



Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Quantitative assay for the detection, screening and reactivity evaluation of nanoceria particles

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ARTICLE INFO

Keywords:

Nanoceria
Nanoparticle detection
Metal oxide selectivity
Colorimetric assay

ABSTRACT

Increasing use of engineered nanoparticles (NPs) in many industrial processes and consumer products requires rapid analytical methodologies to reliably detect and screen samples for the presence of NPs. Here, we report the development, analytical characterization and performance evaluation of a colorimetric assay as a comprehensive test for quantitative detection, screening and reactivity evaluation of nanoceria (cerium oxide, CeO₂) particles in aqueous environments. We provide a critical discussion of the role of environmental conditions including pH, ionic composition, and presence of humic acid and particle type on the overall performance and sensitivity of this assay. The method is based on the strong oxidation ability of nanoceria for organic dyes such as 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid) (ABTS) and 3,3',5,5'-tetramethylbenzidine dihydrochloride hydrate (TMB). Performance characteristics were established with a series of commercially available NPs of varying sizes dispersed in different environments. The results demonstrate that colorimetric assays can be used as a rapid and cost effective way to characterize nanoceria. The method enables identification and selective detection of nanoceria among other metal oxides including Fe₂O₃, TiO₂, Sb₂O₃, ZnO, SiO₂, and Al₂O₃. Applicability of the method for detection of nanoceria in environmental water samples is demonstrated. Recommendations are provided on the selection of the reaction conditions to ensure validity and reliability of measurements. The assay offers an effective and inexpensive alternative to advanced spectroscopic instrumentation, as a screening assay for nanoceria in environmental water. The method can be used as a general tool for the analytical characterization of redox active nanomaterials.

1. Introduction

Cerium oxide (CeO₂) NPs, or nanoceria are extensively investigated in a large number of applications, as polishing agents in the semi-conducting industry, as a fuel additive in diesel particulate filters to reduce toxic emissions [1–4], and more recently as therapeutic agents in biomedicine, and as materials for sensing probes, sorbents and electrochromic coatings. As a result of these applications, nanoceria can be found in a variety of environments where they can interact with and affect biological and environmental processes. Nanoceria can participate in redox reactions, act as a sorbent for toxicants or interact with a variety of environmental and biologically-significant constituents [4–6]. Several studies have reported that these particles can be inhaled causing adverse pulmonary effects [4], induce inflammation [1,2] and promote oxidative stress in a variety of cell lines and model organisms, or can be bio-transformed and internalized by plants [7,8]. Therefore there is a risk that these NPs may cause health, ecological and environmental effects, and there is a need to quantify exposure levels in environmental and biological systems. However, in spite of the

increasing use of these NPs and the knowledge of their potential effects, few analytical methodologies exist to rapidly detect presence and concentration of nanoceria.

General methods to characterize NPs include conventional transmission electron microscopy (TEM) and scanning electron microscopy (SEM) for size and shape, dynamic light scattering (DLS) and ζ -potential analysis for hydrodynamic properties (e.g. agglomeration, surface charge), powder X-ray diffraction (PXRD), X-ray photoelectron spectroscopy (XPS) [9], Fourier Transform Infrared (FTIR) and Raman spectroscopy to determine chemical composition, surface coatings, particle size, crystallinity and surface area. AFM analysis can also be used in conjunction with TEM and SEM to assess particle size [10,11]. Atomic absorption (AAS), atomic emission (AES) and inductively coupled plasma mass spectrometry (ICP-MS) can be used to determine elemental composition. While powerful, these methods are expensive, time consuming and require specialized instrumentation. Therefore, only a few numbers of samples can be analyzed.

In previous research, color based detection was demonstrated for monitoring the catalytic activity of different types of metal and metal

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<http://dx.doi.org/10.1016/j.talanta.2016.10.104>

Received 27 September 2016; Received in revised form 28 October 2016; Accepted 31 October 2016

Available online xxxx

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oxide NPs using a soluble organic dye, methylene blue, and a reducing agent, sodium borohydride [12] but the method showed color response to a large variety of NPs and therefore lacked selectivity. Herein, we report development and performance characterization of a colorimetric assay with tailored selectivity for detection of nanoceria. The method is based on the oxidation ability of nanoceria for organic dyes such as ABTS and TMB, which develop concentration-dependent color changes in presence of nanoceria. Selectivity is enabled by the unique and characteristic redox properties of nanoceria due to the co-existence of the Ce(III/IV) states at the NP surface which provides a distinctive reactivity pathway against soluble organic dyes when compared to other oxides [13,14]. While the redox property is a common feature among nanoceria particles, their reactivity varies with the pH, ionic composition and presence of natural organic material, that can affect their surface properties and stability [15–17]. Therefore, knowledge on how these parameters affect the overall performance of these assays is essential for the future development of analytical methodologies for nanoceria detection.

This work describes development and characterization of visual tests for screening of nanoceria particles in environmental water samples. A critical evaluation of the role of environmental constituents and exposure conditions is presented comparatively for two chromogenic indicators, TMB and ABTS. We demonstrate that these assays are generally applicable for detection of a variety of nanoceria particles, and can be used as a screening tool to assess reactivity and particle content in environmental water. Since both the reactivity and environmental impact are dependent on the type and dose of NPs, and some change with the exposure and storage conditions, inexpensive and widely accessible tools that can be used to rapidly characterize NPs are highly valuable for environmental detection and epidemiological studies.

