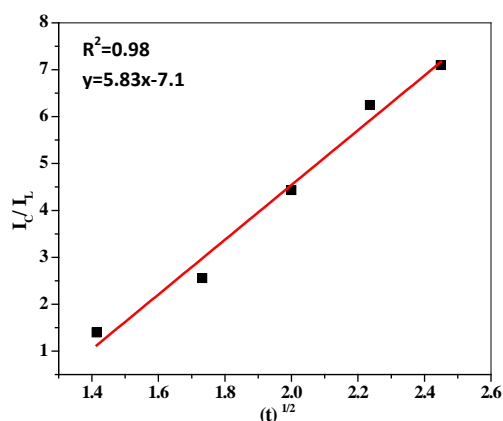
Figure S4 (ii)

**Figure S4:** Cyclic voltammograms of oxidation of catechol ( $10^{-4}$  M) at various scan rates (1 to 100mV/s) at bare gold electrode, Figure S4 (i): Plot of  $E_p$  Vs  $\log v$ , Figure S4 (ii): Plot of  $I_p$  Vs  $v^{0.5}$

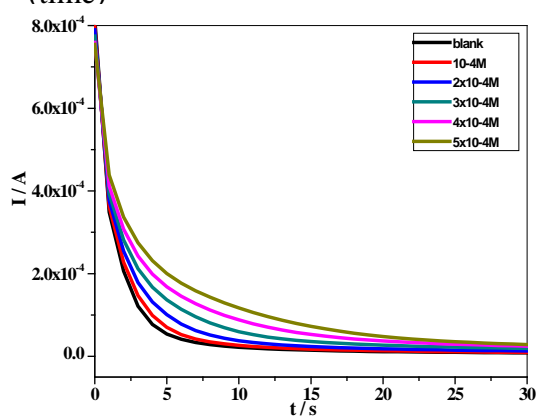


**Figure S5**

**Figure S5:** Current–time curves of AuAC/PEDOT nanocomposite electrode absence and presence of  $10^{-4}$ ,  $2 \times 10^{-4}$ ,  $3 \times 10^{-4}$ ,  $4 \times 10^{-4}$  and  $5 \times 10^{-4}$  M of catechol in 0.1M acetate buffer (pH=6.8) and 5mM Cu(II), Figure S5(i): Dependence of  $I_C/I_L$  on (time)<sup>0.5</sup>

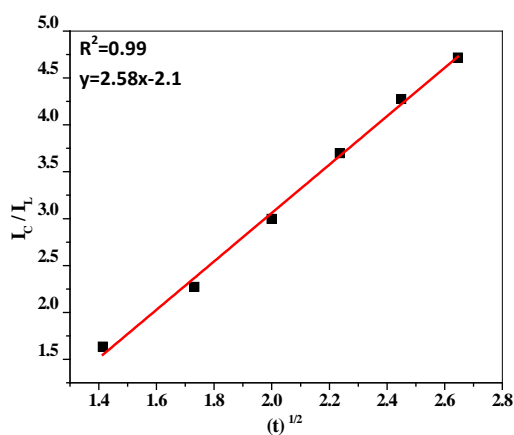


**Figure S5 (i)**

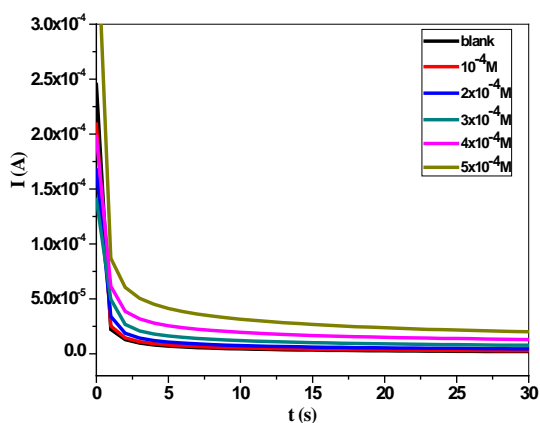


**Figure S6**

**Figure S6:** Current–time curves of PEDOT/Au electrode absence and presence of  $10^{-4}$ ,  $2 \times 10^{-4}$ ,  $3 \times 10^{-4}$ ,  $4 \times 10^{-4}$  and  $5 \times 10^{-4}$  M of catechol in 0.1M acetate buffer (pH=6.8) and 5mM Cu(II), Figure S6(i): Dependence of  $I_C/I_L$  on (time)<sup>0.5</sup>

