Bio-Inspired One-Pot Synthesis of Fibrin-adhered-Reduced Graphene Oxide Conductive Bionanocomposites for Electrochemical Biosensing

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Inspired by the high adhesion behavior of fibrin scaffold in the blood coagulation, we developed novel fibrin fiber-adhered reduced graphene oxide (rGO) conductive bionanocomposites (CBNCs) via one-pot in situ synthesis for high performance electrocatalysis and biosensing. The CBNCs presented porous 3D network structure with rGO nanosheets supported and connected mutually (glued) by fibrin fibers, in turn endowing the CBNCs with good conductivity and mass transfer efficiency. The presence of fibrin not only brought negligible effects on the conductivity of rGO, but also improved their mechanical stability, and as a result, the electrochemical activity of the CBNCs-modified Au electrodes were even superior to that of bare Au electrodes. The CBNCs were then elaborated as the conductive platform to load platinum nanoparticles (PtNPs), which lowered the catalysis potential of H_2O_2 oxidation and promoted the sensitivity to 578 μA cm^{-2} mM^{-1}, being superior to most analogues. Furthermore, glucose oxidase (GOx) and acetylcholinesterase (AChE) were entrapped/adsorbed in the CBNCs to construct amperometric glucose and acetylcholine biosensors, respectively. The acetylcholine biosensor was further adopted to detect paraoxon for food safety. Benefiting from the high adsorbability and catalytic capacity derived from the CBNCs platform, high performance biosensors are expected. The proposed method may open up a new direction for the facile preparation of conductive bionanocomposites.

Introduction

- Researches about conductive nanomaterials in bio-applications are mainly based on the post modification of biological ingredients on preformed conductive materials due to the biological incompatible preparation conditions and the decreased conductivity caused by biomolecules. One-step integration is clearly favorable but has been rarely achieved.
- Fibrin fiber networks generated by blood coagulation possess unique 3D porous structure, biocompatibility and high adhesive ability, which can act as highly efficient supporting matrices for biological components and functional materials.

Methods

Fibrinogen was cleaved by thrombin and transferred into insoluble fibrin fiber networks to entrap rGO nanosheets, yielding fibrin-adhered-rGO CBNCs. Incorporating PtNPs or/and enzymes into the coagulation formed multi-functional fibrin-adhered-rGO CBNCs.

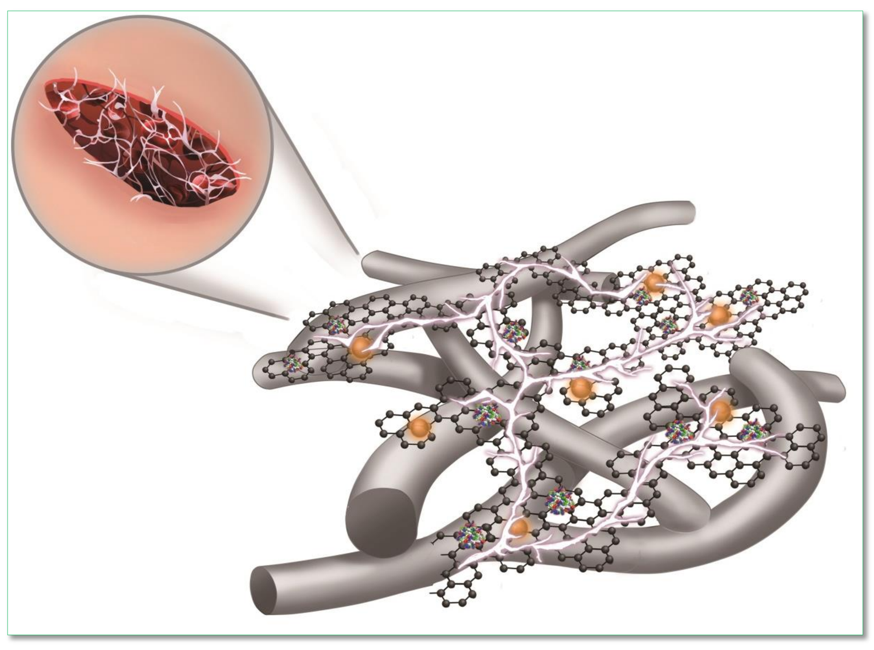

Fig. 1. Illustration of the architecture of fibrin-adhered-rGO-PtNPs-GOx CBNCs.

