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Catalytic degradation of organophosphorous nerve agent simulants by polymer beads@graphene oxide with organophosphorus hydrolase-like activity based on rational design of functional bimetallic nuclear ligand

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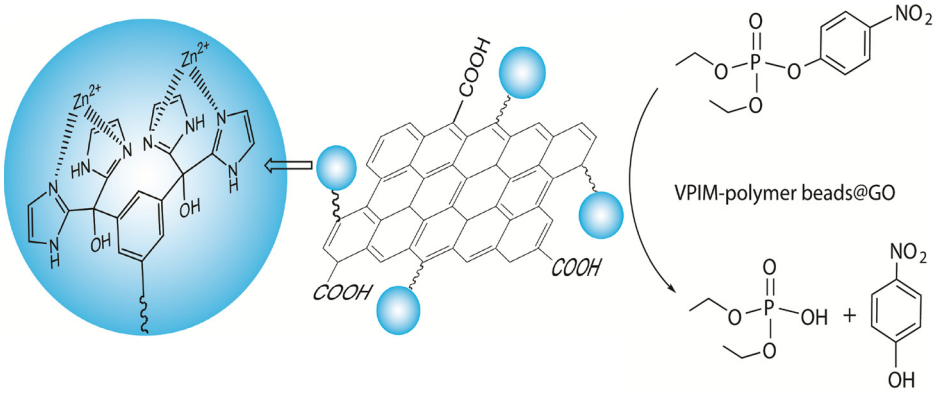
GRAPHICAL ABSTRACT



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ABSTRACT

The degradation of organophosphorous nerve agents is of primary concern due to the severe toxicity of these agents. Based on the active center of organophosphorus hydrolase (OPH), a bimetallic nuclear ligand, (5-vinyl-1,3-phenylene)bis(di(1H-imidazol-2-yl) methanol) (VPIM), was designed and synthesized, which contains four imidazole groups to mimic the four histidines at OPH active center. By grafting VPIM on graphene oxide (GO) surface via polymerization, the VPIM-polymer beads@GO was produced. The obtained OPH mimics has an impressive activity in dephosphorylation reactions (turnover frequency (TOF) towards paraoxon: 2.3 s^{-1}). The synergistic catalytic effect of the bimetallic Zn^{2+} nuclear center and carboxyl groups on surface of GO possibly contributes to the high hydrolysis on organophosphate substrate. Thus, a biomimetic catalyst for efficient degradation of some organophosphorous nerve agent simulants, such as paraoxon and chlorpyrifos, was prepared by constructing catalytic active sites. The proposed mechanism and general synthetic strategy open new avenues for the engineering of functional GOs for biomimetic catalysts.

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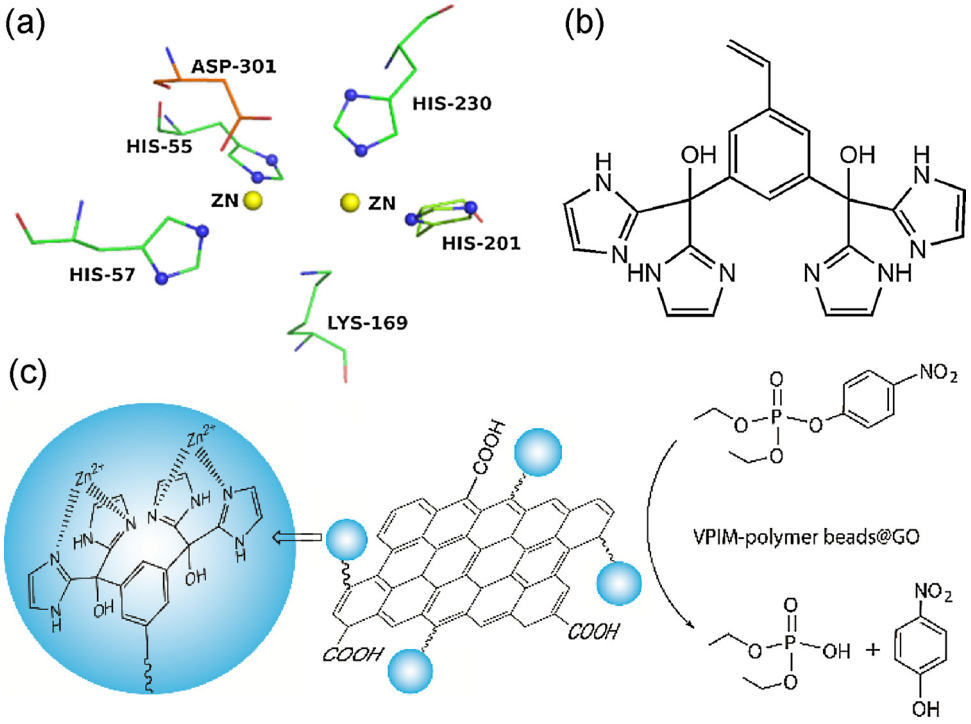

Fig. 1. Active center of organophosphorus hydrolase (PDB code 1HZY, extracted with Autodock 4.2, see ESI† Section 1). (b) Structure of bimetallic nuclear ligand, (5-vinyl-1,3-phenylene)bis(di(1H-imidazol-2-yl)methanol) (VPIM). (c) Reaction showing hydrolysis of paraoxon by VPIM–polymer beads@GO.

