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rGO Quantum Dots/ZnO Hybrid Nanofibers Fabricated Using Electrospun Polymer Templates and Applications in Drug Screen Involved in Intracellular H_2O_2 Sensor

Chi Yang[a,*],Hu Lingwei[b], Hong-Yan Zhu[a], Yong Ling[a],Jin-Hua Tao[a], Chun-Xiang Xu[c,**]

[a]*Department of Pharmacy, Nantong University, Nantong 226001, China*

[b]*Shangqiu Medical College, Shangqiu 476100, Henan, China*

[c]*State Key Laboratory of Bioelectronics, Southeast University, Nanjing 210096, China*

[*]*Corresponding authors.Tel.: +86-513-85051728, E-mail: toyangchi@ntu.edu.cn.*[**]*Corresponding authors. Tel.: +86-25-83790755, xcxseu@seu.edu.cn.*

1. Experimental

1.1. Synthesis of ZnO QDs

ZnO QDs were synthesized by sol–gel method as described elsewhere. [1] In a typical synthesis, 50 mL of ethanol containing zinc acetate (1.0898 g) was boiled and stirred in a distillation apparatus at 80°C for 3 h. After cooling down to 0°C, $LiOH{\cdot}H_2O$ solution (0.50mM) was added dropwise to the reaction solution. Finally, the suspension was placed into an ultrasonic bath in order to destroy the weakly soluble powder. This procedure accelerates the release of OH ions, resulting in immediate reaction to form a stable ZnO cluster solution. White suspension was obtained which was centrifuged at 12000 rpm to separate the precipitates. The white precipitates were redispersed in ethanol and centrifuged again. The process was repeated three times to remove unreacted components or reactants. To provide aqueous stability to ZnO QDs, 0.04 g of precipitates obtained after centrifugation were dispersed in distilled 50 mL water for further use.

1.2. Synthesis of GO QDs

Graphene oxide (GO) was prepared from graphite powder that underwent a preoxidation step by a modified Hummers' method.[2] Typically, 34 mL of H_2SO_4 and 0.75g $NaNO_3$, 1 g of graphite nanoparticles and 5 g of $KMnO_4$ were mixed in 250 mL round-bottom flask. The mixture was then heated to 40 °C and stirred for 6 h and a pink dense suspension was obtained. Subsequently, the reaction mixture was poured onto ice in 4 mL of 30% H_2O_2. The pink suspension quickly changed into a lemon-like yellow suspension. The mixture was transferred to a 1:10 HCl/water solution (500 mL) and then washed with deionized water under centrifugation at 20000 rpm until the pH of the suspensions reached 7. Following 3 h of sonication, the suspension was centrifuged at 10000 rpm for 30 min to collect a stable GO QDs solution from the supernatant.

2. Results and discussion

2.1. Morphology and characterization of QDs

TEM images (Figure S1a) depict that the particle size range is 4–5 nm and the particles obtained are a little polydisperse in nature. The structure of ZnO QDs was further investigated by HRTEM. Figure S1a (with inserted) shows the HRTEM of the ZnO QDs, which is showing (100) plane. The interplanar spacing is found to be 0.28 nm corresponding to the (100) crystal plane.An XRD study was also carried out on the ZnO QDs powder to estimate the crystallite structure and is shown in Figure S1b. The appearance of diffraction peaks corresponding to (100), (002), (101), (102) (110), (103) and (200) planes indicate the hexagonal structure of ZnO QDs in all the samples. This reveals that the particles are crystalline in nature and lie in nanometer regime. No extra peak pertaining to impurity has been observed which implies that ZnO QDs obtained are highly pure. Moreover, the XRD pattern of ZnO QDs fits well to ZnO with wurtzite structure (JCPDS card no. 89-1397).

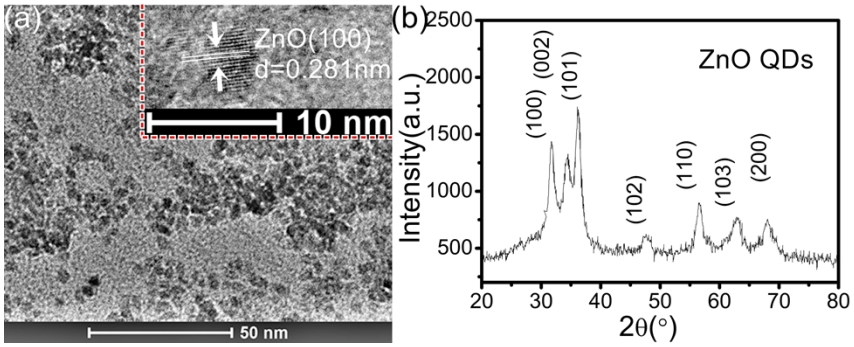

Figure S1 (a) TEM and HRTEM of ZnO QDs (with inserted); (b) XRD patterns of ZnO QDs.

Lattice images obtained at even higher magnifications displayed lattice fringes that can be identified with crystallographic planes of the grapheme oxide quantum dots (GO QDs). For instance, lattice fringes having interplanar spacing of ~0.242 nm, corresponding to GO (100) planes, are highlighted in the Figure S2a.

