Supporting Information

PCN-224/rGO nanocomposite based photoelectrochemical sensor

with intrinsic recognition ability for efficient p-arsanilic acid detection

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Section 1. Supplemental experiments

Humic acid was utilized to investigate the effects of dissolved organic matter on p-ASA detection. The humic acid solution representing the level of simulated natural water was prepared as follows. The humic acid (50 mg) was dissolved in 5 mL of NaOH (1 M), then the mixed solution was diluted by deionized water to reach an apparent concentration of 50 mg/L. Next, 0.1 M HCl was used to adjust the pH of diluted humic acid to 6.0, and the adjusted solution was filtered through 0.45 μ m membrane. Finally, the obtained solution of humic acid was diluted to reach an apparent concentration of 10 mg/L and was employed to prepare experimental background solution containing 0.02 M NaCl. As for preparation of swine manure lixivium, 100 g of fresh swine manure (gained from a pig farm in Heyuan, Guangdong province in China) was dipped in water for 12 h. Then the obtained lixivium was filtered by 0.45 μ m membrane. And the filtered solution was diluted 100 times as experimental background solution.

For practical detection, the prepared simulated natural water and swine manure lixivium were spiked with $1\mu g/L$, $10 \mu g/L$, $100 \mu g/L$ and $1000 \mu g/L$ of *p*-ASA standards respectively. Then the fabricated sensor was used to detect *p*-ASA concentration in two spiked real water samples. The detailed detection process in real samples was similar to that detection in water.

Image: Constrained state stat

Section 2. Supplemental data

Fig. S1 SEM images of PCN-224 (A), PCN/rGO-0.04 (B), PCN/rGO-0.08 (C) and PCN/rGO-0.32 (D).



AFM images, GO and rGO exhibited sheet-like morphology with ultrathin thickness. The thickness of rGO at the ratio of 0.16 and 0.32 is 1.0-1.1 nm and 1.18-1.28 nm, respectively. Thus the thickness of rGO in PCN/rGO composite hardly changed when its ratio increased from 0.16 to 0.32. Thus, the amorphous particles (its ratio at 0.32) is not a result of the thicknesd GO nanosheets. The main cause of damaged crystal structure is that the high density of GO sheets hinder the coordination between TCPP and Zr-O cluster.



Fig. S3 Raman spectra of GO, PCN/rGO-0.16 samples. There are D-band shift at 1350 cm⁻¹ and G-band shift at 1590 cm⁻¹ in the Raman spectra of GO. After compounding with PCN-224, D-band shift and G-band shift remain at the same positions. However, D/G ratio of PCN/rGO-0.16 is smaller than that of pure GO, confirming GO was reduced into graphene to a certain extent during the solvothermal reaction.



Fig. S4 (A) FT-IR spectra of GO (a), PCN-224(b), PCN/rGO (c); (B) N 1s XPS spectra for PCN-224 and PCN/rGO.



Fig. S5 Electrical equivalent circuit of PCN-224 (A) and P CN/rGO (B) based on the EIS plots. For the PCN-224 electrode, we can fit the EIS curve with the equivalent circuit in A, where the electrochemical reaction is controlled by charge transfer. In contrast, for the PCN/rGO, the charge transfer rate at the interface is much fast and the mass transport also control the electrode process. Therefore, the element of Z_W representing the mass transport is added in the equivalent circuit in B.



Fig. S6 Photocurrent response of PCN-224 compounding different GO ratios.



Fig. S7 Photocurrent of PCN/rGO reacted with p-ASA under different temperature (A) and pH values (B).



Fig. S8 Two consecutive linear ranges for detection of *p*-ASA via photocurrent increment on PCN/rGO electrode:









Fig. S9 (A) As 3d XPS spectra for *p*-ASA and PCN/rGO/ASA; (B) Zr 3d and (C) C 1s spectra for PCN/rGO and PCN/rGO/ASA.



Fig. S10 SEM images of PCN/rGO/ASA (A) and PCN/rGO/ASA after PEC testing (B).



Fig. S11 The photocurrent of PCN/rGO/ASA in electrolyte (HEPES buffer) pumped argon (black curve) and air (red curve).



Fig. S12 Tauc plots of PCN/rGO (A) and PCN/rGO/ASA (B)



Fig. S13 Photocurrent response of PCN/rGO electrode in different concentrations of K₃[Fe(CN)₆].



Fig. S14 Temporal evolution of photocurrent of PCN/rGO electrode in electrolyte. In the process of PEC testing, the charging current of double layer is very high when electrode is immersed in electrolyte within the first a few seconds. In order to obtain relatively stable photocurrent response, the "light on" starts at 20 s, then the "light off" begins at 30 s (the illumination occurs at 10-second intervals).

