Supporting Information

An electrochemical aptasensor based on TiO_2/three-dimensional reduced graphene oxide/PPy nanocomposite for the sensitive detection of lysozyme

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1. Preparation of 3D-GO

Graphene oxide (GO) was prepared by a modified Hummers method [1]. Crude GO was dispersed in 200 mL of deionized water and exfoliated with Cell Crusher (900–1000 W, 40 min) for 2 h. Finally, the product 3D-GO was obtained after freeze drying.

2. Preparation of TiO_2 hollow balls

In a typical experiment [2], 12 g of glucose was dissolved in 80 mL of water to form a solution. The solution was then sealed in a 100 mL Teflon-lined autoclave maintained at 180 °C for 4 h. Products were centrifuged (5000 r/min), washed, and dispersed in water for five cycles, after which they were centrifuged, washed, and redispersed in ethanol for five cycles. The obtained carbon spheres were then dried at 80 °C for 2 h in a vacuum.

The starting solution was prepared by mixing 1 mL of $Ti(OBu)_4$ and 20 mL of ethanol. After stirring at 40 °C for 30 min, 0.1 g of colloidal carbon spheres [as prepared in Section (1)] was added to the reaction medium, which was then vigorously stirred for 1 h. When the mixture had cooled to room temperature, it was centrifuged, washed, and dispersed in ethanol for five cycles. The mixture was aged in air at room temperature for 12 h and dried at 60 °C in a vacuum oven. To fabricate TiO_2 hollow spheres, the mixture was heated at a rate of 2 K/min at room temperature and kept at 550 °C for 4 h in a muffle furnace.

3. Chemical structure of GO and TiO_2 nanoballs

Fig. S1 shows the FTIR spectra of GO, water –OH stretching (3400 cm^{-1}), carboxylates or ketones C=O stretching (1728 cm^{-1}), water –OH bending and C=C stretching (1624 cm^{-1}), alcoholic C–OH bending (1401 cm^{-1}), epoxide C–O–C or phenolic C–O–H stretching (1222 cm^{-1}), and C-O stretching (1043 cm^{-1}). The wide peaks at 400–600 cm^{-1} is attributed to the stretching vibration of Ti–O–Ti bonds in crystalline TiO_2.

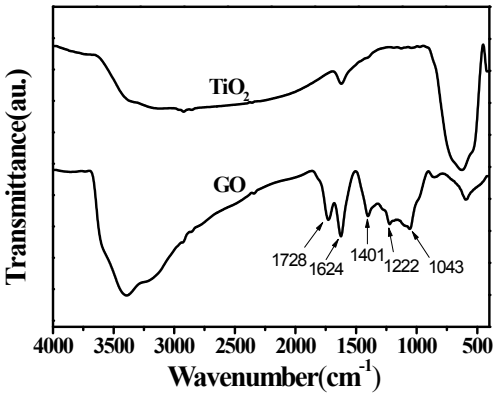

Fig. S1 FTIR spectra of GO and TiO_2

4. Surface morphology of GO and TiO_2 hollow balls

Fig. S2a shows the SEM images of 3D-rGO, which has a typically curved, layerlike structure tens of nanometers in size. The interpenetrating structure could increase the surface active area and loading capacity compared with graphene. This structure also favors molecular diffusion throughout the entire GR monolith. Thus, 3D-rGO was used as the platform matrix for the deposition of TiO_2 particles to fabricate nanocomposites. SEM images show that pristine TiO_2 has evident particle aggregation (Fig. S2b). Figs. 2c and 2d show the TEM images of GO and TiO_2.

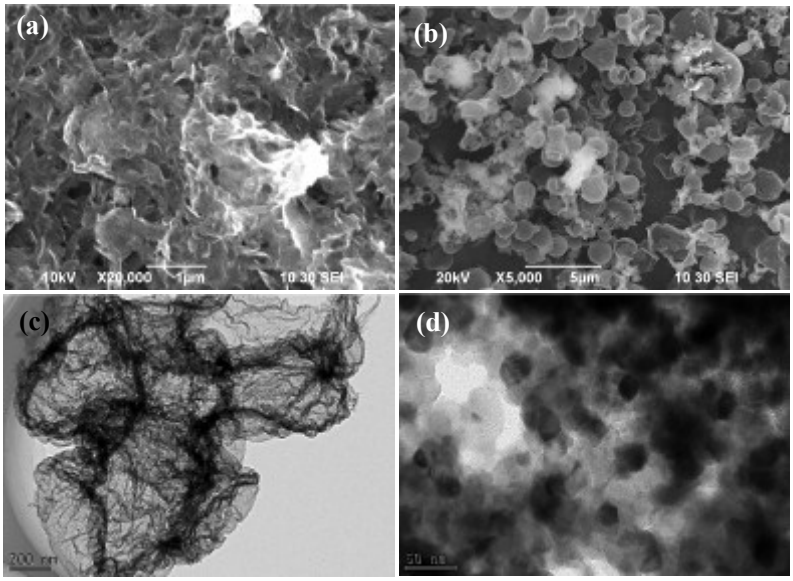

Fig. S2 SEM images of (a) GO and (b) TiO_2. TEM images of (c) GO and (d) TiO_2.

