Electronic Supplementary Material (ESI) for Analytical Methods.
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Supplementary Data

For

Graphene quantum dots incorporated $NiAl_2O_4$ nanocomposite based molecularly imprinted electrochemical sensor for 5-hydroxymethyl furfural detection in coffee samples

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Apparatus

ZEISS EVO 50 SEM, JEOL 2100 TEM, Bruker-Tensor 27 FTIR spectrometer and a PHI 5000 Versa Probe type x-ray photoelectron spectrometer were used for SEM, TEM, FTIR and XPS measurements, respectively.

GCE cleaning procedure

Surface cleaning of GCE electrodes was done using solutions containing alumina. These solutions are in different diameter sizes (0.1 μm and 0.05 μm) and the particles on the surface were removed by the interaction of the electrodes with these solutions, respectively. After these solutions of different sizes were dripped onto the electrodes, cleaning processes were started with the help of electrode cleaning pads (grain size 4000). After the interaction with the solutions was completed, the electrodes were sonicated twice with ultrapure water and isopropyl alcohol, respectively. Finally, it was dried at room temperature and made ready for use.

Linearity

$$LOQ = 10.0\ S / m$$

$$LOD = 3.3\ S / m$$

S: Standard deviation of the intercept and m*:* Slope of the regression line

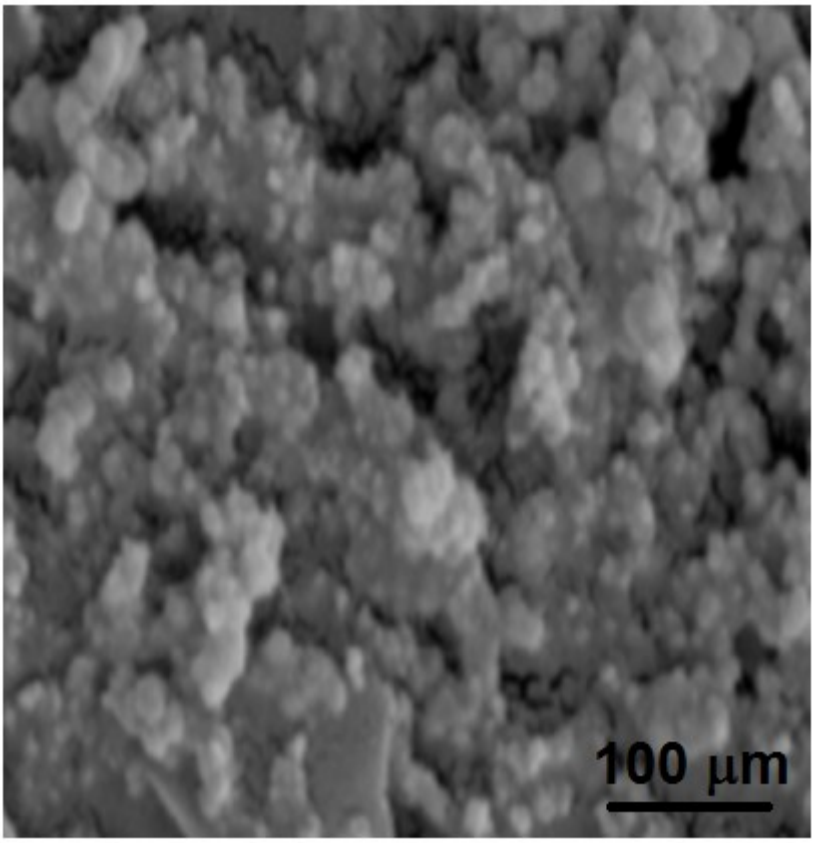

Fig. S1. SEM image of GQDs-$NiAl_2O_4$ nanocomposite

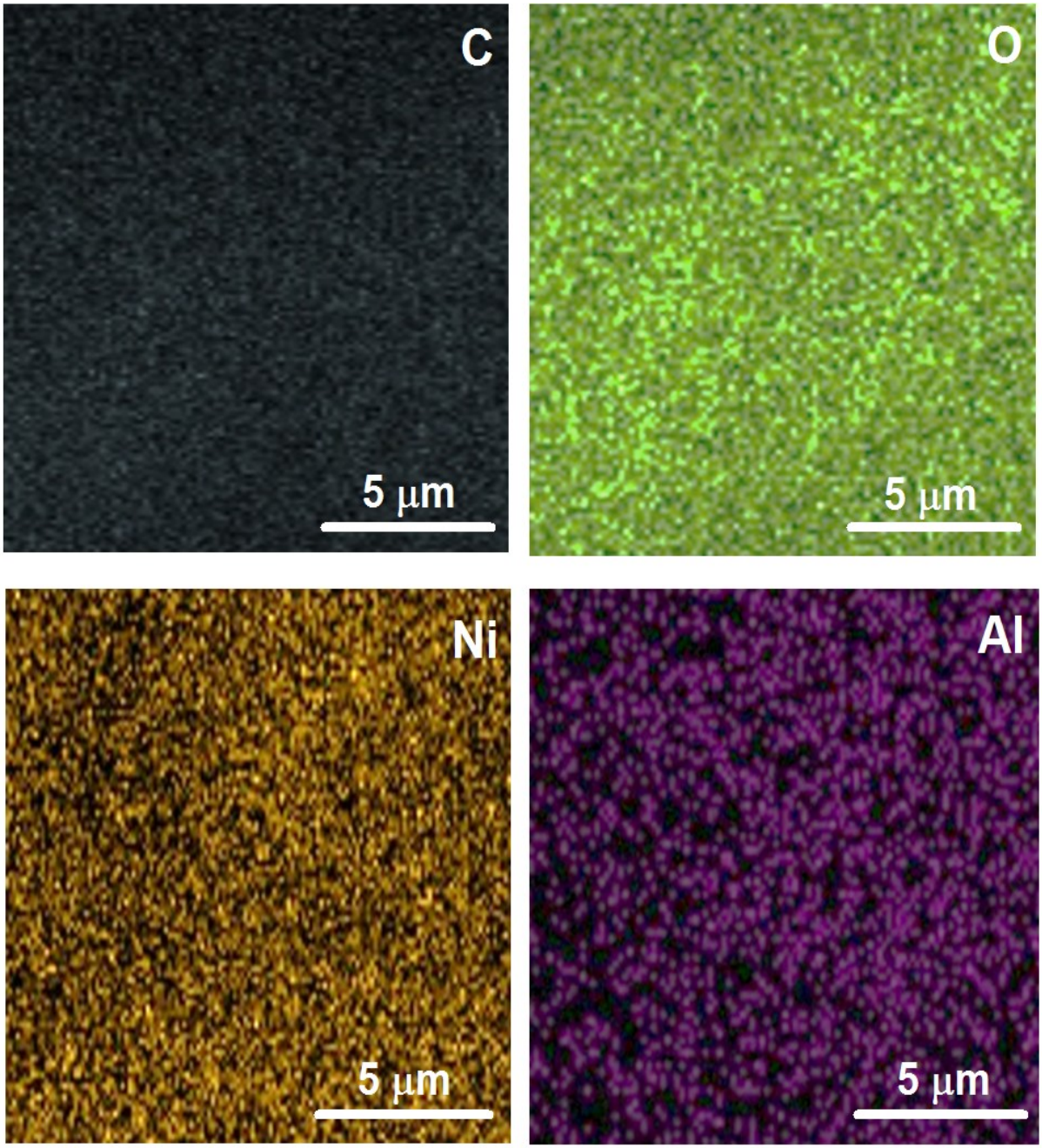

Fig. S2. SEM-EDX mapping of (A) nickel, (B) aluminum, (C) oxygen and (D) carbon elements on GQDs-$NiAl_2O_4$ nanocomposite