Section 3. Supplemental mechanism investigation

The process of calculating parameters related semiconductor electrochemistry is as follows: (I) The plots with $1/C^2$ vs. applied potential at the constant frequency of 10 kHz for PCN/rGO and PCN/rGO/ASA were obtained according to the Mott-Schottky equation:¹

$$\frac{1}{C^2} = \left(\frac{2}{e\varepsilon\varepsilon_0 N_A A^2}\right) \left[V - V_{fb} - \frac{k_B T}{e}\right]$$
(1)

where C is capacitance, e is the electronic charge $(1.602 \times 10^{-19} \text{ C})$, ε_0 is the permittivity of vacuum (8.854×10⁻¹² F/m), ε is the relative permittivity of semiconductor (ε ~15.0 for the PCN/rGO), k_B is Boltzmann's constant (1.38×10⁻²³ J/K), T is the absolute temperature (298 K), N_A is the carrier density, A is the active area of the electrode (0.28 cm²), V is the applied potential and V_{fb} is the flat band potential. The fitted linear equations obtained from Mott-Schottky plots

(Fig. 5B) were $y_1 = 1.61 \times 10^{10} x_1 + 3.72$ and $y_2 = 1.17 \times 10^{10} x_2 + 1.74$ for PCN/rGO and PCN/rGO/ASA. Based on equation (1), the value of V_{fb} can be measured by intercept at zero on the potential axis of Mott-Schottky plot. The V_{fb} calculated from the above fitted equations was - 2.3 V and -1.5 V (vs. Ag/AgCl) for PCN/rGO and PCN/rGO/ASA. The V_{fb} is considered to be close to the conduction band (CB) edges of the n-type semiconductor,² thus the CB positions of PCN/rGO and PCN/rGO/ASA were about -2.3 V and -1.5 V (vs. Ag/AgCl), respectively (see Fig. 5C).

(II) The carrier density, N_A, was estimated from the slope of the Mott-Schottky plots using the following equation:³

$$N_A = \frac{2}{e\varepsilon\varepsilon_0 S_{MS} A^2} \tag{2}$$

where S_{MS} is the slope which can be obtained from the above fitted equations $(1.61 \times 10^{10} \text{ for PCN/rGO}, 1.17 \times 10^{10} \text{ for PCN/rGO/ASA})$ and A is the active area of the electrode (0.28 cm²). Hence, the charge carrier density was calculated to be $5.84 \times 10^{20} \text{ cm}^{-3}$ for PCN/rGO and $8.04 \times 10^{20} \text{ cm}^{-3}$ for PCN/rGO/ASA.

(III) The width of depletion layer (W) can be calculated according to the equation:⁴

$$V_{SC} = -\left(\frac{e_0 N_D}{2\varepsilon\varepsilon_0}\right) W^2 \tag{3}$$

where V_{SC} is space-charge capacitance of semiconductor (equal to band bending). V_{SC} was found to be 2.2 V and 1.4 V for PCN/rGO and PCN/rGO/ASA based on the difference between conduction band edge and bias voltage. Hence the width of depletion layer estimated from equation (3) was 2.5×10^{-7} cm and 1.69×10^{-7} cm for PCN/rGO and PCN/rGO/ASA, respectively. (IV)The strength of the electric field (E) is determined by the ratio of potential difference (band bending) to the width of the depletion layer:

$$E = \frac{V_{SC}}{W} \tag{4}$$

In terms of equation (4) and the above calculation results, the E are 8.84×10^6 V/cm and 8.22×10^6 V/cm for the PCN/rGO and PCN/rGO/ASA, respectively.

References

1. C. Li, Y. Li and J.-J. Delaunay, A novel method to synthesize highly photoactive Cu₂O

microcrystalline films for use in photoelectrochemical cells, *ACS Appl. Mater. Interfaces*, 2013, **6**, 480-486.

- J. Lin, Y. Dong, Q. Zhang, D. Hu, N. Li, L. Wang, Y. Liu and T. Wu, Interrupted chalcogenide-based zeolite-analogue semiconductor: atomically precise doping for tunable electro-/photoelectrochemical properties, *Angew. Chem.*, 2015, **127**, 5192-5196.
- J. N. Nian, C. C. Tsai, P. C. Lin and H. Teng, Elucidating the conductivity-type transition mechanism of p-type Cu₂O films from electrodeposition, *J. Electrochem. Soc.*, 2009, 156, S163-S163.
- K. Rajeshwar, in *Fundamentals of Semiconductor Electrochemistry and Photoelectrochemistry*, ed. S. Licht, Wiley-VCH, Weinheim, 2001, pp. 10.