

Supplementary materials

Ultrafast synthesis of gold/proline-functionalized graphene quantum dots and its use for ultrasensitive electrochemical detection of p-acetamidophenol

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1 Experimental

1.1 Synthesis of amino acid-GQD

Amino acid-GQD was prepared by the pyrolysis of citric acid and amino acid, in which amino acid is cysteine (Cys), alanine (Ala), aspartic acid (Asp), glutamic acid (Glu), phenylalanine (Phe), glycine (Gly), histidine (His), isoleucine (Ile), lysine (Lys), leucine (Leu), methionine (Met), asparagine (Asn), proline (Pro), glutamine (Gln), arginine (Arg), serine (Ser), threonine (Thr), valine (Val), tryptophane (Trp) or tyrosine (Tyr).¹ In a typical procedure, the mixture of citric acid (2.5 mmol) and amino acid (2.0 mmol) was dissolved in ultrapure water (2 mL). The resulting mixture was heated at 200°C for 3.5 h. The collected sample was neutralized with 1 M NaOH solution to pH 7 and then dialyzed in ultrapure water for two days to remove unreacted reagents.

1.2 Preparation of GNs/amino acid-GQD

The HAuCl₄ solution (0.06 mg mL⁻¹, 99 mL) was transferred into a flask. After the solution was heated to refluxing state, rapidly added the amino acid-GQD solution (50 mg mL⁻¹, 1.0 mL). The refluxing state was kept until the colour of the solution remain unchanged and then cooled to ambient temperature. To

obtain GNs/amino acid-GQD, the solution was centrifugated to remove unreacted HAuCl_4 and amino acid-GQD.²

1.3 Electrochemical measurements