Results and Discussion

Fibrin-adhered-rGO CBNCs presented as unique homogeneous hydrogel-like composites leaving clear supernatant, indicating full encapsulation of rGO (the mass ratio of fibrinogen and rGO was 1 : 0.8).

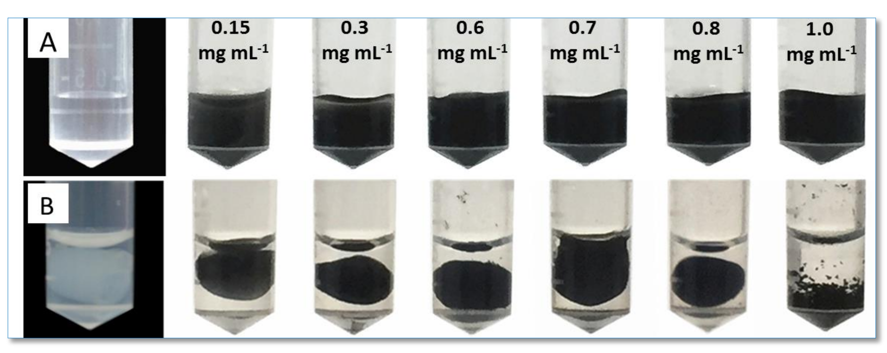

Fig. 2. Photographs of fibrin and fibrin-adhered-rGO CBNCs before and after the coagulation.

Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images showed porous networks with rGO nanosheets supported and connected mutually (glued) by fibrin fibers, endowing the CBNCs-modified Au electrodes with high electrochemical activity that were even superior to that of bare Au electrodes.

