Development of surface imprinted core–shell nanoparticles and their application in a solid-phase dispersion extraction matrix for methyl parathion

Lei Tan [a,b], Weiming Li [c], He Li [a], Youwen Tang [a,*]

[a] Key Laboratory of Theoretical Chemistry of Environment, Ministry of Education, Department of Chemistry, South China Normal University, Guangzhou 510006, China
[b] Guangzhou Center for Disease Control and Prevention, Guangzhou 510440, China
[c] Guangdong Key Laboratory of Green Processing of Natural Products and Product Safety, School of Light Industry and Food Science, South China University of Technology, Guangzhou 510641, China

ARTICLE INFO

ABSTRACT

Applying molecular imprinting techniques to the surface of functionalized SiO_2 allows the preparation of molecularly imprinted polymers (MIPs) with accessible, high affinity and surface exposed binding sites. This paper demonstrates a new strategy for producing such hybrid organic–inorganic surface imprinted silica nanoparticles for specific recognition of methyl parathion. The technique provides surface grafting imprinting in chloroform using amino modified silica nanoparticles as supports, acrylamide as the functional monomer, γ-methacryloxypropyl trimethoxy silane as the grafting agent, and methyl parathion as a template. The amino propyl functional monomer layer directs the selective occurrence of imprinting polymerization at the silica surface through copolymerization of grafting agents with functional monomers, but also acts as an assistive monomer to drive the template into the formed polymer shells to create effective recognition sites. The resulting MIPs-SiO_2 nanoparticles display three-dimensional core–shell architectures and large surface areas. The molecularly imprinted shell provides recognition sites for methyl parathion, with the materials exhibiting excellent performance for selecting the template. Using MIPs-SiO_2 nanoparticles as a matrix of solid-phase dispersion extraction sorbents, trace amounts of methyl parathion are selectivity extracted from pear and green vegetable samples while simultaneously eliminating matrix interferences, attaining recoveries of 84.7–94.4% for the samples.

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1. Introduction

Pesticide pollution is a serious concern for both human health and the environment. Contamination of agriculture products and groundwater with organophosphate pesticides is a major concern owing to the biological persistence, toxicity, and mutagenicity of such contaminants [1,2]. Methyl parathion is one of the most dangerous and yet most commonly used organophosphate pesticides in agricultural, household, and urban insecticide applications. As a result, the development of ultrasensitive assays for the real-time detection of this pesticide has become a focus of environmental monitoring and scientific research. In spite of the rapid development of various technologies for pesticide analysis, highly efficient sample preparation with sensitive high-performance liquid chromatography detection remains the method of choice, especially for complex samples and trace level analysis [3,4].

Barker introduced matrix solid-phase dispersion (MSPD) technology two decades ago for the extraction of drug residues from animal tissue [5]. Since then, the technique has attracted considerable attention from scientific and industrial communities owing to its inherent simplicity, reusability, robust polymer network, and cost-effectiveness, and the technology has experienced rapid development [6,7]. In recent years, the greatest innovation in MSPD has been the development of unusual supporting materials. Molecular imprinting technology is one of the most promising strategies among the various approaches studied for producing biomimetic receptors for molecular recognition [8]. Molecular imprinting is based on the assembly of a cross-linked polymer matrix around an imprint molecule that is held in place, either covalently or noncovalently, by judiciously chosen functional monomers. The key feature of molecularly imprinted polymers (MIPs) is their engineered selectivity for binding to an analyte of interest. The majority

of the literature to date has focused on molecular imprinting in organic polymers due to the easy availability of various monomers. The problem is that such organic polymers may shrink or swell by controlled amounts in response to stimuli such as solvent exposure and applied voltage [9,10]. In contrast, MIPs prepared from the sol–gel process have already been proposed that can form a confined and rigid structure to offer superior binding specificity to a target molecule. The recent growth in interest of imprinted sol–gel materials prepared by sol–gel reaction has led to a growing activity in this field, but the material's limited porosity and lack of modifiable chemical functionality constrains its development and breadth of application [11,12]. One possibility is to introduce organ silicon precursors into sol–gel based MIPs so that the silica gel can be grafted with certain functional groups. Unfortunately, the commercially availability of organ silicon is quite limited. A better alternative is to directly utilize organic functional monomers bearing a vinyl group and reacting with a sol–gel precursor through condensation, which provides an elegant strategy to overcome the difficulties arising from molecular imprinting on polymers.

The crushing of bulk polymers is a time-consuming and wasteful process that results in irregular sizes and shapes, where this irregularity leads to poor recognition performance. Instead, surface imprinting can be applied to avoid the disadvantages that arise from bulk polymerized MIPs [13]. A fundamental strategy of surface imprinting is to locate the molecularly imprinted sites on the surface of nanostructures, thereby improving sensitivity for the recognition of target molecules [14]. In comparison with bulk imprinting, the transfer of template molecules is much easier and the binding kinetics is less restricted. Previous research has shown that molecularly imprinted polymer shells with tunable thicknesses can be easily grafted from the surfaces of silica nanoparticles. Generally, there are two laboratory-based methods employed for surface molecular imprinting on silica particles. The first method is a sol–gel reaction that employs 3-aminopropyltriethoxysilaneas the functional monomer [15–17]. The second method involves chemical immobilization of organic initiators, chain transfer agents, or meth acrylic bonds at the surface of silica particles, and subsequent copolymerization with functional monomers in the solution phase [6,18–20]. Although much progress has been made in the application of surface imprinted nanomaterials, the design of novel functionalized nanoparticles with well-defined nanostructures and surface properties remains an area of intense research interest [21–23].