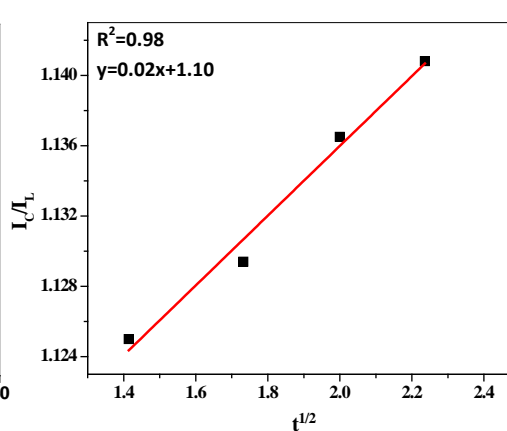


**Figure S6 (i)**

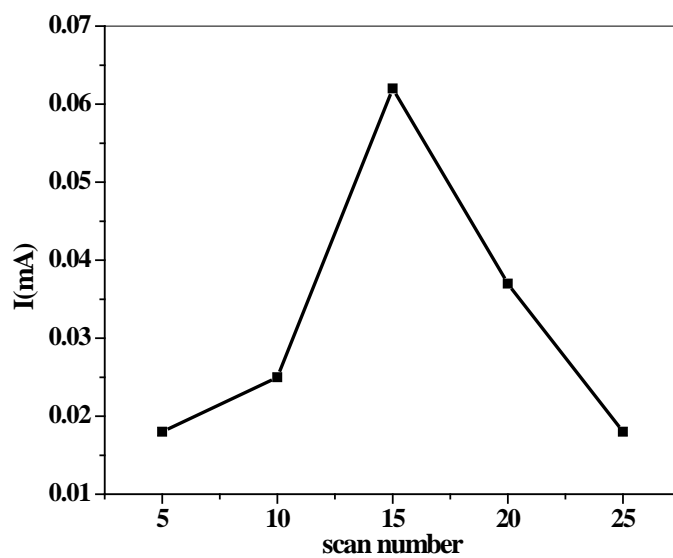


**Figure S7**

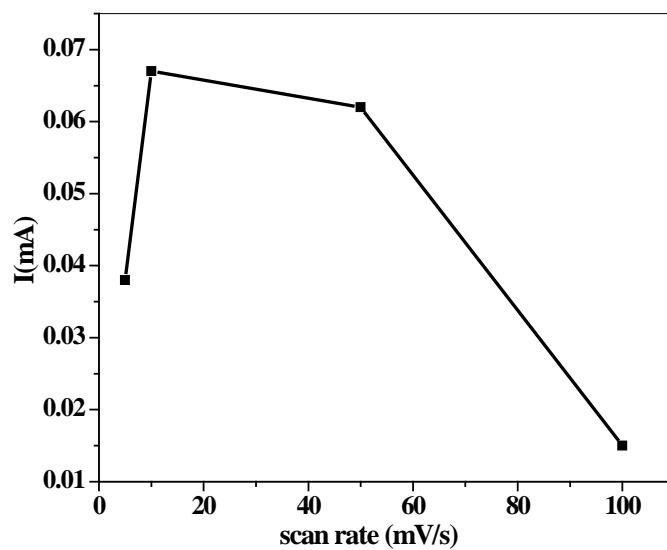
**Figure S7:** Current–time curves of bare gold electrode absence and presence of  $10^{-4}$ ,  $2 \times 10^{-4}$ ,  $3 \times 10^{-4}$ ,  $4 \times 10^{-4}$  and  $5 \times 10^{-4}$  M of catechol in 0.1M acetate buffer (pH=6.8) and 5mM Cu(II), Figure S7(i): Dependence of  $I_C/I_L$  on (time)<sup>0.5</sup>



