Electronic Supplementary Material (ESI) for Nanoscale. This journal is © The Royal Society of Chemistry 2017

Supporting information

One-pot Synthesis of Dendritic Pt₃Ni Nanoalloys as NonenzymaticElectrochemical Biosensors with High sensitivity and Selectivity for DopamineDetection *Ge Gao*,^{*a*}*ZongkuiZhang*,^{*c*} *Kai Wang*,^{*b*}*QiangYuan*,^{*a*}**and XunWang*^{*b*}*

To whom correspondence should be addressed E-mail: qyuan@gzu.edu.cn; wangxun@mail.tsinghua.edu.cn

^aCollege of Chemistry and Chemical Engineering, Guizhou University, Guiyang, Guizhou province 550025 (P.R. China)
^bDepartment of Chemistry, Tsinghua University, Beijing 100084 (P.R. China)
^cGuizhou University Hospital, Guizhou University, Guiyang, Guizhou province 550025 (P.R. China)

Experimental Materials

Chemicals: Platinum(II)acetylacetonate (Pt(acac)₂,97%), nickel(II)acetylacetonate (Ni(acac)₂, 95%) were purchased from Sigma-Aldrich. Polyvinyl pyrrolidone (PVP-8000), sodium chloride (NaCl, AR), potassium chloride (KCl, AR), sodium sulfate(Na₂SO₄, AR), sodium nitrate (NaNO₃, AR), sodium phosphate dibasic (Na₂HPO₄, AR), potassium phosphate monobasic (KH₂PO₄, AR), glucose (Glu, AR), ascorbic acid (AA, AR) and N,N-Dimethylacetamide (DMAC,AR) were purchased from China Medicine Shanghai Chemical Reagent Corp. Dopamine (DA, 97%) and uric acid (UA, 98%) was purchased from Ark Pharm. Pt black was purchased from Johnson Matthey. Chemicals were used as received without further purification. The super pure water (18M Ω cm) was used as solvent. 0.1 M (pH 7.2) phosphate buffer solution (PBS) was prepared by using NaCl, KCl, Na₂HPO₄ and KH₂PO₄.

Experimental Methods

Synthesis of dendritic Pt₃Ni nanoparticles: In a typical synthesis, 13.5 mg Pt(acac)₂, 3.0 mg Ni(acac)₂ and 36.0 mg NaCl were added into 7.0 mL of DMAC containing 0.2 g Polyvinyl Pyrrolidone (PVP-8000) and stirred for 15 minutes. Then the resulting green solution was transferred to a 12 mL Teflon-lined stainless-steel autoclave. The sealed vessel was then heated at 180°C for 8 h before it was cooled to room temperature. The products were separated via centrifugation at 10000 rpm for 20 minutes and washed 3-4 times with ethanol. The collected product was redispersed in ethanol. By adjusting the amount of Pt(acac)₂ and Ni(acac)₂, the Pt₉Ni (13.5 mg Pt(acac)₂, 1.0 mg Ni(acac)₂) and Pt₅Ni₅ (13.5 mg Pt(acac)₂, 9.0 mg Ni(acac)₂) nanocrystals can be obtained.

Characterization: The X-ray diffraction (XRD) patterns of the samples were recorded on a Bruker D8 Advance diffractometer with Cu K_a radiation (λ =1.5418 Å) with graphite monochromator (40 KV, 40 mA). The size and morphology of the NCswere determined by a HITACHI H-7700 transmission electron microscope (TEM) at100 kV, and a FEI Tecnai G2 F20 S-Twin high-resolution transmission electronmicroscope (HRTEM) equipped with energy dispersive spectrometer (EDS) analyses 200 kV. The high-angle annular dark-field scanning TEM (HAADF-STEM) wasdetermined by a FEI Tecnai G2 F20 S-Twin HRTEM operating at 200 kV. The inductively coupled plasma mass spectrometry (ICP-MS) analysis of samples wasperformed on IRIS Intrepid II XSP (ThermoFisher).

Electrochemical sensing experiment of DA: Electrochemical experiments were controlled by CHI 760E electrochemical analyzer (CHI Instruments, Shanghai, Chenghua Co., Ltd.). The super pure water (18 M Ω cm) purified through a Milli-Q Lab system (Nihon Millipore Ltd.) was used as solvent. A conventional three-electrode cell was used here, including a glassy carbon electrode (GCE, Φ =5 mm) as the working electrode, platinum foil as the counter electrode and an Ag/AgCl (saturated KCl) electrode as the reference electrode. All potentials given in this work were referred to the Ag/AgCl electrode at room temperature (25 °C). The electrolytic solution was bubbled with nitrogen for 15 min prior to the initiation of electrochemical experiments. The GCE was prepared by a simple casting method. Prior to use, the GCE was successively polished with 0.1 and 0.05µm alumina powder to obtain a mirror like surface, it was then cleaned in an ultrasonic bath. Then, the prepared Pt₃Ni nanoalloyor Pt black ink was spread on the pre-polished mirror-like surface of GCE and then dried under infrared lamp, respectively. The sensing measurements were all carried out in 0.1 M PBS solution (PH=7.2) using amperometric detection at a working potential of 0.30 V under constant stirring.



Fig. S1. TEM images of the as-synthesized dendritic Pt_3Ni nanocrystals.



Fig. S2. HRTEM images of the as-synthesized dendritic Pt_3Ni nanocrystals. (White arrow 1, 2 and 3 stands for the defects such as corner, low-coordination atom and boundary.)

| Sample | Element | Atom% | Atom% |
|---------------------------------|---------|---------------|----------------------|
| | | feeding radio | (result from ICP-MS) |
| Pt ₉ Ni | Pt | 90 | 91 |
| | Ni | 10 | 9 |
| Pt ₅ Ni ₅ | Pt | 50 | 52 |
| | Ni | 50 | 28 |
| Pt ₃ Ni | Pt | 75 | 76 |
| | Ni | 25 | 24 |

Table S1 The composition of the as-synthesized PtNi nanocrystals calculated from ICP-MS.



Fig.S3 TEM images and XRD patterns of the as-synthesized Pt_9Ni (a, b and c) and Pt_5Ni_5 (d, e and f) nanoalloys.



Fig. S4. TEM images of the as-synthesized products under the same synthesis conditions of dendritic Pt_3Ni nanoalloys. (a) Without NaCl; (b) In the presence of NaF; (c) In the presence of NaBr and (d) In the presence of NaI.



Fig.S5 TEM image of commercial Pt black. The size of commercial Pt black is from 3.0 nm to 5.0 nm.



Fig. S6 (a) Cyclic voltammetric curves (CVs) of Pt_9Ni , Pt_5Ni_5 , Pt_3Ni and the commercial Pt black in 0.1 M HClO₄. (b) CVs of Pt_9Ni , Pt_5Ni_5 , Pt_3Ni and the commercial Pt black in 0.1 M PBS +1.0 μ M DA. (c) The magnified image of the DA test regions from 0.299 to 0.302V in positive scan.



Fig. S7 TEM images of Pt₃Ni nanoalloys after amperometric current-time test of DA.