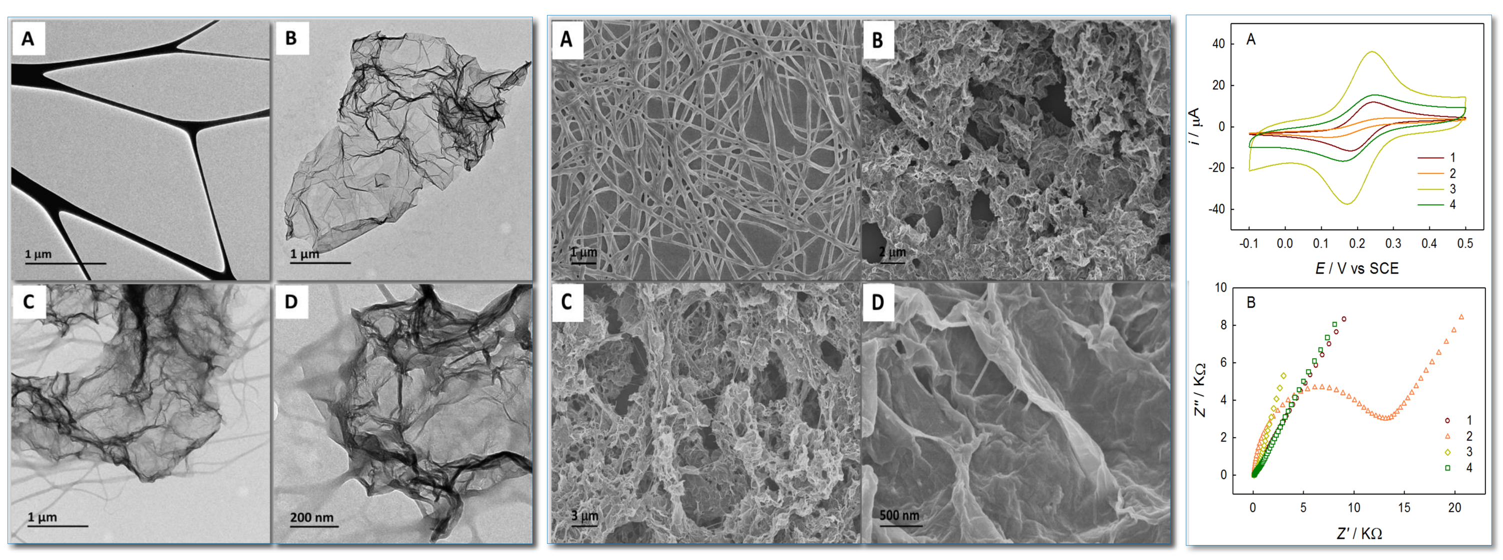

Fig. 3. (Left) TEM and (middle) SEM images of (A) fibrin, (B) rGO and (C, D) fibrin-adhered-rGO CBNCs. (Right) Cyclic voltammetry and electrochemical impedance spectroscopy of (1) bare Au, (2) fibrin/Au, (3) rGO/Au, (4) fibrin-rGO/Au electrodes.

Due to the unique structure, fibrin-adhered-rGO-AChE CBNCs preserved the high conductivity and catalytic capacity of rGO toward the oxidation of thiocholine, the electro-active product of ATCl hydrolysis, and thus, the high sensitive detection for organophosphorus pesticides based on the inhibition of AChE electrochemical method were expected.

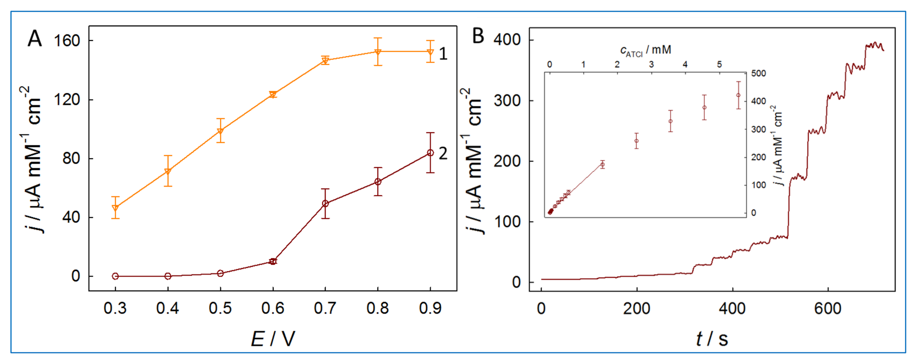

Fig. 4. (A) The static current responses of (1) fibrin-adhered-rGO-AChE CBNCs/Au and (2) AChE/Au electrodes to 1 mM ATCl. (B) Chronoamperometric responses to successive additions of ATCl at 0.7 V and (inset) calibration curves on fibrin-adhered-rGO-AChE CBNCs/Au electrodes.

- PtNPs were entrapped densely in fibrin-adhered-rGO CBNCs (fibrin-adhered-rGO-PtNPs CBNCs) due to the ultra-high immobilization ability from fibrin and rGO. Benefiting from the excellent electro-catalytic capacity for H_2O_2 oxidation deriving from the composites, fibrin-adhered-rGO-PtNPs CBNCs based electrochemical sensors exhibited good performance for H_2O_2 detection (sensitivity: 578 μA cm^{-2} mM^{-1}, the limit of detection (LOD): 0.77 μM).
- Further, GOx were loaded in fibrin-adhered-rGO-PtNPs CBNCs to construct fibrin-adhered-rGO-PtNPs-GOx CBNCs based biosensors for the detection of glucose, which also showed comparable performance with other analogue based biosensors (sensitivity: 92.8 μA cm^{-2} mM^{-1}, LOD: 0.5 μM).

