Supplementary information

Platinum-nickel bimetallic nanoclusters ensemble-on-polyaniline nanofilm for enhanced electrocatalytic oxidation of dopamine

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Supplementary information contains:

Figure S7. Current vs. Concentration calibration chart of Pt (orange) and $Pt_{0.75}Ni_{0.25}$ (green) hybrid electrodes from amperometric detection of DP in 0.1 M PBS.

Figure S8. Specific oxidation of DP in the presence of ascorbic acid (analyte selectivity test).

Supplementary text. Chronoamperometric measurements.

Tables

Table S1. Summary of structural results of Ni-K edge EXAFS refinements of pure Ni and $Pt_{0.75}Ni_{0.25}$ NCs deposited on SiO_2/Si wafer.

		Pure Ni NCs			$Pt_{0.75}Ni_{0.25}$ NCs		
N_i	Shell	CN_i	R_i(Å)	A_i(Å^2)	CN_i	R_i(Å)	A_i(Å^2)
1	Ni_{Ox}-O	2.4(6)	2.015(2)	0.011(7)	2.0(7)	1.99(2)	0.01(1)
2	Ni_M-Ni_M	1.8(8)	2.46(2)	0.009(8)	0.8(5)	2.48(3)	0.01(2)
3	Ni_M-Pt_M	-	-	-	2(1)	2.66(3)	0.01(1)
4	Ni_{Ox}-Ni_{Ox}	2(1)	2.91 (2)	0.01(1)			
5	Ni_M-Ni_M	2(1)	3.40(3)	0.01(1)			
		E_f=10(1)		R=39%	E_f= 9(2)		R=57%

N_i: Shell number, **CN_i:** Coordination number of atom in the N_i^{th} shell, **R_i:** Radial distance of atoms in the N_i^{th} shell [Å], **A_i**: Debye-Waller term of the N_i^{th} shell ($A=2\sigma^2$ with σ^2= Debye-Waller factor) [Å^2], **Ni_{Ox}**: Ni atoms in oxides and hydroxides, **Ni_M**: Ni in metal phase. **E_f:** contribution of the wave vector of the zero-photoelectron relative to the origin of k [eV], **R: R** factor (%).

Table S2. Binding energies of different oxide and metal phases derived from Pt 4f and Ni 2p XPS spectra of $Pt_{0.75}Ni_{0.25}$, pure Pt and pure Ni NCs deposited on SiO_2/Si Wafer.

NCs	Chemical Phases	BE (eV)
$Pt_{0.75}Ni_{0.25}$ NCs		**4f 7/2**
	Pt^{o}	71.1
	Pt^{+2}	72.3
	Pt^{+4}	73.0
		2p 3/2
	Ni^{o}	852.3
	Ni^{+2}	853.4
	Ni^{+2} (OH)	855.8
	Ni^{+3}	860.9
Pt NCs		**4f 7/2**
	Pt^{o}	71.4
	Pt^{+2}	72.3
	Pt^{+4}	73.9
		2p 3/2
Ni NCs	Ni^{o}	852.1
	Ni^{+2}	853.4
	Ni^{+2} (OH)	855.9
	Ni^{+3}	860.5

Figures

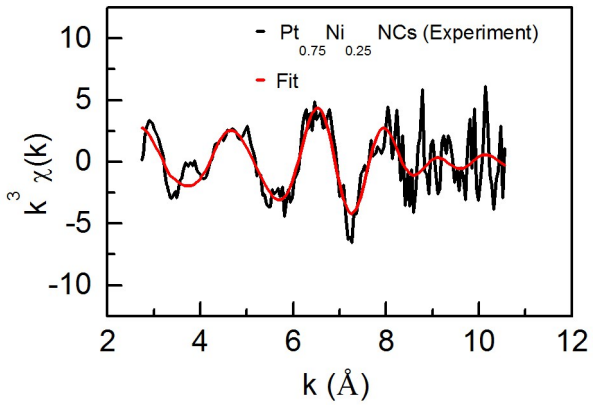

Figure S1. Best fit of Ni K-edge k^3-weighted EXAFS spectra of $Pt_{0.75}Ni_{0.25}$ NCs deposited on SiO_2 /Si wafer.

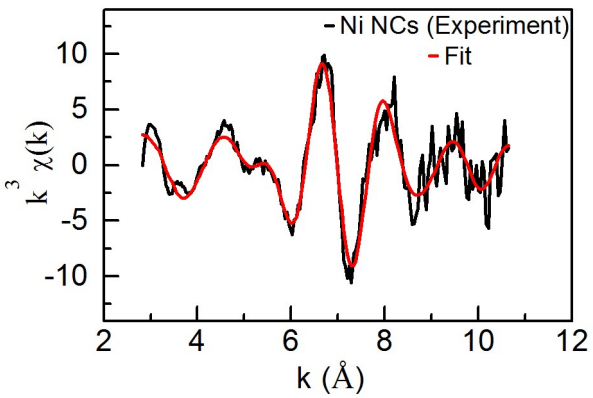

Figure S2. Best fit of Ni K-edge k^3-weighted EXAFS spectra of pure Ni NCs deposited on SiO_2/Si wafer.