2. Experimental

2.1. Chemicals and materials

Cerium(IV) oxide NPs (CeO₂, 10–20 nm), 20 wt% colloidal dispersion in 2.5% acetic acid and 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid) (ABTS, 98%) were purchased from Alfa Aesar. 3,3',5,5'-Tetramethyl-benzidine dihydrochloride hydrate (TMB, 98%), humic acid (HA, sodium salt 45–70% technical, and nitric acid (HNO₃, 68–70%) were purchased from Acros. Citric acid anhydrous and Tris(hydroxymethyl)aminomethane hydrochloride (Tris-HCl, ≥99.0%) were purchased from Sigma. Sodium hydroxide, sodium acetate, and acetic acid glacial were purchased from J.T. Baker, and sodium citrate dihydrate (90–100%) was purchased from Mallinckrodt Baker, Inc. Silica colloidal (SiO₂, 35 nm, acidic) was purchased from NYACOL nano technologies, Inc. Titanium dioxide (TiO₂, 10–30 nm), and zinc oxide NPs (ZnO, 10–30 nm) were purchased from SkySpring Nanomaterials, Inc. Iron oxide (Fe₂O₃, 20–40 nm), and antimony oxide (Sb₂O₃, 80–200 nm) nanopowders were purchased from US Research Nanomaterials, Inc, where alpha-alumina nanopowder (Al₂O₃, 300 nm) was purchased from SPI Metallography Supplies. All reagents were used without further purification, and all solutions were prepared with ultrapure water (Millipore, Direct-Q system, 18.2 MΩ cm).

To test the applicability of this method for detection of varying types of nanoceria we have tested the following commercially available nanoceria particles: (A) Alfa Aesar, #40125, 10–20 nm (20% in H₂O, colloidal dispersion stabilized in 0.4 M acetate), (B) Alfa Aesar, #47240, < 5 nm (20% in H₂O, NP dispersion, high pH), (C) Sigma-Aldrich, #MKBD9924, < 25 nm (10 wt% dispersion in water), (D) SkySpring, #2110CG, 10–30 nm, (nanopowder), (E) Sigma-Aldrich, #544841, < 25 nm (nanopowder). Their characteristics are summarized in Table S1.

2.2. Solutions and buffers

Effect of pH and buffer solutions were evaluated using acetate, citrate, and Tris buffers. The acetate buffers (pH 3.6, 4, 4.5, 5, and 5.5) were prepared from 0.2 M sodium acetate-acetic acid and the pH was adjusted using 1 M HNO₃ or 1 M NaOH. The citrate buffers (pH 3.4, 5.5, 6, and 7.4) were prepared from 0.2 M sodium citrate dihydrate-citric acid and the pH was adjusted using 1 M HNO₃ or 1 M NaOH. Tris buffers (pH 7.5, 8, 8.5, and 9) were prepared from 0.2 M Tris-HCl and the pH was adjusted using 3 M NaOH in distilled water. The NP dispersion was diluted in deionized water, and sonicated for 5 min prior to all experiments.

The effect of ionic strength was tested with NaCl solutions at concentrations ranging from 1 to 1000 mM in deionized water. The effect of pH and ionic strength were determined for nanoceria at a concentration of 25 mg L⁻¹. To investigate the effect of HA, particles were dispersed in humic acid solutions at concentrations of 1, 5, 10, and 50 mg L⁻¹ prepared in deionized water. The effect of ionic strength and HA was determined for ABTS and TMB at concentrations of 0.13 mM and 1.3 mM, respectively. Solutions of dyes were prepared fresh each day and were stored on ice until use.

2.3. Application to environmental water samples

The applicability of this method was evaluated in three different water samples, which were collected from the local Raquette River, Potsdam, NY; Norwood beach, Norwood, NY; and tap water. The water samples were filtered using a 0.2 μm syringe filter before use. For analysis, the samples were spiked with a nanoceria at a concentration of 10 mg L⁻¹.

2.4. Measurement procedure

Experiments were performed in 1.5 mL cuvettes using UV–vis spectroscopy. The optimized procedure for the colorimetric measurement consists in the addition of 100 μl of 2 mM ABTS or 200 μl of 10 mM TMB, to the sample cell containing NP suspension at varying concentrations. The dye was left to react with the NPs until a constant absorbance value was achieved. Experiments to optimize the methodology were carried out with nanoceria dispersions prepared in deionized water.

2.5. Instrumentation

UV–vis spectrophotometric measurements were performed with a Shimadzu UV-2401PC spectrophotometer equipped with a 1 cm path length cell. Zeta potential (ζ-potential) was measured at 25 °C with a Brookhaven Zeta Plus analyzer. A JEOL JSM-2010 instrument was used for high resolution transmission electron microscopy (HRTEM). TEM analysis was performed on aliquots of nanoceria particles placed on a copper HRTEM grid and dried under vacuum.

3. Results and discussion

3.1. Method principle

The nanoceria colorimetric detection assay is based on monitoring of the oxidation of the organic dyes ABTS and TMB by the NPs. The spectroscopic behavior of ABTS and TMB in the absence and presence of nanoceria dispersion is shown in Fig. 1. The assay is based on the ability of nanoceria to act as an oxidizing agent for the oxidation of organic dyes [18,19]. Here we employ this concept to develop an analytical quantification assay to characterize nanoceria containing samples. The nanoceria particles used to optimize the assay have an average diameter of 19.5 ± 4.3 nm measured by DLS with a dispersity of 0.418 ± 0.195, also confirmed by HRTEM analysis. Addition of

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