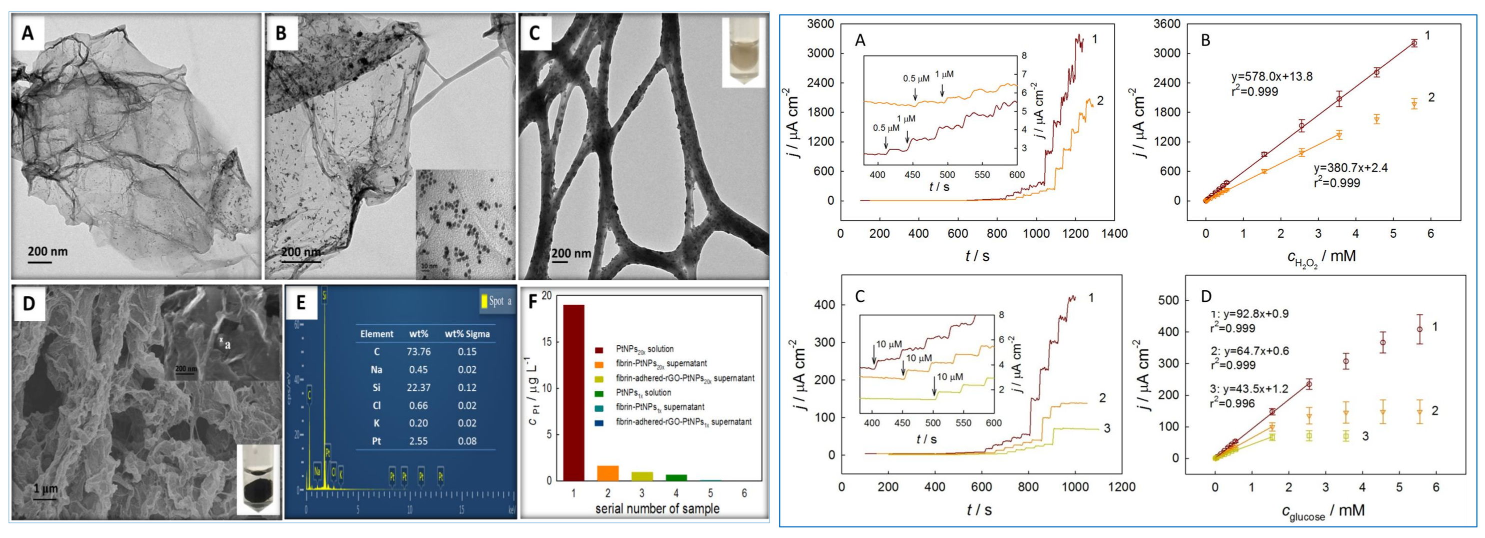

Fig. 5. (Left) (A, B) TEM, (D) SEM images and (E) energy dispersive spectrometer mapping of fibrin-adhered-rGO-PtNPs CBNCs. (C) TEM image of fibrin-PtNPs biocomposites. (Right) (A) Chronoamperometric responses to successive additions of H_2O_2 at 0.7 V and (B) calibration curves on (1) fibrin-adhered-rGO-PtNPs CBNCs/Au and (2) fibrin-adhered-rGO CBNCs/Au electrodes. (C) Chronoamperometric responses to glucose at 0.7 V and (D) calibration curves on (1) fibrin-adhered-rGO-PtNPs-GOx CBNCs/Au, (2) fibrin-adhered-rGO-GOx CBNCs/Au and (3) fibrin-GOx BNCs/Au electrodes.

Conclusions

- We have developed fibrin-adhered-rGO conductive bionanocomposites via one-pot synthesis under facile conditions, which is expected to be applied as versatile approach for the preparation of high performance conductive bionanocomposites.
- The CBNCs platform showed high immobilization ability toward both nanomaterials and biomolecules applied for high performance electrochemical-/bio-sensing.

Reference

Han, F.; Qi, X.; Li, L.; Bu, L.; Fu, Y.; Xie, Q.; Guo, M.; Li, Y.; Ying, Y. and Yao, S., Adv. Funct. Mater., 2014, 24: 5011-5018.

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