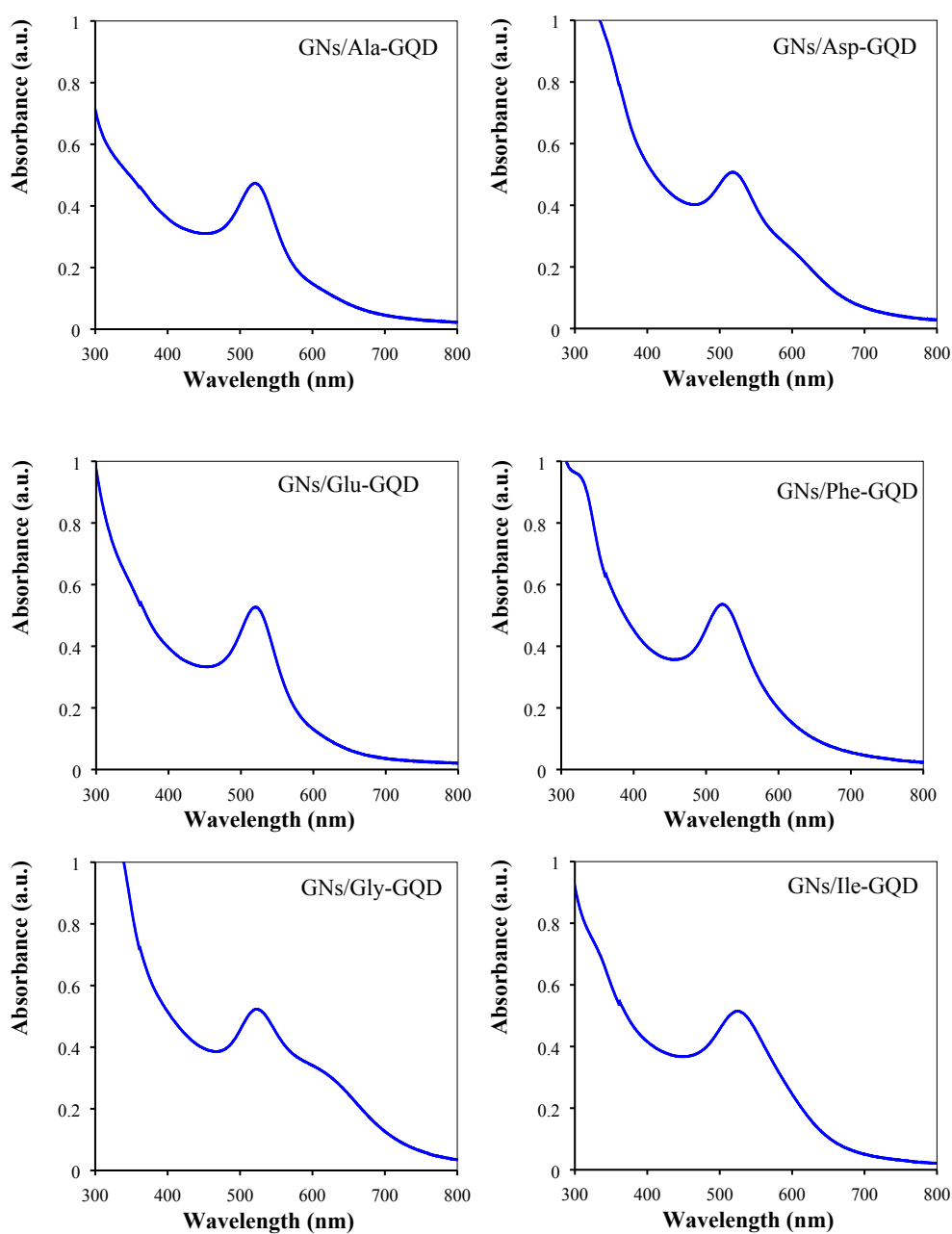
Electrochemical experiments were performed with a CHI830D electrochemical workstation (Shanghai, China). Conventional three electrode system was used for differential pulse voltammetry (DPV) with Ag/AgCl (saturated KCl) electrode as the reference electrode, platinum wire as the counter electrode, and bare or modified glassy carbon electrode (GCE, 1.0 mm in diameter) as the working electrode. Before use, GCE was polished successively with 1.0, 0.3, and 0.05 μm alumina powder, and sonicated in a 6.0 M of nitric acid/ultrapure water and ethanol/ultrapure water for 5 min. Then, the GCE as working electrode was subjected to cyclic scanning in 0.5 M of sulphuric acid solution in a potential range from -0.1 V to 1.0 V. When the cyclic voltammogram was almost unchanged, the electrode was taken out, cleaned with ultrapure water and dried in a stream of nitrogen. The treated GCE was modified with different gold nanoparticles to prepare different sensor using the following procedure: the GNs/amino acid-GQD was dissolved in ultrapure water to make up 0.2 mg ml^{-1} solution, then 10 μl mixture was dropped on the surface of GCE, after that 2 μl of chitosan solution was carefully spreading on the surface of modified GCE and dried in air before use. In the study, electrochemical experiment was carried out under room temperature, and all experimental solution was degassed by nitrogen for at least 15 min. Then, a nitrogen atmosphere was maintained during electrochemical measurements.