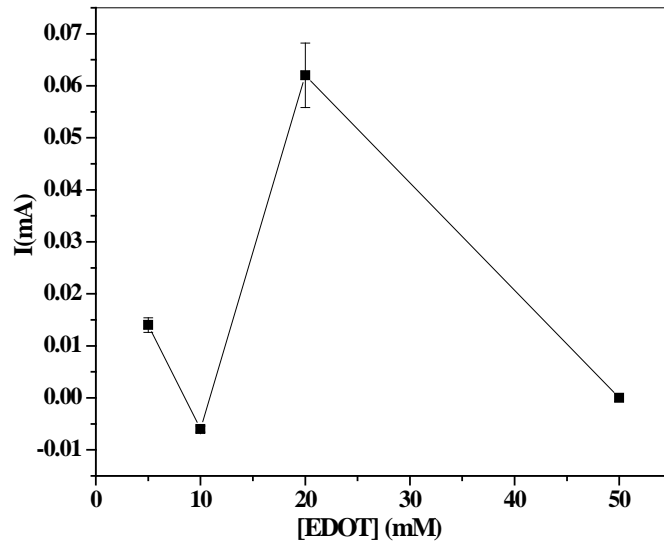
**Figure S7 (i)**



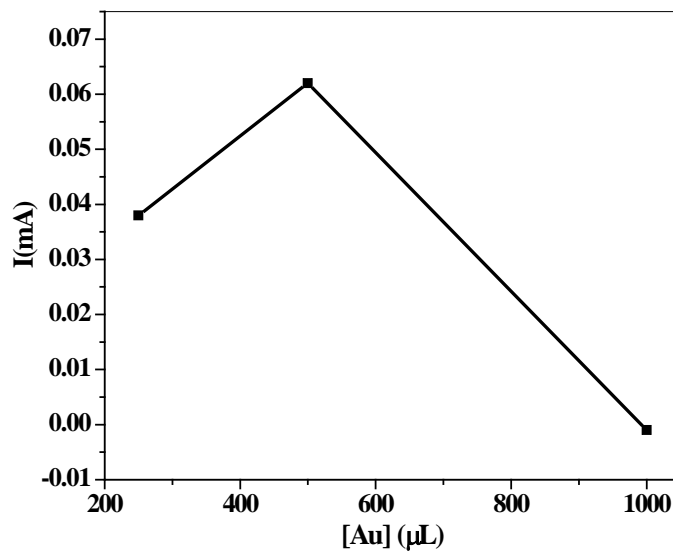
**Figure S8:** Effect of scan number of PEDOT film formation on the peak current of catechol ( $10^{-6}$ M)



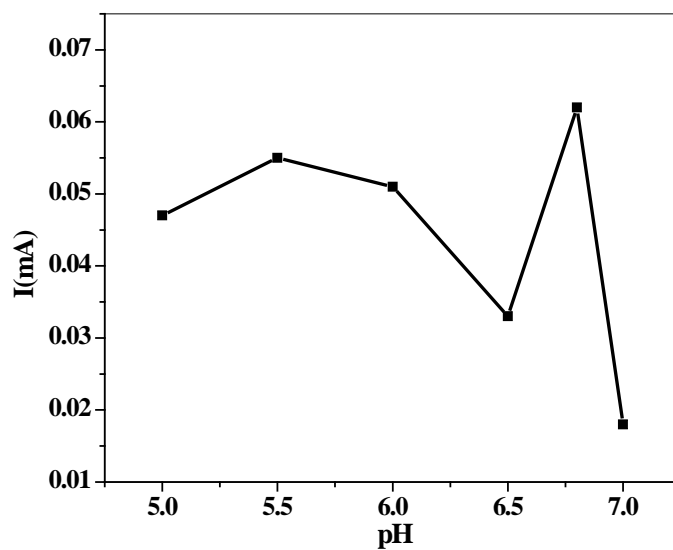
**Figure S9:** Effect of scan rate during PEDOT film formation on the peak current of catechol ( $10^{-6}$ M)



