Supporting Information

Laser-Induced Graphene/Gold Nanoparticle Hybrid Sensor for Enhanced Electrochemical Detection of Paracetamol

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Reagents and instruments

Paracetamol (Acetaminophen, AP), potassium ferricyanide ($K_3[Fe(CN)_6]$), and potassium ferrocyanide ($K_4[Fe(CN)_6]$) were purchased from Damas-beta (Shanghai, China). The polyimide film (25 μm, DuPont, USA), silver/silver chloride ink (EN-06B8, Enson, China), silver ink (JLL-20, JuLong, China), polyethylene terephthalate (PET) film (10 μm), screen-printed carbon electrodes (SPCE), and screen-printed gold electrodes (SPAE) were all bought on Taobao. The glassy carbon electrode (GCE) was acquired from ChenHua Instrument Co. Ltd. Phosphate buffered saline (10 mM KCl, pH = 7.4), chloroauric acid trihydrate ($HAuCl_4 \cdot 3H_2O$), catechol (CC), resorcinol (RC), hydroquinone (HQ), ethanol, and acetone were purchased from Sigma Aldrich, China. Dopamine (DA), L-ascorbic acid (AA), and urea (UA) were sourced from Macklin, Shanghai, China. All the reagents mentioned above are of analytical grade. Ultrapure water (≥18 MΩ·cm) was produced by the Hitachi water purification system (Shanghai, China).

The scanning electron microscope (SEM) images were captured using a Zeiss Gemini SEM 300. Powder X-ray diffraction (PXRD) was performed on a SmartLab SE diffractometer (Rigaku, Tokyo, Japan) with Cu Kα radiation. Raman spectra were collected using a Renishaw inVia Raman microscope. X-ray photoelectron spectroscopy (XPS) was conducted on a Thermo Fisher ESCALAB 250Xi using an Al Ka laser (Thermo Fisher Scientific, USA). Contact angle images were obtained using a Theta Flex (BioLin, Sweden).

Preparation of AuNPs/LIG electrode

First, a 10.6 μm CO_2 laser was used to mark out the working electrode area of the three-electrode system on a 100 μm PI substrate. Then, 100 mM $HAuCl_4$ solution was drop-cast onto the obtained LIG working electrode at a loading volume of 10 μL. After the chloroauric acid precursor solution dried at room temperature, a second laser treatment was conducted under the same conditions as the first to obtain an AuNPs/LIG composite nanoelectrode. The settings for both laser treatments were: laser power of 2.5 W, speed of 150 $mm \cdot s^{-1}$, line spacing of 0.08 mm, and the laser mode was vector mode. Once the laser-marked electrode was prepared, screen printing technology was utilized to quickly print conductive silver paste and silver/silver chloride paste, which served as the reference electrode and connection wires in the three-electrode system, through pre-designed screen meshes and a scraper, followed by curing in an oven at 80°C for 5 minutes. Finally, a layer of PET film was applied over the AuNPs/LIG electrode as a passivation layer to isolate the working electrode area. The pattern of the three-electrode system was pre-designed using CAD software.

Electrochemical detection using AuNPs/LIG electrodes

To investigate the preparation conditions of AuNPs/LIG and the effect of external strain on electrochemical behavior, cyclic voltammetry (CV) measurements were conducted within a voltage range of -0.2 V to +0.6 V in a 0.1 M KCl solution containing 5.0 mM $K_3[Fe(CN)_6]^{3-/4-}$. In a 0.1 M PBS solution with a pH of 7, differential pulse voltammetry (DPV) was employed at a scan rate of 0.05 V/s to detect the electroactivity of acetaminophen within the range of -0.2V to +0.6V.

Actual sample analysis

Tylenol brand phenacetin-containing tablets were purchased from a pharmacy, and one tablet was ground into powder. According to the acetaminophen content indicated in the instruction manual, it was prepared into a standard concentration for testing. Tap water was directly sampled from the laboratory's water pipe. After filtering out physical impurities with a 0.45 μm filter, the tap water samples were diluted and adjusted to pH using a 0.1 M PBS solution (pH=7.0) at a ratio of 1:1 (v:v). The standard addition method was used to analyze acetaminophen in the tap water samples. The formula for determining the recovery rate is: Recovery Rate (%) = Test Concentration / Added Concentration × 100%.