1. Introduction

Organophosphorous nerve agents are considered the most toxic compounds of synthetic chemical derivatives because of their phosphorylating mode of acetylcholinesterase inhibition, which can lead to asphyxiation [1]. To date, these nerve agents are still being used for chemical weapons or pesticides for agricultural production. Recent global military events and terroristic attacks have called the urgent need to efficiently destruct these chemicals. Organophosphorus hydrolase (OPH, also known as phosphotriesterase) can efficiently decompose the phosphate ester bond of these types of nerve agents [2,3]. However, whether in the natural or recombinant strains, OPH is not only low in content, but is also unstable, easily inactivated, and difficult to prepare [4,5].

Inspired by nature, the design of a biocatalyst mimicking the active center of an enzyme to substrate selectivity at the molecular level is an extremely challenging issue [6–8]. The catalytic participation of amino acid residues (His 55, His 57, His 201, His 230, Asp 301, and Lys 169) of OPH active center (Fig. 1a) has been largely explored [9]. Studies show that Asp 301 plays an important role on shuttle protons [10], and four histidines contribute to the formation of the bimetallic center [11,12]. Moreover, both metal ions in OPH active center are required for optimum catalytic activity [13]. The catalytic functions for one or both metal ions possibly include (1) polarization of the P═O or P═S bond of the organophosphate substrate for nucleophilic attack, (2) activation of water in the form of a hydroxide that bridges the two divalent cations, and (3) neutralization of the developing negative charge on the leaving group during P—O bond cleavage [14]. Therefore, the mimicry of bimetallic nuclear center is the point of OPH mimics [15–20].

Many biomimetic catalysts employ hydroxide bridged dimers of bimetallic nuclear as catalysts, such as, metal complexes [15], metal organic frameworks [16–18], and several nanomaterials [19,20] which hydrolyze organophosphorus triesters and achieve high catalytic efficiency. However, the design of these catalysts only focused on the bimetal nuclear center of OPH active sites. In fact, the amino acid residues (i.e, four histidines, carboxylated lysine and aspartic acid) at OPH active sites should be a focus. Therefore, in general, some of these biomimetic catalysts with high efficiency need bases, such as *N*–methylmorpholine (NMM) [19] and *N*–ethylmorpholine (NEM) [17], as co-reactants.

Owing to the large surface and abundant functional groups on surface [21,22], such as –C═O, –C—OH and –O═C–O–, carbon nanomaterials have exhibited nanoenzyme properties [23–25], or have been used as substrate to create artificial enzyme [26–28]. Active site-engineered graphene oxide (GO) as OPH mimetics has been designed and synthesized by polymerization using 1–vinylimidazole (1–VI) for the rapid degradation of nerve agents with good stability [29]. The cooperative effect of the imidazole groups, the —COOH groups on GO surface, and zinc ions are responsible for the high catalytic performance of OPH. However, the formation of the bimetallic nuclear center needs further confirmation.

In this work, we attempted to directly introduce the designed and synthesized ligand (5-vinyl-1,3-phenylene)bis(di(1H-imidazol-2-yl)methanol) (VPIM) containing four imidazole groups (Fig. 1b), considering that OPH active site consists of four histidines. Thus, the coordination environment of the metal ions is expected to be controlled in advance, and a bridged OH^- for a nucleophilic attack can be formed (Fig. 1c). Then, the designed bimetallic nuclear ligand was grafted on GO via polymerization to produce an OPH mimics.

2. Experimental

2.1. Chemicals and general methods

Paraoxon, dimethyl 5-aminoisophthalate, dimethyl 5-bromoisophthalate, trimethylolpropane trimethacrylate (TMPTMA), potassium vinyltrifluoroborate, (1, 1′-Bis(diphenylphosphino) ferrocene) dichloropalladium (II), complex with dichloromethane ($PdCl_2$(dppf) CH_2Cl_2), and 2,2′-azoisobutyronitrile (AIBN) were purchased from Sigma–Aldrich (Shanghai, China). Imidazole, 2-hydroxyethyl methacrylate (HEMA), *n*-butyllithium solution, chlorotrimethylsilane, sodium hydride (NaH), hydroxybenzotriazole (HOBt), *N*,*N*'-