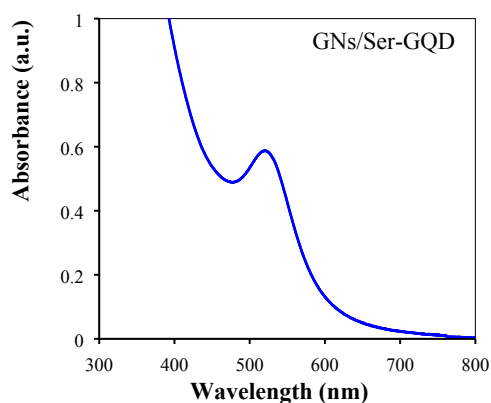
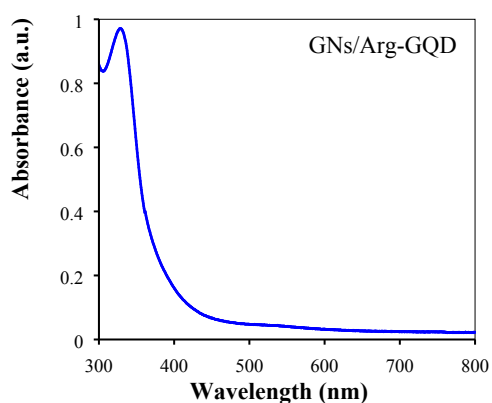
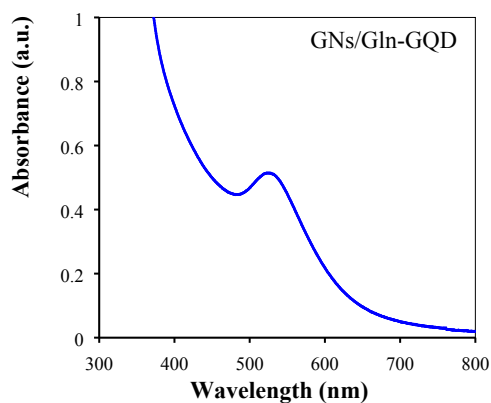
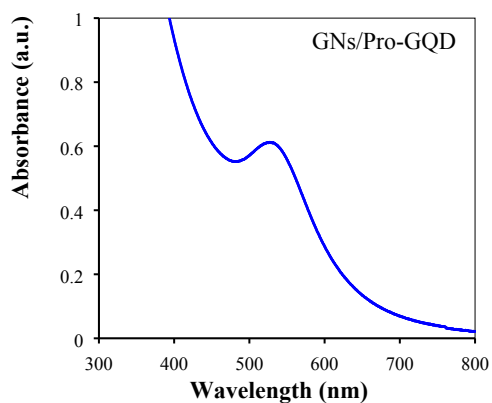
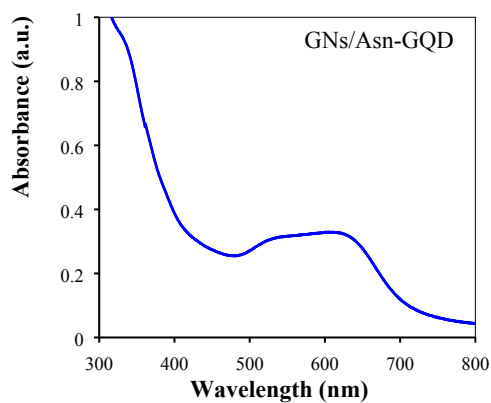
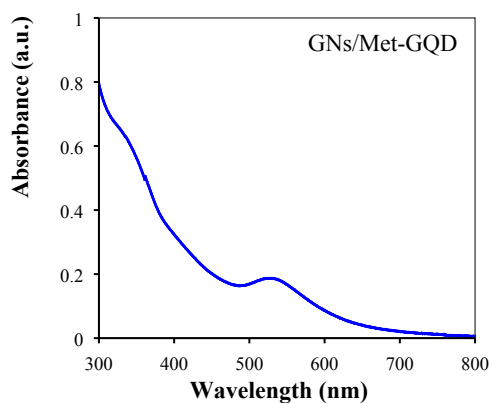
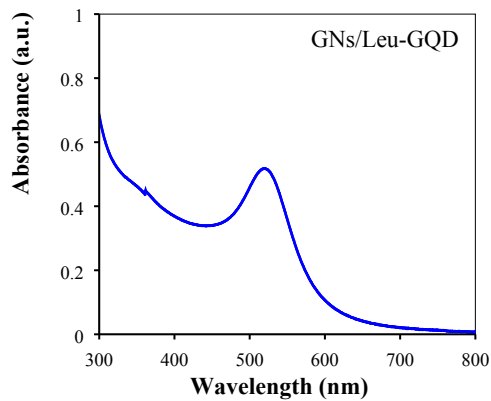
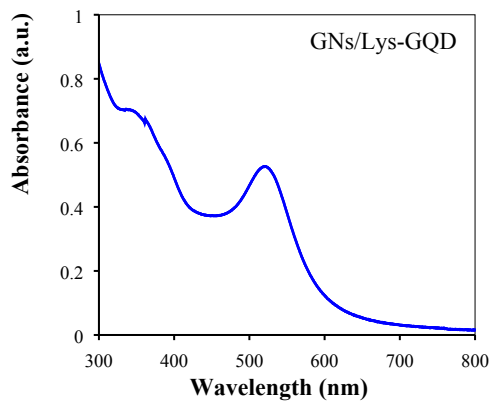
1.4 Materials characterization