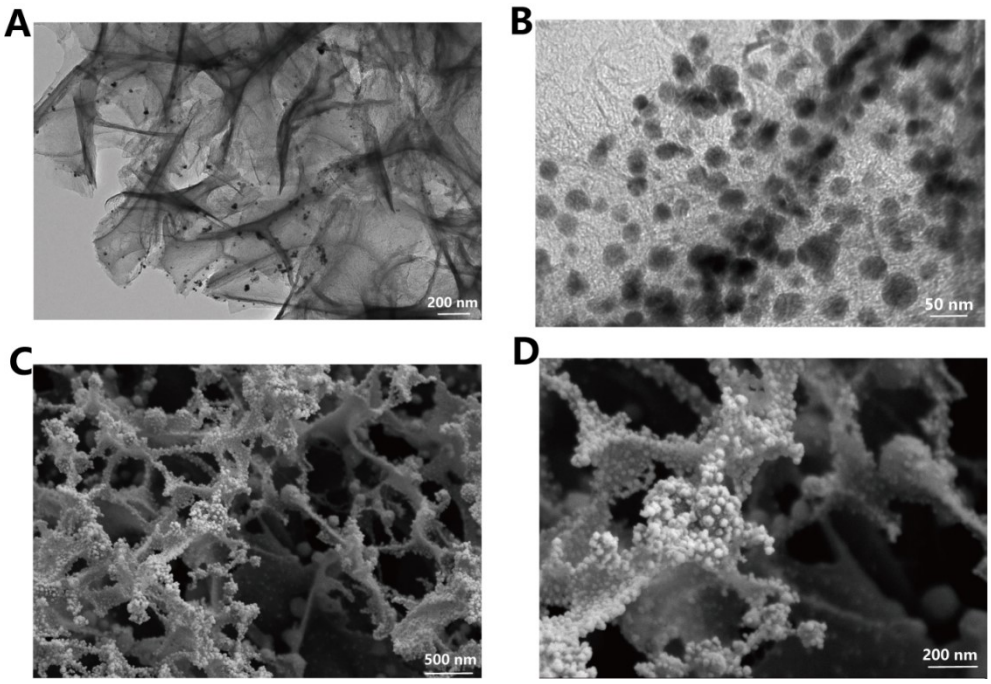

Fig. S1 Characterization of AuNPs/LIG electrodes: (A, B) TEM image; (C, D) SEM images.

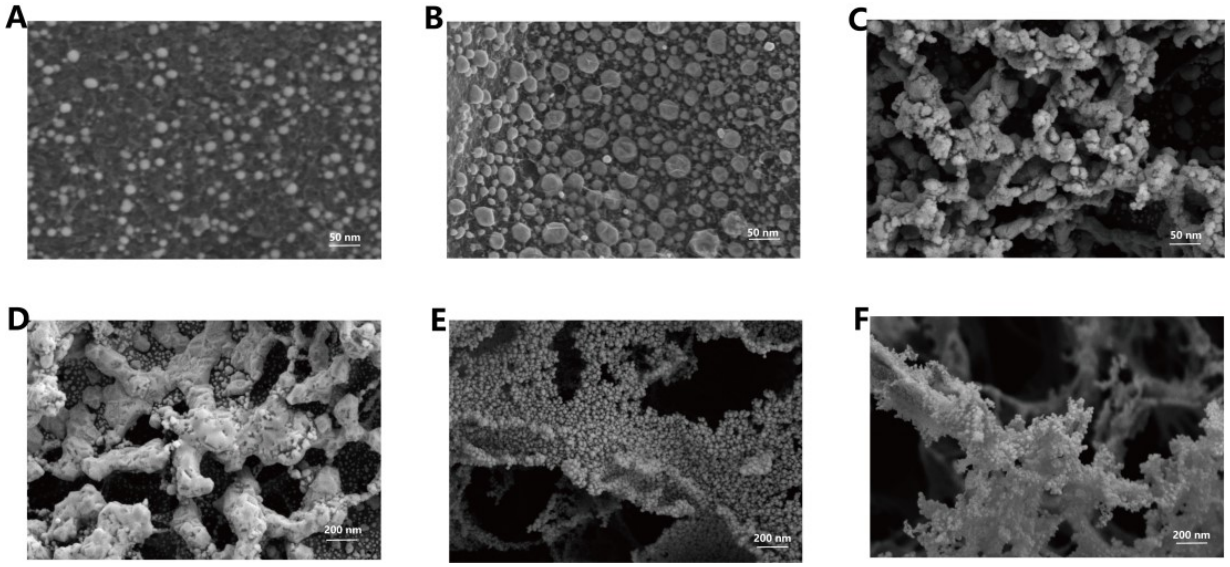

Fig. S2 SEM images of AuNPs/LIG fabricated with different laser parameters: (A) 2.0 W; (B) 2.5 W; (C) 3.0 W. SEM images of secondary laser engraving at different speeds: (D) 100 mm·s^{-1}; (E) 150 mm·s^{-1}; (F) 200 mm·s^{-1}.