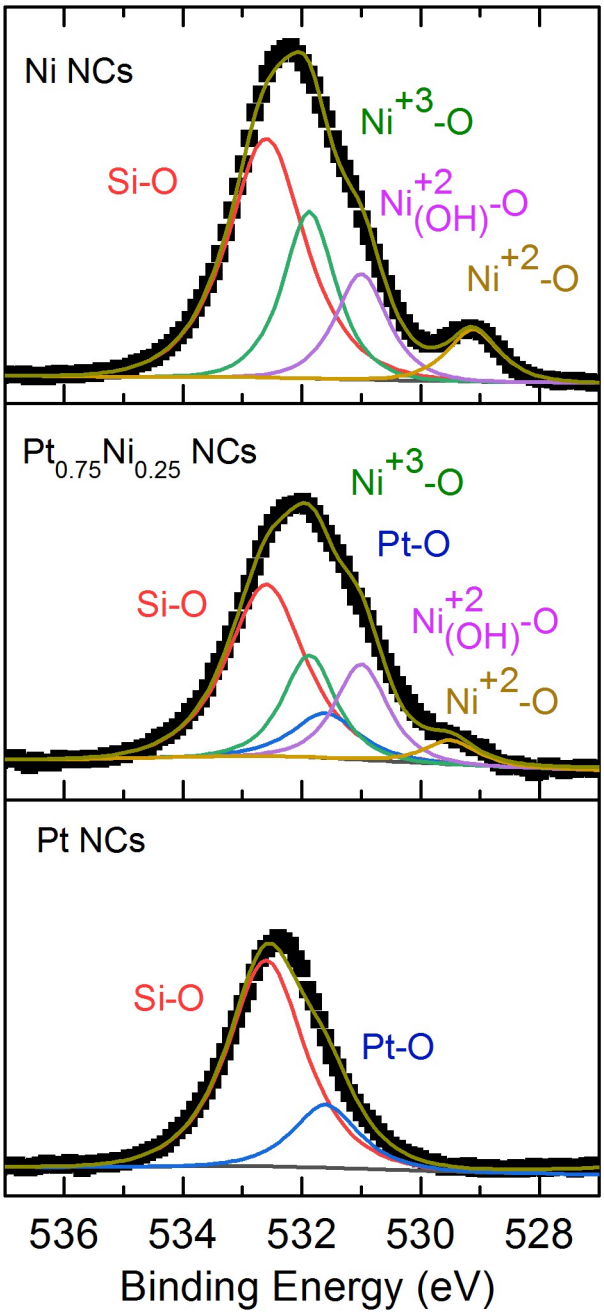

Figure S3. XPS spectra of O1s core levels of $Pt_{0.75}Ni_{0.25}$, Pt and Ni NCs on silica wafer.

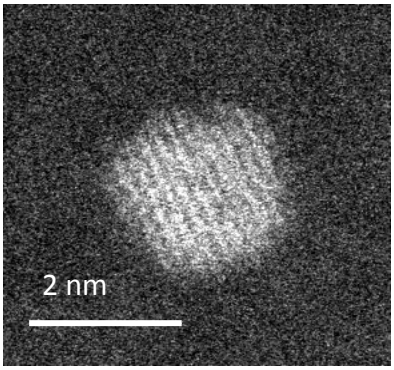

Figure S4. Atomic mass contrast HAADF-STEM image of a $Pt_{0.75}Ni_{0.25}$ NC.

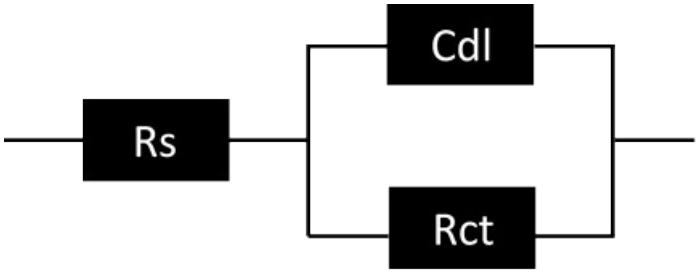

Figure S5. Randle Circuit model used for EIS data fitting where, Rs is the solution resistance, Cdl the double layer capacitance and Rct the charge transfer resistance.

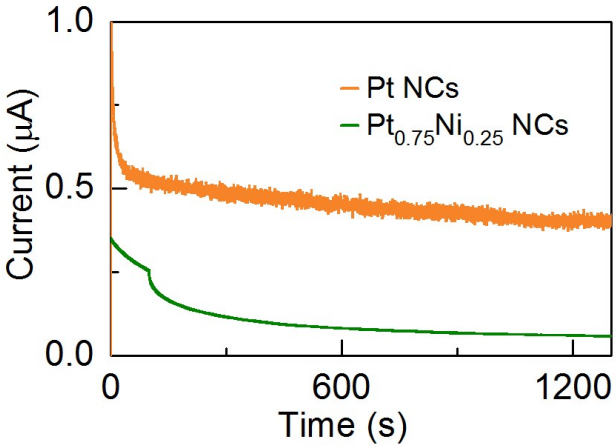

Figure S6. Amperometric background signal of $Pt_{0.75}Ni_{0.25}$ NCs (green) and Pt NCs (orange) supported PANI electrodes under DP free conditions.