Transmission electron microscope (TEM) was performed by a JEOL 2010. X-ray diffraction (XRD) was measured on the D8 Advance with a Cu $\text{K}\alpha$ radiation. Raman measurements were carried out using a InVia

laser micro-Raman spectrometer with a 785 nm laser excitation. UV-vis absorption spectra were recorded by a TU-1901 spectrometer in absorbance mode. X-ray photoelectron spectroscopy (XPS) measurement was performed using a PHI 5700 ESCA spectrometer with monochromated Al KR radiation ($h\nu=1486.6$ eV). Fluorescence spectra were recorded on a Cary Eclipse fluorescence spectrophotometer (VARIAN, America) with an excitation wavelength of 380 nm.

2 Supplementary data





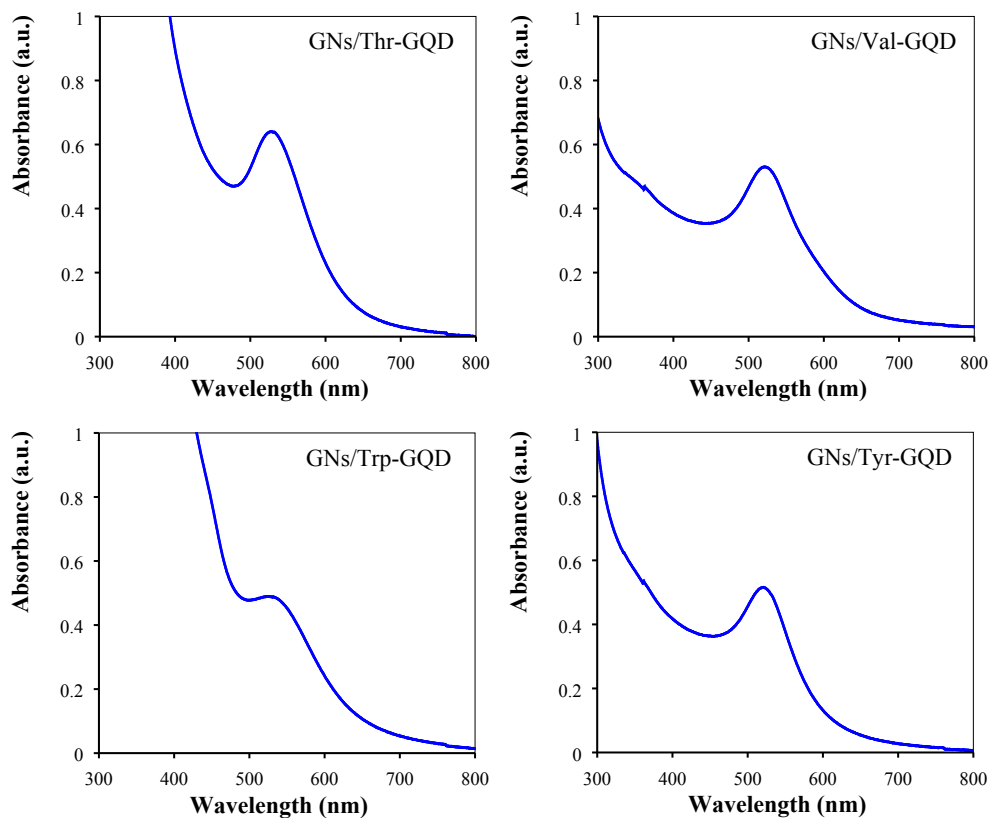


Fig. s1. UV-vis absorption spectra of the GNs/amino acid-GQD solution.

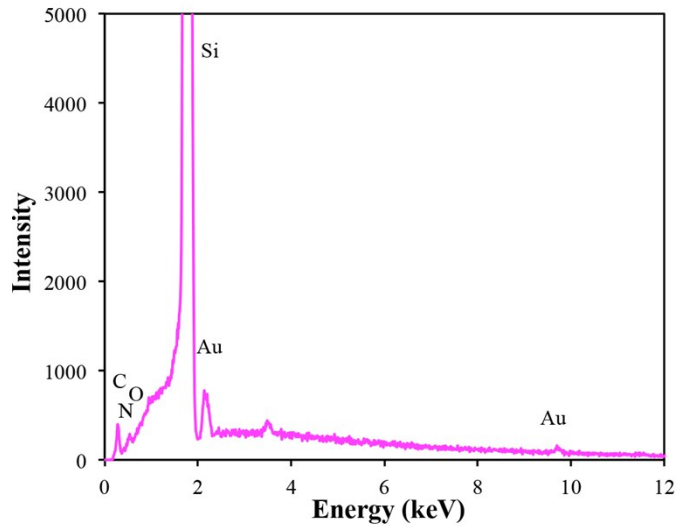


Fig. s2 EDX pattern of GNs/Pro-GQD

References

- 1 X. Wu, F. Tian, W.X. Wang, J. Chen, M. Wu, I. Ju and X.J. Zhao, *J. Mater. Chem. C*, 2013, 1, 4676–4684.
- 2 I. Mihalache, A. Radoi, C. Munteanu, M. Kusko and C. Kusko, *Org. Electron.*, 2014, 15, 216.