Raman scattering is highly sensitive to the electronic structure of carbon based materials, [3,4] The Raman spectra of GO QDs are shown in Figure S2b. The spectrum of GO QDs has two bands at 1577 cm^{-1} and 1343 cm^{-1}, which correspond to the GO (G) and diamondoid (D) bands, respectively.

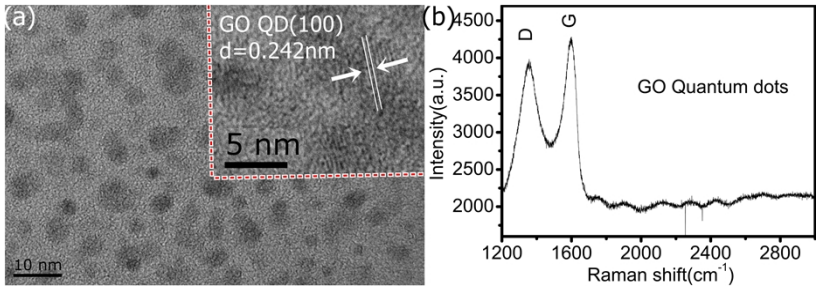

Figure S2 (a) TEM and HRTEM of GO QDs (with inserted); (b) Raman spectra of GO QDs.

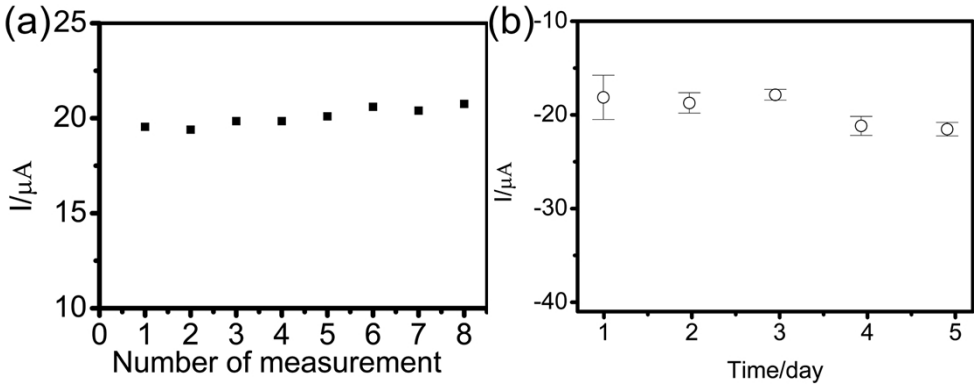

Figure S3 (a) Reproducibility test for the rGO QDs/ZnO hybrid nanofibers electrode monitored 8 times with the addition of 0.2 μM H_2O_2 at −0.4 V versus SCE in 0.1 M PBS (pH 7.2);(b) Stability test for rGO QDs /ZnO hybrid nanofibers electrode at −0.4 V versus SCE in 0.1M PBS (pH 7.2) over 5 days.

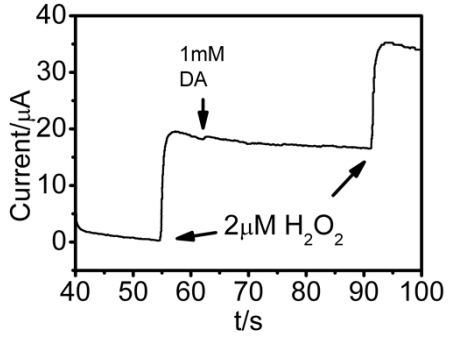

Figure S4 Amperometric responses of the rGO/ZnO electrode toward 2 μM H_2O_2 and containing 1mM DA.

The selectivity of the electrode toward the electrocatalytic reduction of H_2O_2

Table S1 Interference experiments with the proposed H_2O_2 biosensor.

Interferent	I(Interferent)/I(H_2O_2,2μM),%		
	-0.3V	-0.35V	-0.4V
AA(1mM)	0.4	0.5	0.4
UA(1mM)	0.15	0.12	0.11
DA(1mM)	0.45	3	0.15
O_2	8	0.6	0.5
$O_2^{\cdot-}$(20μM)	-	-	5
ClO^-(20μM)	-	-	6
NO(20μM)	-	-	10
HNO(20μM)	-	-	3

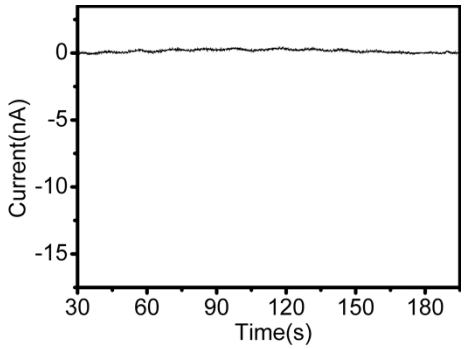

Figure S5 Measurements of electrode response upon the addition of 0.2 μM TBB in the cell-free detection solution.

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