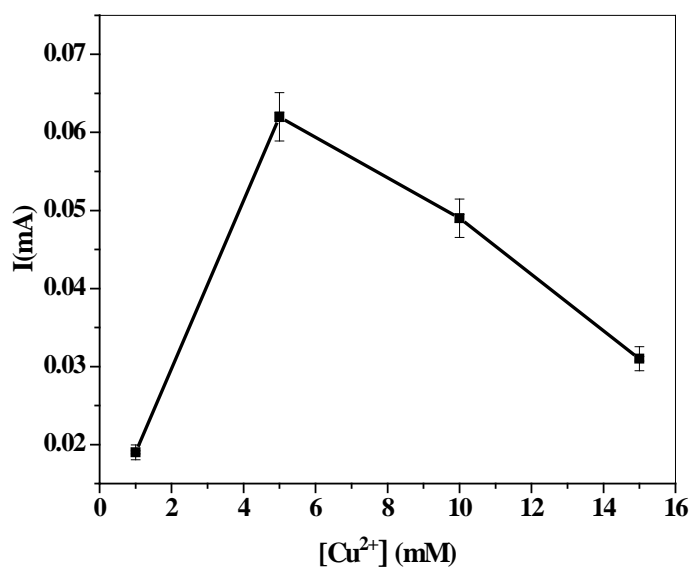
**Figure S10:** The effect of EDOT concentration on the peak current of catechol ( $10^{-6}$ M)



