

Electronic Supplementary Information

Pt-Ni nanoframes functionalized with carbon dots: an emerging class of bio-nanoplatfoms

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Experimental details

1.1 Preparation of CDs and CDs–COOH

Photoluminescent CDs were prepared via a facile one-step hydrothermal treatment according to our previous method.¹ Briefly, citric acid (3.15 g) and ethylenediamine (1 mL) was mixed in 30 mL deionized water. Then, the mixture was transferred into a poly-(tetrafluoroethylene) (Teflon)-lined autoclave (50 mL) and heated at 200 °C for 5 h. After cooling to room temperature, the brown-black and transparent solutions were subjected to dialysis (molecular weight cutoff = 3500) against deionized water for 12 h in order to obtain pure CDs. Then, 100.0 mg of the as-synthesized CDs were dispersed in 50 mL of aqueous solution containing 5.0 g of NaOH and 5.0 g of ClCH₂COONa, followed by sonication at 900 W for 6 h. Then the color of CDs suspensions changed from faint yellow to saffron yellow during the reaction, probably due to further reduction of the CDs under the drastic alkaline conditions. After the treatments, the as-received CDs–COONa was neutralized with dilute HCl and dialysed against deionized water overnight to remove any ions. Finally, the resulting products were freeze-dried under vacuum at –50 °C before use.

1.2 Preparation of hydrophobic Pt-Ni nanoparticles (PNnp), PNnp–NH₂ and chemical corrosion to Pt-Ni nanoframe (PNnf–NH₂)

PNnp: The monodispersed hydrophobic Pt-Ni nanoparticles were prepared by hot injection of metal precursors in oleylamine according to a solvothermal method reported by Niu et al.² Briefly, H₂PtCl₆·6H₂O (100 mg/ml, 0.4ml) and

$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (100 mg/mL, 0.35 mL) were mixed with one milliliter of oleylamine in a 10 mL flask. The mixture was heated at 160 °C to evaporate water under strong stirring for 1 h, forming a transparent green solution. 15 mL of oleylamine was preheated in a three-necked flask at 160°C for 1 h under argon atmosphere and further raised to 265 °C. The precursor solution was injected into the three-necked flask immediately after reaching 265 °C. Finally, the mixture was maintained at 365 °C for 1 h under argon atmosphere and then cooled to room temperature. The products were collected by centrifugation (10000 rpm, 5 min) and washed with hexane and ethanol (1/1 v/v) for several times. After that, the resultants were thoroughly redispersed in 20 mL of cyclohexane.

PNnp-NH₂: The monodispersed hydrophobic Pt-Ni nanoparticles (PNnp) were treated with polyethylenimine ethylenediamine branched (PEI) to introduce amino groups and render them hydrophilic. In brief, the as-synthesized hydrophobic (10 mg) PNnp was dispersed in 2 mL cyclohexane, and 1 mL aqueous solution containing of 10 mg PEI was added with vigorous stirring for 24 h in the room temperature. Then, the PNnp-NH₂ was thoroughly transferred into water solution, which may be contributing to electrostatic interaction or hydrogen bond. To remove excess polymer, the solution was repetitively centrifugated at 15,000 rpm for 10 min and the large aggregations were removed through a 0.22 μm drainage membrane. Finally, the as-obtained PNnp-NH₂ were further dispersed in deionized water with a concentration of 5 mg mL⁻¹.

PNnf-NH₂: The chemical corrosion process were successfully synthesized via a

classical method. 10 mg PNnp-NH₂ was dispersed into 2 mL deionized water, and 2 mL acetic acid was added with vigorous stirring for 2 h in 90 °C. After washed with water/ethanol (1/1 v/v), the PNnf-NH₂ was collected by centrifugation (10000 rpm) and re-dispersed in deionized water with a concentration of 5 mg mL⁻¹.

1.3 Preparation of CDs-PNnf bio-nanoplatforms.

Briefly, the as-prepared CDs-COOH (2 mL, 5 mg mL⁻¹) were dissolved in 10 mL Tris-HCl buffer (0.1 M, pH = 7.4) containing 10 mg of EDC and 5 mg of NHS to activate the surface carboxylic acid group in an ice-bath, followed by 2 h vigorous stirring. Then, PNnf-NH₂ Tris-HCl (2 mL, 5 mg mL⁻¹) was added, and the mixture was treated with ultrasonication for 12 h. The as-obtained nanoconjugates was washed three times and re-dispersed with Tris-HCl buffer. Finally, the CDs-PNnf lyophilized and stored in a freezer for further use.

1.4 Cytotoxicity of the CDs-PNnf nanoconjugates

In vitro cytotoxicity of CDs-PNnf on live cells were carried out on a battery of MTT 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide) assays on the MCF-7 breast cancer cells with different time line. These cells were seeded in 96-well assay plates at a density of 1×10⁴ cells per well and incubated for 24 h. Then, different concentrations of CDs-PNnf (0, 5, 10, 20, 50, 100, 150 µg mL⁻¹) were added into the wells. After incubation for an additional 12 h/24 h/48 h, the medium was removed and washed three times with PBS (phosphate-buffered). Following,

MTT (10 μL , 5 mg mL^{-1}) was added to each well and the plate was incubated at 37 $^{\circ}\text{C}$ for 3–4 h. Next, 100 μL DMSO was added to each well to dissolve the dark blue crystal. The absorbance was examined with a microplate reader (Biorad, USA) at a wavelength of 570 nm. The following formula was used to calculate the cell viability: cell viability (%) = (mean of the Abs. value of the treatment group/mean Abs. value of the control) \times 100%.