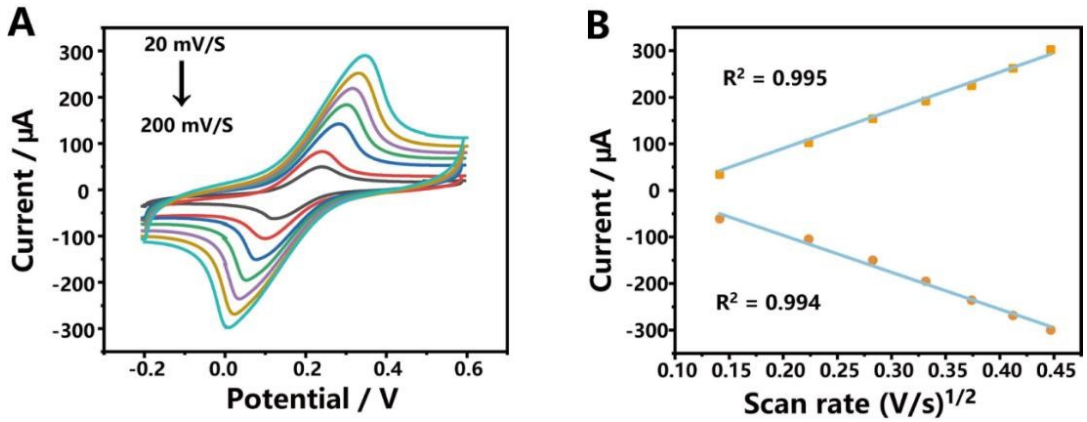

Fig. S3 (A) Cyclic voltammograms (CVs) of the AuNPs/LIG electrode in a solution containing 0.1 mmol/L KCl and 5 mM $[Fe(CN)_6]^{3-/4-}$ at different scan rates: 20, 50, 80, 110, 140, 170, 200 mV/s; (B) Plot of peak current versus the square root of scan rate.

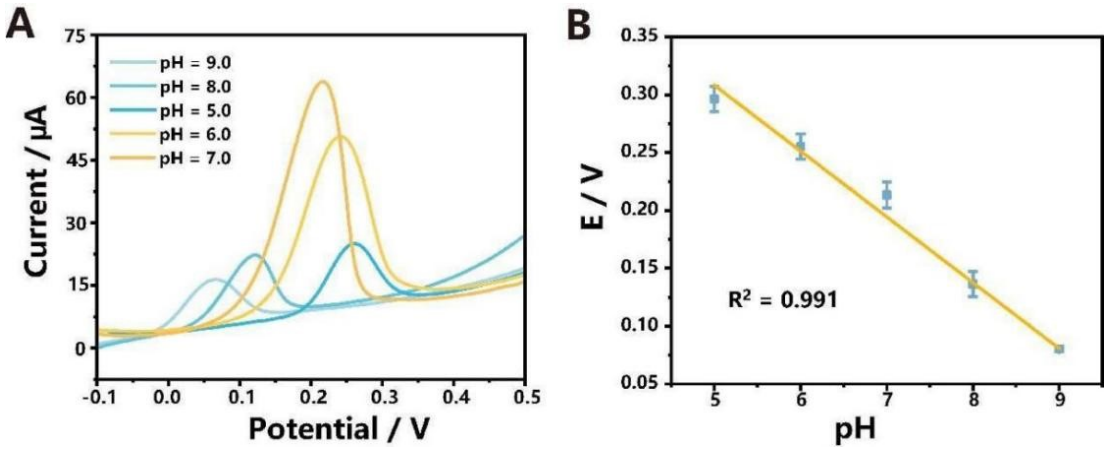

Fig. S4 (A) Cyclic voltammograms (CVs) of the AuNPs/LIG electrode in a PBS buffer solution (pH=7.0) containing 0.1 mmol/L paracetamol at different scan rates: 20, 50, 80, 110, 140, 170, 200 mV/s; (B) Plot of pH versus potential.