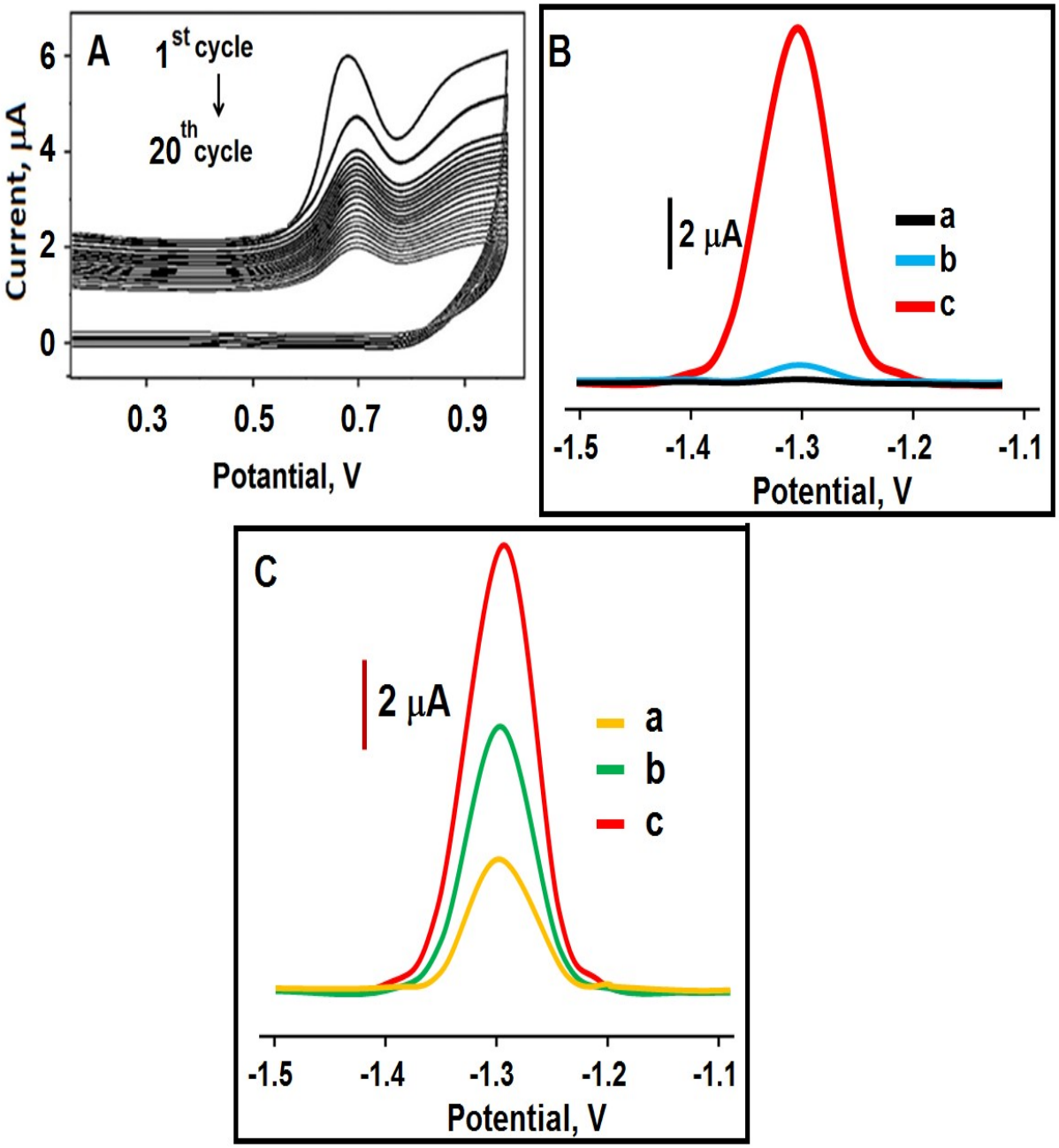

Fig. S3. (A) 100.0 mM Py polymerization containing 25.0 mM HMF on GQDs-$NiAl_2O_4$/GCE (Scan rate: 100 mV s^{-1}), (B) SWVs of the prepared electrodes in this study: (a) MIP/GQDs-$NiAl_2O_4$/GCE in blank buffer solution (pH 11.0), (b) NIP/GQDs-$NiAl_2O_4$/GCE after rebinding of 5.0 ng L^{-1} HMF in 0.1 M PBS (pH 11.0), (c) MIP/GQDs-$NiAl_2O_4$/GCE after rebinding of 5.0 ng L^{-1} HMF in 0.1 M PBS (pH 11.0) (Parameters are frequency of 100 Hz, pulse amplitude of 25 mV, scan increment of 5 mV), (C) SWVs of different molecularly imprinting electrodes after rebinding of 5.0 ng L^{-1} HMF in 0.1 M PBS (a) MIP/$NiAl_2O_4$/GCE, (b) MIP/GQDs/GCE, (c) MIP/GQDs-$NiAl_2O_4$/GCE (Parameters are frequency of 100 Hz, pulse amplitude of 25 mV, scan increment of 5 mV)