1.5 Cell imaging with the CDs–PNnf nanoconjugates

Imaging of cells was examined with a confocal laser scanning microscope (excited at 405 nm). For the imaging of MCF-7, cells were co-incubated with 100 μg mL^{-1} CDs-PNnf RPMI1640 solution at 37 $^{\circ}\text{C}$ for 24 h.

1.6 Quantum yield (QY) measurements

Fluorescence Quantum yield of CDs and CDs–COOH were measured by comparing their integrated PL intensities. Quinine sulfate in 0.1 M H_2SO_4 (quantum yield 54%) was used as a standard as described. The Quantum yields were calculated using following equation:

$$Q = Q_R \frac{I A_R n^2}{I_R A n_R^2}$$

where Q is the QY, I is the integrated intensity, A means the UV-vis absorption intensity. The R refers to the reference, and n presents the refractive index with 1.33 as the default for both quinine sulfate and CDs solvent. Noteworthy, the optical density is kept under 0.05 to avoid inner filter effects.

1.7 Cell incubation

The human breast cancer cell (MCF-7) were maintained in a RPMI-1640 medium supplemented with FBS (10%), L-glutamine (2 mM), antibiotic-antimycotic solution (1%) and non-essential amino acids (1%) in 5% CO₂ at 37 °C.

1.8 Materials and characterization

All the chemicals were used as received without further purification. ethylenediamine (99.5%), sodium hydroxide (96%), citric acid (99.5%), sodium chloroacetate(98%), N-hydroxysuccinimide (NHS, 97%) and 1-(3-dimethylamino-propyl)-3-ethylcarbodiimide hydrochloride (EDC, 98%) were purchased from Aladdin Company. Oleylamine(98%), chloroplatinic acid hexahydrate(H₂PtCl₆·6H₂O), Nickel(II) nitrate hexahydrate(Ni(NO₃)₂·6H₂O, 98.5%), polyethylenimine ethylenediamine branched (PEI), acetic acid(100%)were provided by Sigma-Aldrich. Deionized water was used throughout.

The size and morphology of the nanoparticles were characterized on a JEM-2010F high resolution transmission electron microscope operated at 120 kV. Fourier transform infrared spectroscopy (FTIR) was measured in the spectral range from 4000 to 400 cm⁻¹ with a Thermo Nicolet 6700 spectrometer (Thermo Fisher Scientific, United States) using the pressed KBr pellet technique. Photoluminescence (PL) spectra were recorded on a Shimadzu RF-5301 spectrophotometer. Cellular fluorescent images were recorded using a Confocal Laser Scanning Microscope (FV1000, Olypmus Corporation, Japan). UV-Vis spectra were recorded on a

spectrophotometer (2500-PC, Shimadzu, Japan) at room temperature. All data are expressed as the mean result \pm standard deviation (SD), and all figures were acquired from three independent experiments with consistent results.

References :

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2. Niu, Z. Q.; Becknell, N.; Yu, Y.; Kim, D.; Chen, C.; Kornienko, N.; Somorjai, G. A.; Yang, P. D. Anisotropic phase segregation and migration of Pt in nanocrystals en route to nanoframe catalysts. *Nat. Mater.* **2016**, 1188-1194.

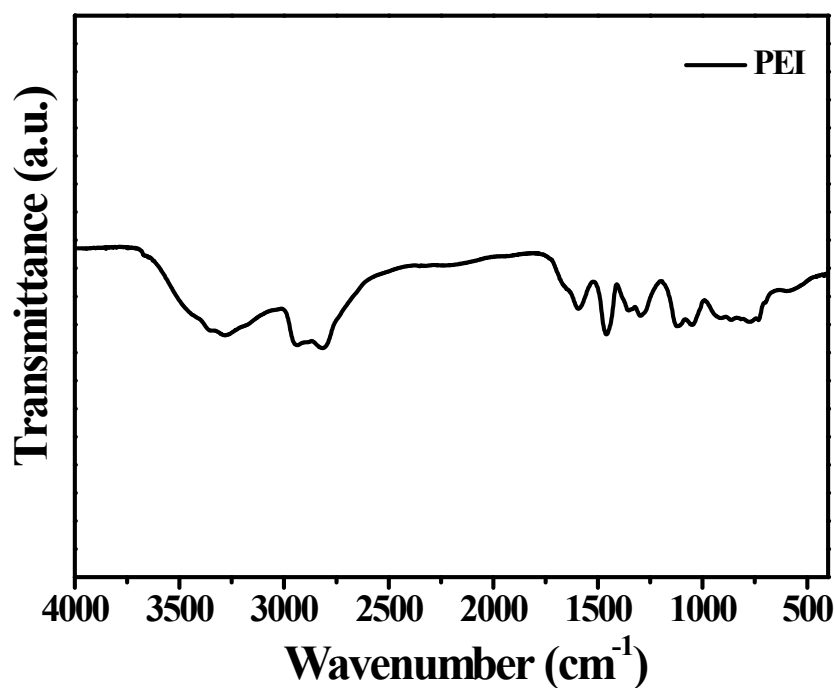


Figure S1. FT-IR spectrum of PEI.