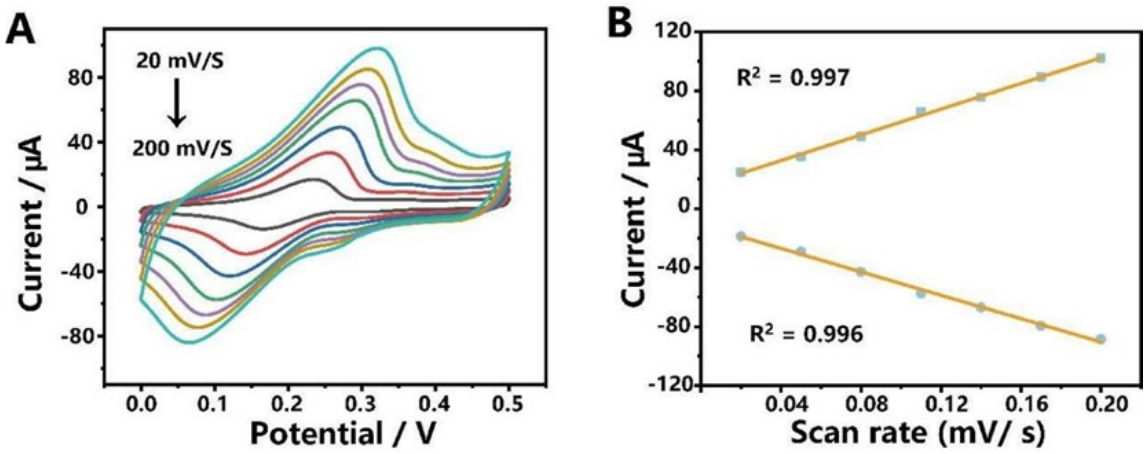

Fig. S5 (A) Cyclic voltammograms (CVs) of the AuNPs/LIG electrochemical sensor in a PBS buffer solution (0.01 mol/L, pH=7.0) containing 1 mmol/L paracetamol at different scan rates: 20, 50, 80, 110, 140, 170, 200 mV/s; (B) Plot of peak current versus scan rate.

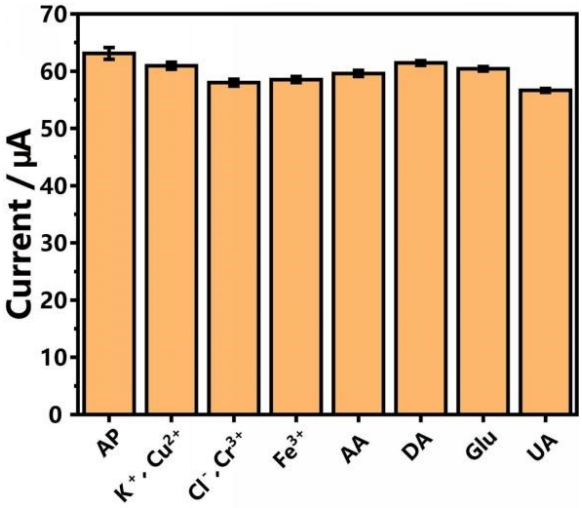

Fig. S6 Effect of 10 mM organic or inorganic ions on the current value of AuNPs/LIG response to paracetamol. AP- paracetamol; AA- Ascorbic acid; DA- Dopamine; UA- Uric acid.

Table S1 Comparison between reported methods and our method for detecting paracetamol.

Electrode	Detection object	Linear range	Detection limit	Application scenario	Reference
S-CTFs@$NiCo_2O_4$	PA	2 ~ 360 μM	0.18 μM	Actual water sample	[12]
	4-PA		0.35 μM		
NH_2-UiO-66/WC	PA	1 μM ~ 150 μM	0.17 μM	Actual water sample	[20]
	PAP		0.35 μM		
GMA	PA	0.1 μM ~ 150 μM	0.057 μM	tablet	[41]
N-GSEC	PA	0.1 ~ 250 μM	0.01 μM	-	[15]
	4-PA	0.05 ~ 100 μM	0.025 μM		
AuNPs/LIG	PA	0.1 μM ~ 100 μM	0.065 μM	Tab water and tablet	This study

Table S2 Comparison with other laser synthesis methods.

Electrode	Detection object	Linear range	Detection limit	Application scenario	Reference
LIG	Paraquat	0.5 - 35 μM	0.54 μM	Actual water sample	[42]
LIG/PtNPs	glucose	300 nM - 2.1 mM	4.622 μA/mM	Sweat	[43]
LIG/Ag NPs	H_2O_2	0.1 - 10 mM	7.9 μM	Whole and skimmed milk	[44]
Co@3D NPC	clozapinealben	0.15 - 20 μM	2.8 nM	Soothing tea	[45]

	dazole	0.1 - 7 μM	2.5 nM	and pure milk	
AuNPs/LIG	PA	0.1 μM - 100 μM	0.065 μM	Tab water and tablet	This study

Table S3. Detection of paracetamol in actual samples

Sample	Spiked (μM)	Found (μM)	HPLC (μM)	Recovery rate (%)
Tablet	10	10.68	12.78	106.8%
	20	20.12	22.89	100.6%
	50	52.33	52.27	104.66%
	80	82.16	81.58	102.7%
Tap water	10	9.78	10.77	97.8%
	20	19.25	22.17	96.25%
	50	48.76	49.59	97.52%
	80	78.63	78.32	98.29%