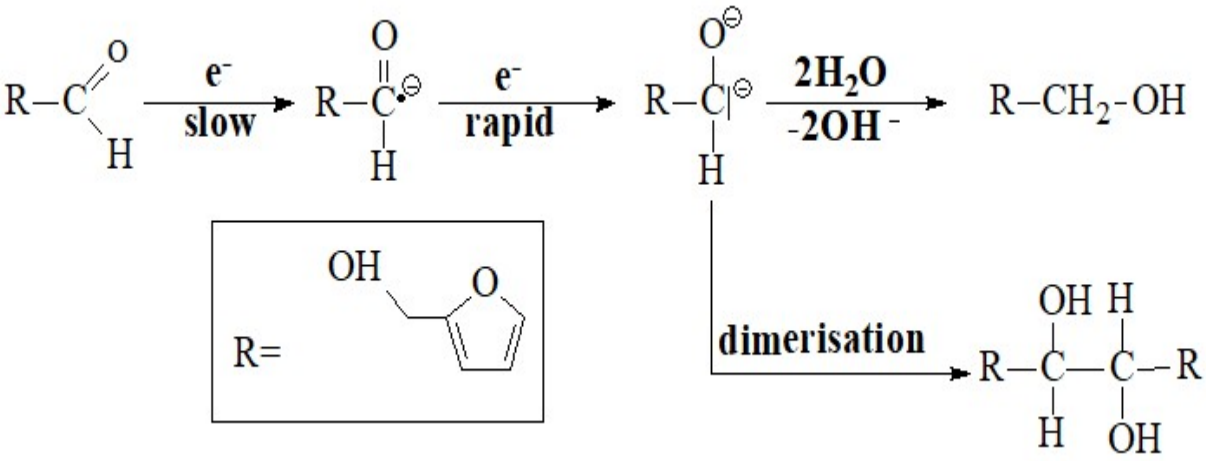

Fig. S4. The proposed electro-reduction mechanism for HMF at MIP/GQDs-$NiAl_2O_4$/GCE

3.4. Optimization studies

3.4.1. pH effect

The pH effect is an important factor that affects the sensor signals depending on the ambient conditions. When we looked at Fig. S5A, the sensor signal values increased up to pH 11.0 Thus, 11.0 was chosen as the ideal pH.

3.4.2. Mole ratio HMF to Py monomer effect

Secondly, mole ratio HMF to Py monomer effect was investigated (Fig. S5B). In the preparation of molecularly imprinted sensors, it is necessary to carefully adjust the monomer ratio. There is a high probability of non-specific interactions in large proportions of monomer concentrations. At low monomer concentrations, the number of binding sites of the analyte molecule is low and significantly affects the sensitivity of the sensor. The highest sensor signal appears to be obtained when using 100.0 mM Py and 25.0 mM HMF.

3.4.3. Desorption time effect

It is very important to completely remove the analyte molecule from the electrode surface in the preparation of molecularly imprinted sensors. In the case of sensor preparation, the adsorption-desorption kinetics primarily affects the performance of the sensor. Consequently, a good optimization of the elution time is required. Several desorption times were tried for optimization and the most optimal signal value was obtained at 20 min (Fig. S5C).

3.4.4. Scan cycle effect

The thickness of the prepared electrode surface is very important in electrochemical sensor applications. Film thickness is an important factor that directly affects sensor performance. During the sonication process on the electrode surface with low film thickness, it is likely that the nanocomposite material will break off from the electrode surface. Therefore, molecularly imprinted electrodes with different film thickness were prepared and the highest signal was obtained in the electrode with 20^{th} scan cycle (Fig. S5D).