5. CV measurements of samples at different stages and lysozyme detection

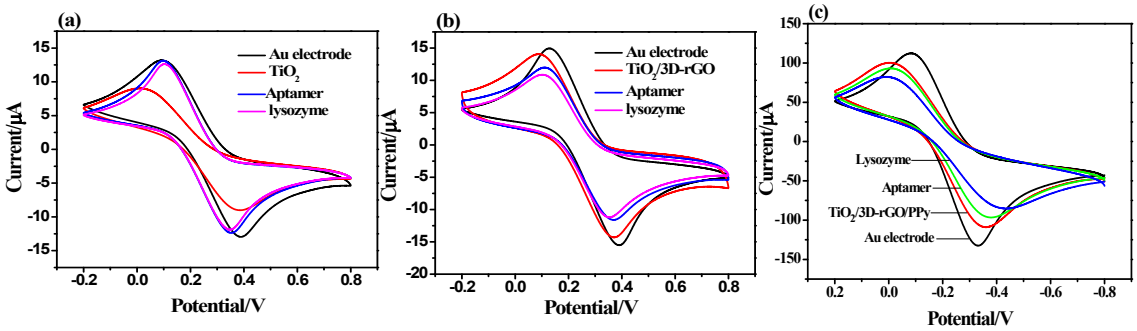

Fig. S3 CV Curves of bare Au electrode vs. (a) TiO_2, (b) TiO_2/3D-rGO, and (c) TiO_2/3D-rGO/PPy nanocomposite-modified Au electrode, immobilized aptamer, and aptamer coordinated with lysozyme (0.5 ng mL^{-1}).

6. Kinetic behavior of the lysozyme adsorption onto the developed aptasensor

The result showed that the DNA G-quadruplexes could be removed from the TiO_2/rGO/PPy matrix at the very beginning. After 2 h, the adsorption curve reached to equilibrium. Comparing with the current response of the TiO_2/rGO/PPy electrode

immobilized with aptamer, the reserved △I of 8.6 mA was observed, indicating that quite much DNA G-quadruplexes could be remained even after 10 h.

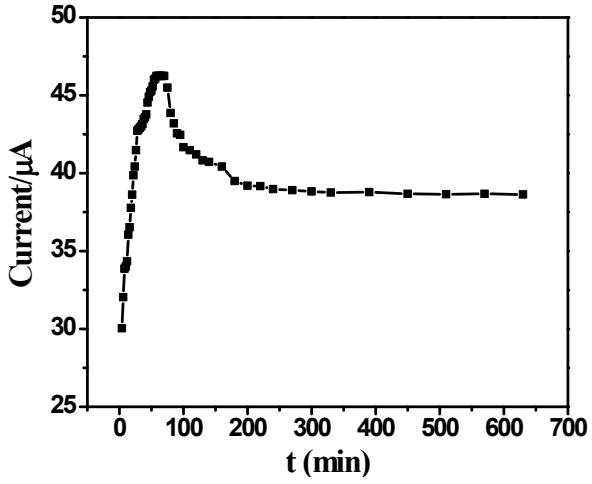

Fig. S4 The dependence of the current response of the lysozyme detection using the developed aptasensor on the incubation time.

7. Thermogravimetric analysis (TGA) of TiO_2/3D-rGO/PPy nanocomposite

The thermogravimetric analysis (TGA) was performed in N_2 flow using a thermogravimetric analyzer (Diamond TG/DTA). The samples were heated from 20 °C to 800 °C at a rate of 10 °C min^{-1}. TGA curves of TiO_2, 3D-rGO, TiO_2/3D-rGO and TiO_2/3D-rGO/PPy nanocomposite were summarized in **Fig. S5**. The products have a little mass loss up to 150 ℃ due to the deintercalation of H_2O. [3] The decomposition of PPy is probably between 150 ℃ and 450 ℃. [4] The mass loss for TiO_2, 3D-rGO, TiO_2/3D-rGO and TiO_2/3D-rGO/PPy are 5, 23.5, 20, and 47 wt.%, respectively. Based on the above TG analyses, the amount of TiO_2, 3D-rGO, PPy, and adsorbed water in the TiO_2/3D-rGO/PPy nanocomposite were approximately calculated to be about 7, 59, 25 and 9 wt.%, respectively.

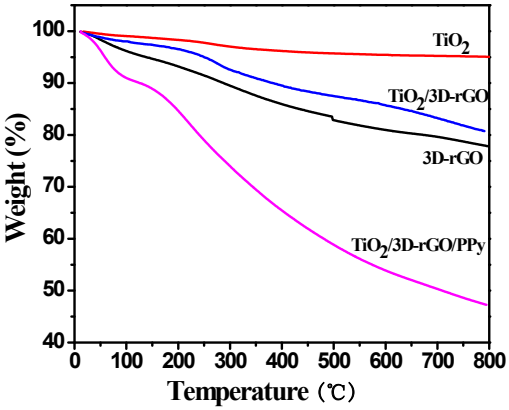

Fig. S5 TGA curves of TiO_2, 3D-rGO, TiO_2/3D-rGO, and TiO_2/3D-rGO/PPy nanocomposite.

References

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