In recent years, parathion imprinted materials have been largely reported in literature. Alizadeh reported the preparation of parathion imprinted polymer using a computational approach. The MIP was used as a solid-phase extraction adsorbent for parathion separation and determination in aqueous samples [24]. Li and co-workers reported the electrodeposition of a methyl parathion imprinted silicate film onto a glassy carbon electrode using tetraethylorthosilicate as the silicon precursor and vinyltriethoxysilane as the functional monomer [25]. Baldim et al. prepared parathion imprint polymers and used them to extraction of parathion from real samples before analysis by gas chromatography [26]. In this paper, we demonstrate the feasibility of an alternative strategy for producing surface imprinted hybrid organic–inorganic silica nanoparticles for the specific recognition of methyl parathion. We use amino propyl modified SiO_2 as the support, acrylamide as the functional monomer, γ-methacryloxypropyl trimethoxy silane as the grafting agent and methyl parathion as the template to produce surface graft imprinting at the surface of silica nanoparticles. The spherical particles function as a selective sorbent in a solid-phase dispersion extraction procedure for the cleanup of methyl parathion, allowing for simple and cost-efficient sample preparation.

2. Experimental

2.1. Chemicals and instruments

All chemicals used were of at least analytical grade. Methyl parathion (MP) (98%), methamidophos (98%), malathion (98%), and simetryn (98%) were purchased from Sima-lab company (Tianjin, China). Tetraethylorthosilicate (TEOS), 3-amino-propyltriethoxysilane (APTES), γ-methacryloxypropyl trimethoxy silane (KH570, MPS), methacrylic acid (MAA), acrylamide (AAM), Azo-bis-isobutyronitrile (AIBN) and ethylene glycol methacrylate (EGDMA) were purchased from Tianjian Chemical Reagents Co., Ltd. The HPLC grade organic solvents chloroform, acetic acid, and methanol were purchased from Kermel (Tianjin, China). Other chemicals were purchased from Shanghai Chemical Reagent Company and without further purification.

The morphology and microstructure of the SiO_2 and MIPs-SiO_2 were characterized by high-resolution transmission electron microscopy (HRTEM) on a JEM-2100HR (JEOL, Japan). UV–vis absorption spectra were recorded with A Shimadzu UV-Vis 1700 Spectrophotometer. Fourier transforms infrared (FT-IR) spectra (4000–400 cm^{-1}) in KBr were recorded on a PE Spectrum One FT-IR Spectrometer (Foster City, CA, USA). HPLC analysis was performed using a liquid chromatography system containing a LC-20AT pump, a SPD-20A UV–vis detector (Shimadzu, Japan).

2.2. Synthesis and chemical modification of silica nanoparticles

The procedure for synthetically producing the monodispersed spherical silica nanoparticles used in this work is similar to the method previously described in literature [18]. Ethanol (50.0 mL) was added to a 100 mL round bottom flask, along with a magnetic stirring bar. Concentrated ammonium hydroxide solution (2.0 mL) and water (6.3 mL) were added, and stirred at 700 rpm. TEOS (2.25 mL) was then added and the resultant mixture stirred overnight. The resulting colloidal suspension was centrifuged, and the precipitate was rinsed with ethanol at least three times before being dried under vacuum. Amino propyl modification of silica nanoparticles was carried out with 3-amino-propyltriethoxysilane, as described in previous literature [19]. One hundred milligram of silica nanoparticles and 2 mL of APTES were added into 50 mL anhydrous toluene, and the mixture refluxed for 12 h under dry nitrogen. The resulting APTES-modified silica nanoparticles were separated by centrifuge, and then washed with ethanol three times.

2.3. Synthesis of imprinted silica nanoparticles

Typically, NH_2–SiO_2 nanoparticles were first dispersed in 5 mL dry chloroform by ultrasonic vibration. Acrylamide, KH570, Methyl parathion, and AIBN were then dissolved into the above solution. The mixing solution was purged with nitrogen for 20 min and stirred for 5 h before TEOS (0.3 mL of TEOS dissolved in 1 mL methanol) and 0.3 mL of HAC (1 mol L^{-1}) were added into the solution. The reaction was allowed to proceed under magnetic stirring for 6 h. In all preparations, the amount of amino modified SiO_2 and KH570 were kept constant. For comparison, four molar ratios between the template and monomer of 1:1, 1:2, 1:4, and 1:8 were tested. The resulted imprinted nanoparticles were labeled as MIPs1-SiO_2, MIPs2-SiO_2, MIPs3-SiO_2 and MIPs4-SiO_2. To remove methyl parathion templates from the polymer shell, the MIPs-SiO_2 nanoparticles were extracted with a methanol/acetic acid solvent (9:1, v/v). The NIPs-SiO_2 particles were prepared using the same procedure but in the absence of the template.