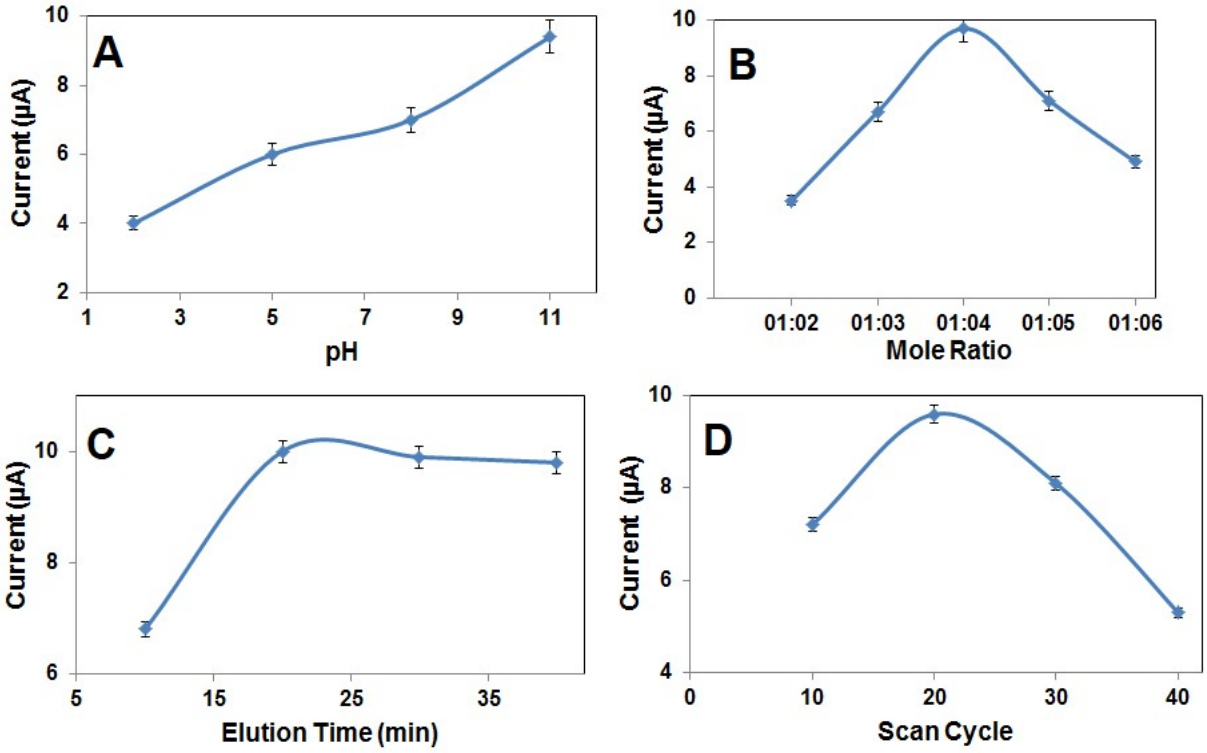

Fig. S5. Effect of (A) pH, (B) mole ratio, (C) desorption time, (D) scan cycle on signals of SWVs (in presence of 5.0 ng L^{-1} HMF) (n = 6)

Table S1. Recovery results of HMF (n=6)

Sample	Added HMF (ng L^{-1})	Found HMF (ng L^{-1})	*Recovery (%)
Coffee	-	1.071 ± 0.003	-
	2.000	3.073 ± 0.006	100.07 ± 0.01
	5.000	6.069 ± 0.002	99.97 ± 0.03
	8.000	9.070 ± 0.008	99.99 ± 0.01

*Recovery = Found HMF, ng L^{-1} / Real HMF, ng L^{-1}

Table S2. k and k′ values of HMF imprinted electrodes (MIP/GQDs-$NiAl_2O_4$/GCE and NIP/GQDs-$NiAl_2O_4$/GCE)

	MIP		NIP		
	ΔI (µA)	***k**	**ΔI (µA)**	***k**	****k′**
HMF	10.00	-	0.50	-	-
5-MT	0.50	20.00	0.30	1.67	12.20
FUR	0.40	25.00	0.20	2.50	10.00
GLU	0.30	33.33	0.15	3.33	10.10
AA	0.20	50.00	0.10	5.00	10.00
MGO	0.10	100.00	0.05	10.00	10.00

Analyte concentrations: 5.0 ng L^{-1} HMF, 500.0 ng L^{-1} 5-MT, 500.0 ng L^{-1} FUR, 500.0 ng L^{-1} GLU, 500.0 ng L^{-1} AA and 500.0 ng L^{-1} MGO; *k = ΔI_{HMF} / $\Delta I_{\text{interfering chemical}}$ and **k′ = k_{MIP} / k_{NIP}

