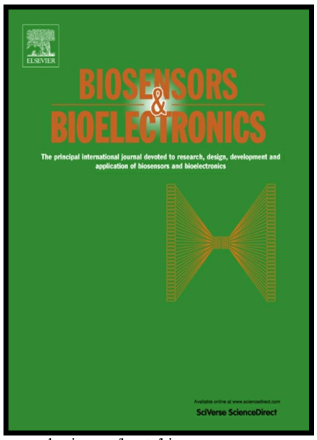

Polyacrylic acid-coated cerium oxide nanoparticles: an oxidase mimic applied for colorimetric assay to organophosphorus pesticides

Shi-Xiang Zhang, Shi-Fan Xue, Jingjing Deng, Min Zhang, Guoyue Shi, Tianshu Zhou

PII: S0956-5663(16)30470-5
DOI: http://dx.doi.org/10.1016/j.bios.2016.05.040
Reference: BIOS8730

To appear in: *Biosensors and Bioelectronic*

Received date: 26 February 2016
Revised date: 28 April 2016
Accepted date: 11 May 2016

Cite this article as: Shi-Xiang Zhang, Shi-Fan Xue, Jingjing Deng, Min Zhang Guoyue Shi and Tianshu Zhou, Polyacrylic acid-coated cerium oxid nanoparticles: an oxidase mimic applied for colorimetric assay t organophosphorus pesticides, *Biosensors and Bioelectronic* http://dx.doi.org/10.1016/j.bios.2016.05.040

Polyacrylic acid-coated cerium oxide nanoparticles: an oxidase mimic applied for colorimetric assay to organophosphorus pesticides

Shi-Xiang Zhang, Shi-Fan Xue, Jingjing Deng, Min Zhang,* Guoyue Shi, Tianshu Zhou*

School of Ecological and Environmental Sciences, School of Chemistry and Molecular Engineering, East China Normal University, 500 Dongchuan Road, Shanghai 200241, China.

Corresponding author:
Min Zhang, Email: mzhang@chem.ecnu.edu.cn
Tianshu Zhou, Email: tszhou@des.ecnu.edu.cn

Abstract:

It is important and urgent to develop reliable and highly sensitive methods that can provide on-site and rapid detection of extensively used organophosphorus pesticides (OPs) for their neurotoxicity. In this study, we developed a novel colorimetric assay for the detection of OPs based on polyacrylic acid-coated cerium oxide nanoparticles (PAA-CeO_2) as an oxidase mimic and OPs as inhibitors to suppress the activity of acetylcholinesterase (AChE). Firstly, highly dispersed PAA-CeO_2 was prepared in aqueous solution, which could catalyze the oxidation of TMB to produce a color reaction from colorless to blue. And the enzyme of AChE was used to catalyze the substrate of acetylthiocholine (ATCh) to produce thiocholine (TCh). As a thiol-containing compound with reducibility, TCh can decrease the oxidation of TMB catalyzed by PAA-CeO_2. Upon incubated with OPs, the enzymatic activity of AChE was inhibited to produce less TCh, resulting in more TMB catalytically oxidized by PAA-CeO_2 to show an increasing blue color. The two representative OPs, dichlorvos and methyl-paraoxon, were tested using our proposed assay. The novel assay showed notable color change in a concentration-dependent manner, and as low as 8.62 ppb dichlorvos and 26.73 ppb methyl-paraoxon can be readily detected. Therefore, taking advantage of such oxidase-like activity of PAA-CeO_2, our proposed colorimetric assay can potentially be a screening tool for the precise and rapid evaluation of the neurotoxicity of a wealth of OPs.

Keywords: Oxidase mimic; Colorimetric assay; PAA-CeO_2; Acetylcholinesterase; Organophosphorus pesticides

1. **Introduction**

Organophosphorus pesticides (OPs) have been widely used in agriculture for many years, which are released globally into the environment, our food, and water supplies each year (Watson *et al*., 2006). The toxicity of OPs poses instant and lethal effects on human and mammal due to the nonreversible phosphorylation and inactivation of acetylcholinesterase (AChE) in central nerve system. The inhibition of AChE could cause the accumulation of neurotransmitter acetylcholine, thus inducing serious clinical complications including respiratory tract, fibrillation and ultimately leading to death. Due to their acute highly toxicity (Quinn *et al*., 1987; Tang *et al*., 2016), it is highly important to develop facile and simple approaches for the determination of OPs in view of public safety and environmental protection. Several analytical techniques have been reported to detect OPs, such as gas chromatograph-mass spectrometry (GC-MS) (Lacorte *et al*., 1994), liquid chromatography (LC) (Hernandez *et al*., 2005), enzyme activity inhibition methods (Pundir *et al*., 2012), and immunoassays (Jennifer *et al.*, 2010). But most of them are time-consuming and usually require highly trained technicians, which are not suitable for rapid analysis in on-site conditions. For immunoassays, due to the deficient of specific antibodies for OPs, a sensitive detection of OPs is difficult. In this respect, alternative and flexible methods based on enzyme-activity inhibition have been developed. Compared with classical methods, colorimetric sensors depending on its superior properties such as simple, facileness and real-time have attracted increasing interests in recent years (Kousba *et al*., 2003). For example, Li *et al.* has used gold nanoparticles (AuNPs) as colorimetric probe to achieve visual detection of OPs (Li *et al*., 2011). In addition, Sun *et al.* has reported that nerve agents and highly toxic OPs could be colorimetrically determined based on the catalytic reaction of AChE and the aggregation of lipoic acid (LA)-capped AuNPs (Sun *et al.*, 2011). Although the aforementioned AuNPs-based methods have high sensitivity, lots of physical parameters, such as ion concentration, pH and temperature, may induce the nonspecific aggregation of AuNPs due to their instability (Ghosh *et al.*, 2007). Therefore, it is still desirable and significant to develop more robust, sensitive and selective colorimetric assays for OPs. It is reported that cerium oxide (CeO_2) has found applications in many fields, especially in catalysis (Xu *et al*., 2013). Crystalline CeO_2 nanoparticles can be prepared by many methods with the reaction conditions of high temperature and high pressure, such as hydrothermal (Yu *et al*., 2004), solvothermal synthesis (Gu *et al*., 2007), and thermal decomposition (Lin *et al*., 2010). A mild and facile method for the synthesis of CeO_2 would be favorable to its extensive applications. Thus, the synthesis of biocompatible dextran-coated CeO_2 and its enhanced stability in aqueous solution has been reported (Perez *et al*., 2008). Furthermore, it is also revealed that polymer-coated CeO_2, e.g. polyacrylic acid-coated CeO_2 (PAA-CeO_2), is a more robust redox nanocatalyst for biochemical applications, because it is not susceptible to denaturation or decomposition (Asati *et al*., 2009). PAA-CeO_2 has an intrinsic oxidase-like activity in aqueous solution, which can readily oxidize some organic substrates without any oxidizing agent (e.g. hydrogen peroxide, H_2O_2). This unique aqueous oxidase-like activity of PAA-CeO_2 can be employed as a powerful tool for new potential applications in biotechnology, environmental chemistry, and so on.

Enlightened by the above facts, we herein proposed a novel colorimetric assay for the detection of OPs utilizing PAA-CeO_2 as an oxidase mimic and OPs as inhibitors to suppress the activity of AChE (Scheme 1). PAA-CeO_2, AChE, acetylcholine (ATCh) and a colorimetric substrate (e.g. 3,3',5,5'-tetramethylbenzidine, TMB) were applied to construct the sensing system for the monitoring of OPs. Firstly, highly