**Figure S11:** The effect of AuAC concentration on the peak current of catechol ( $10^{-6}$ M)

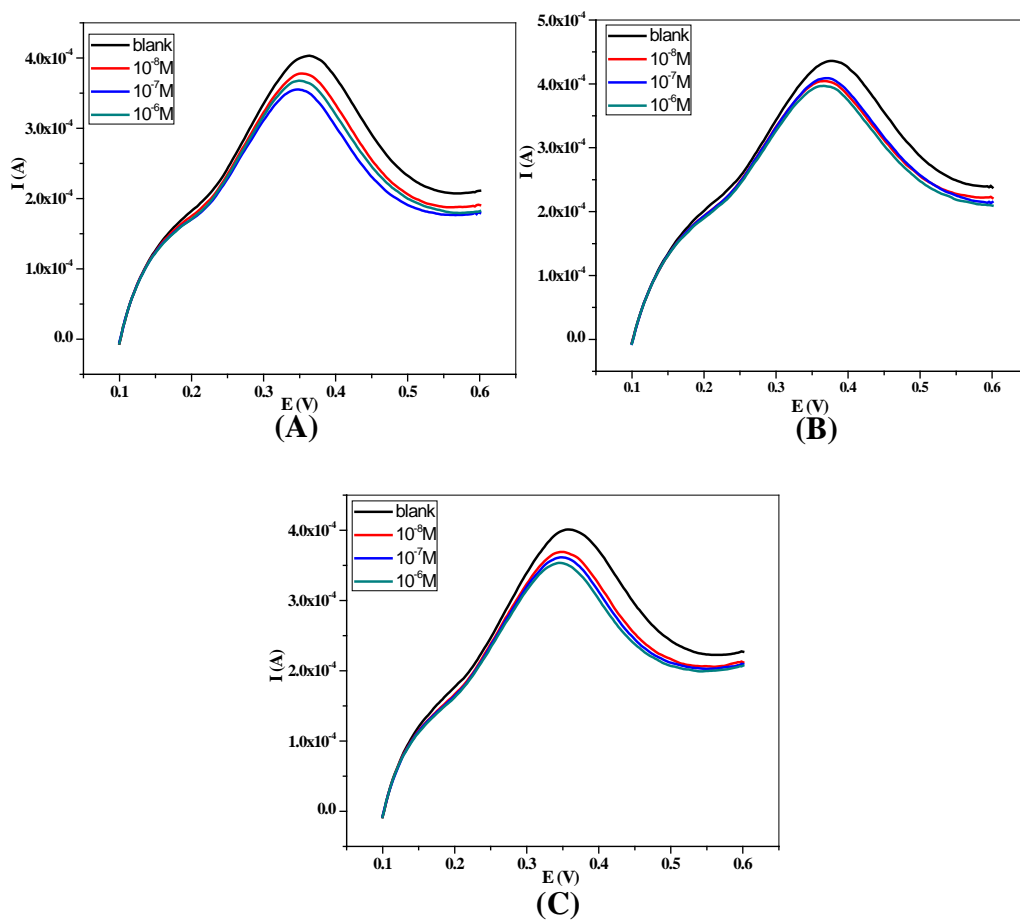


**Figure S12:** The effect of solution pH on the peak current of catechol ( $10^{-6}$ M)



**Figure S13:** The effect of  $\text{Cu}^{2+}$  concentration on the peak current of catechol ( $10^{-6}$ M)





**Figure S14:** Linear sweep voltammograms for real sample analysis A) well water B) river water C) tap water of blank,  $10^{-8}$ M,  $10^{-7}$ M and  $10^{-6}$ M concentrations of catechol.

**Table S1:** Investigated and optimized conditions for the formation of AuAC/PEDOT nanocomposite modified electrode

Parameters	Investigated range	Optimal conditions
EDOT concentration (mM)	5 to 50	20
Scan number	5 to 25	15
Gold cluster concentration (mL)	0.25 to 1	0.5
Scan rate (mV/s)	10 to 100	50

**Table S2:** Sequential optimization of analytical parameters for catechol determination

Analytical parameters	Tested range	Optimal condition
<b>A. Chemical</b>		
(i) Supporting electrolyte		0.1M CH <sub>3</sub> COONa
(ii) pH	5–7	6.8
(iii) Copper ion concentration (mM)	1–15	5
<b>B. Instrumental</b>		
(iv) Scan rate (mV/s)	10–100	50
(v) Cathodic potential scan limit (V)	0.05–0.2	0.1
(vi) Anodic potential scan limit (V)	0.5–0.7	0.6

**Table S3:** Comparison with reported electrochemical sensors for the determination of catechol

Electrochemical technique	Electrode modification	Calibration range ( $\mu\text{M}$ )	Limit of detection ( $\mu\text{M}$ )	References
DPV	PEDOP/MWCNTs-Pd/GC E	0.01–6000	0.026	[40]
DPV	carbon nanofibers/gold nanoparticles/Au	5.0–350	0.36	[41]
DPV	poly(glutamic acid) Modified GC Electrode	1–80	0.8	[42]
SWV	screen printed graphite electrode	1–100	0.29	[43]
Amperometry	Au/TiO <sub>2</sub> nanorod composites-modified BDD electrodes	5–200	1.4	[44]
Amperometry	DeniLite laccase immobilized Pt electrode	0–58	0.07	[45]
CV	AuNP-SAMs/Au	4–20	4	[46]
CV	Molecularly Imprinted Conducting Polymer/Au	0.228–144	0.228	[32]
Amperometry	CNT-Tyr composite	0–150	10	[47]
CV	MIP/Au	0–100	0.029	[33]
Amperometry	poly(aniline-co-p-aminophenol) film	5–500	0.8	[48]
Amperometry	montmorillonite modified graphite electrode	10–1000	1.13	[49]
DPV	$\beta$ -cyclodextrin-cobalt ferrite nanocomposite	1–200	0.12	[50]
DPV	Bis(1,10-phenanthroline)copper(II)bis(tetracyanoquinodimethanide) in poly-L-lysine film	0.01–20	0.003	[51]
DPV	(PEDOT)/graphene oxide (GO) hybrid film	2 to 400	1.6	[52]
LSV	AuAC/PEDOT/Au	$1 \times 10^{-4}$ –10	$6.3 \times 10^{-6}$	Present method

(CV: Cyclic voltammetry, SWV: Square wave voltammetry, DPV: Differential pulse voltammetry).