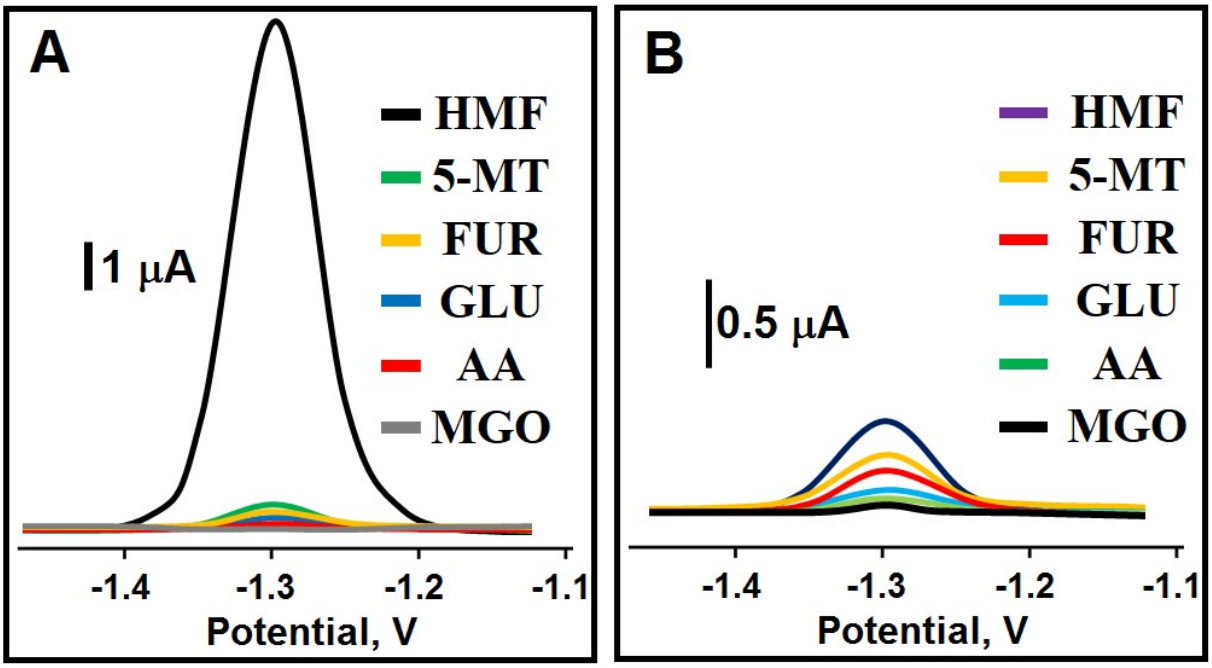

Fig. S6. SWVs of (A) MIP/GQDs-$NiAl_2O_4$/GCE and (B) NIP/GQDs-$NiAl_2O_4$/GCE in 5.0 ng L^{-1} HMF, 500.0 ng L^{-1} 5-MT, 500.0 ng L^{-1} FUR, 500.0 ng L^{-1} GLU, 500.0 ng L^{-1} AA and 500.0 ng L^{-1} MGO (Parameters are frequency of 100 Hz, pulse amplitude of 25 mV, scan increment of 5 mV)

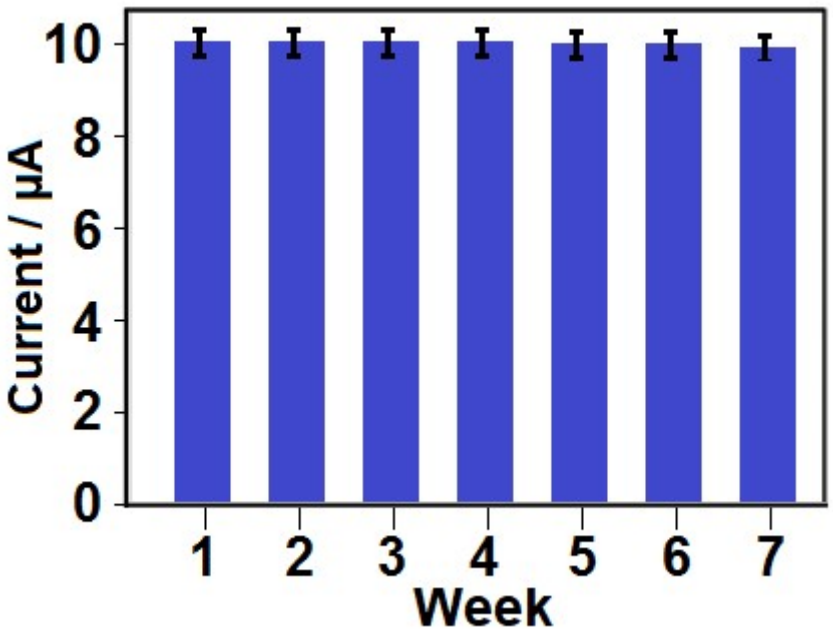

Fig. S7. Stability test of MIP/GQDs-$NiAl_2O_4$/GCE including 5.0 ng L^{-1} HMF (n = 6)