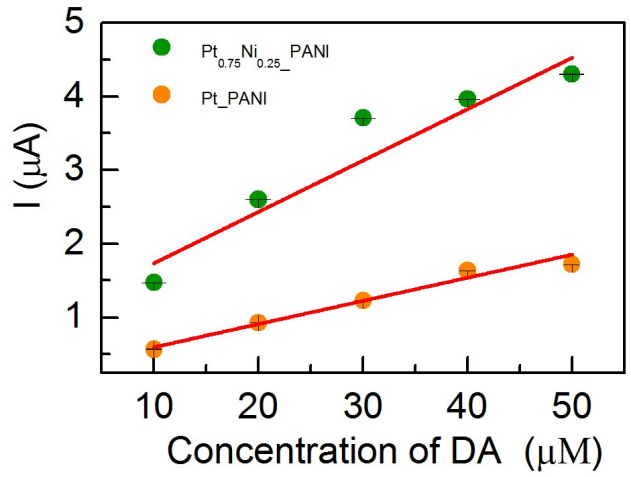

Figure S7. Current vs. Concentration calibration chart of Pt (orange) and $Pt_{0.75}Ni_{0.25}$ (green) hybrid electrodes from amperometric detection of DP in 0.1 M PBS.

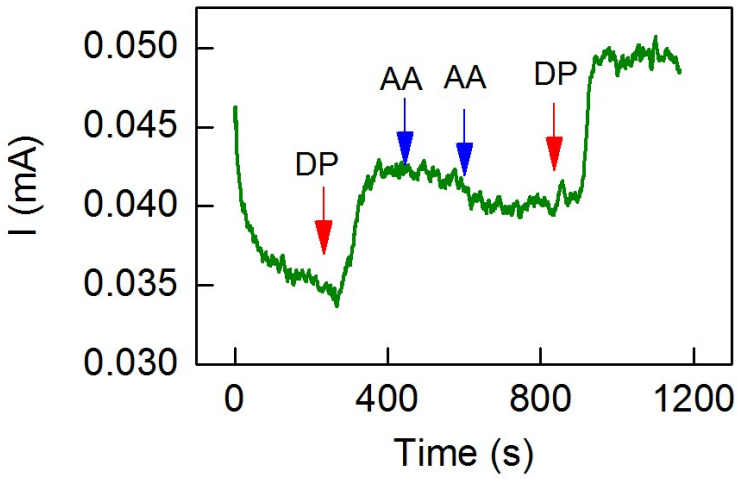

Figure S8. Specific oxidation of DP in the presence of ascorbic acid (analyte selectivity test).

Supplementary text

Chronoamperometric measurements were performed under different concentrations of DP with PBS as electrolyte by applying for 1800s oxidation potentials of 0.19 V and 0.45 V for $Pt_{0.75}Ni_{0.25}$ NCs and Pt NCs hybrid electrodes, respectively (Figure S5). A decrease in the background signal of $Pt_{0.75}Ni_{0.25}$ NCs compared to that of Pt NCs is observed under DP free PBS condition.

A linear relationship was obtained between the current response and the concentration of the DP in the 5 to 50 µM range (Figure 7). The linear regression equation can be applied with a correlation coefficient of R2 = 0.91 and 0.97 for $Pt_{0.75}Ni_{0.25}$ and Pt, respectively. The sensitivity (slope of calibration curve) and limit of detection (LOD) calculated (S/N=3) for the $Pt_{0.75}Ni_{0.25}$ NCs-PANI hybrid was 0.137A/µM.cm^2 and 0.1 µM, respectively. The sensitivity of $Pt_{0.75}Ni_{0.25}$ NCs was found to be around 4 times higher than that of pure Pt NCs (0.033A/µM. cm^2). Also, the LOD plummeted from 0.6 µM (Pt NCs) to 0.1 µM ($Pt_{0.75}Ni_{0.25}$ NCs). The detection limitation of PANI Pt and $Pt_{0.75}Ni_{0.25}$ NCs hybrid electrodes is in the human body DP reference range,[1] and is comparable and often better than most of the reported research works on bare Pt or CP modified with Pt.[2,3,4]

Beyond activity and stability, selectivity is an important criterion. Ascorbic Acid (AA) molecules always coexist in the physiological fluid along with DP and known to have similar oxidation potential causing strong interference in electrochemical detection of DP.[5] To test whether PANI- $Pt_{0.75}Ni_{0.25}$ NCs electrodes can electro-oxidize AA, an amperometric experiment (Figure S8) was performed at 0.19 V. Addition of 1 mM AA into the electrolyte containing 100 µM DP with a current response of 0.08 µA did not produce any additional current response. This demonstrates that PANI-NCs hybrid electrodes are immune against interference from the AA molecule highlighting their highly specific DP detection capability.

References

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