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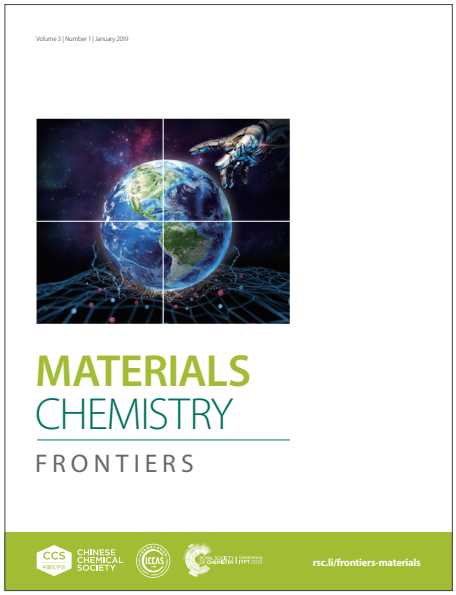

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ARTICLE

Enhance of an efficient sensitivity for the diclhovors detection by a low-weighted gelator based bolaamphiphile amino acid derivatives decorated with a hybrid graphene quantum dots/enzyme/ hydrogel

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Going beyond an efficient sensitivity of optical biosensor motivates the exploration of amplification strategy that incorporated the biosensor system in the supramolecular hydrogel. We established the novel fluorescent hybrid materials comprising graphene quantum dots and enzymes supported in L-phenylalanine derived bis(urea) supramolecular hydrogels (**GQDs**/**Enz**/**Gels**) for detection of organophosphate. Addition of acetylcholinesterase (AChE) and choline oxidase (ChOx) during the formation of the self-assembled **GQDs**/**Gel** materials, resulted in enzyme-functionalized gel networks. Significant turn-off fluorescence of the encapsulated **GQDs** in the hydrogels was due to the hydrogen peroxide generated from the active enzymatic reaction. Addition of the insecticide dichlorvos to the **GQDs/Enz/Gels** materials resulted in the recovery of the fluorescence in proportion to the concentration of dichlorvos, with a detection limit of 2.61×10^{-8} M which outperforms analogous in solution by 100-fold improvement and a wider linear range of 1.25×10^{-8} – 1.25×10^{-4} M compared to biosensor in solution. These hybrid hydrogels show promising sensitivity for detection of oxy-form organophosphate pesticide and expectedly offer scope for the development of rapid and environmentally friendly techniques.

Introduction

Supramolecular, or low molecular weight gels, and particularly hydrogels, have wide ranging applications in areas such as controlled drug release[1-2], enzyme stabilization and immobilization[3-5], pharmaceutical polymorph control [6-8], anion or metal ion sensing [9-13], and as biosensors [14-16]. Supramolecular hydrogels arise from the self-assembly of low molecular weight gelators (LMWG) and large amount of water (typically higher than 99% by mass) using non-covalent interactions. Bolaamphiphilic molecules comprise of at least two parts including a hydrophobic skeleton such as alkyl chains, a steroid, or a porphyrin and two hydrophilic groups on both ends which are symmetric or asymmetric end group. Most bolaamphiphiles with the hydrophobic spacers have been designed as low molecular mass gelators[17-19] which is a technical advantage in terms of the low concentration required for formation of aqueous or organic gels. For gel formation, the interaction between bolaamphiphilic based gelator stemmed from the hydrogen bonds, hydrophobic effect, π–π stacking interaction. These noncovalent interactions of bolas can form self-assemble to generate the sheets, micelles, vesicle, fibers and nanotubes. [20-22] Work of Minghua Liu[23] demonstrated the novel bolaamphiphilic gelators with L-glutamic acid as end group, connecting with the rigid aromatic substituents by varying the different lengths of alkyl chains as spacers which greatly changes the gelation property and the gel structures. Particularly, the even-odd alkyl chain would influence to the gelating and self-assembly under the hydrogen bonding from amide groups and a strong π–π stacking interaction. Arindam Banerjee[24] reported the metal-ion-induced, pH-responsive hydrogel formation using phenylalanine-based bolaamphiphilic molecule. One of these metallo-hydrogels showed a benefit for encapsulation of vitamin B12 molecules with slowly releasing under various pH system. Moreover, there are the research presenting that inorganic silica gel and gold particles exhibited much more stable under an organic Bolaamphiphilic molecules monolayer. A technical advantage of the Bolaamphiphilic molecules is attractive in terms of the low concentration at which aqueous or organic gels are formed[25]. Non-chemically crosslinked hydrogels have been extensively studied in the context of enzyme encapsulation and stabilization[3]. However, a flexible and porous structure is required to facilitate full penetration of the enzyme into the substrate and therefore, solid-phase substrates such as metal nanoparticles, or even a mobile gel-type networks without well-defined pores, have seen less success[26-28]. Hence, the immobilization of amphiphilic GQDs and enzymes into hydrogels remains of great interests for amplifying a signal to give high sensitivity for sensing applications and maintaining enzymatic activity in biological applications. Considerably, carbon dots mediated through the hydrogel encapsulation show advantageously in high fluorescent intensity compared to those in solution.[29-30] Its benefit of high sensitivity for sensing application is of great merits.

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