

Nanosphere Reactive Oxides for Environmental Remediation

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INTRODUCTION

Nanoparticles have been demonstrated to have useful absorption and catalytic activities but it is difficult to take advantage of these properties in the real world due to their small size. For example, in a water treatment column, they can simply suspend and flow away with the water or clog any filter that might be used to keep them in place. In fluidized catalytic beds they tend to escape from a reactor along with the fluidizing gases. In this paper, readily-prepared spherical aggregates of nanoparticles will be reported as a practical solution for the combination of nanoparticle reactivity with physical properties that are conducive for use in industrial and water-purification processes.

Initially these nanosphere reactive oxides were developed to address the removal of arsenic from water. Arsenic's toxicity to man and other living organisms has led to serious environmental problems and difficulties in procuring suitable drinking water in many parts of the world. In well-oxidized waters arsenic is present predominately as arsenate ($\text{H}_2\text{AsO}_4^{-1}$ and $\text{H}_2\text{AsO}_4^{-2}$) while under reducing conditions it is usually present as arsenite (H_3AsO_3 and $\text{H}_2\text{AsO}_3^{-1}$) [1]. Since the reduction and oxidation reactions of arsenic are particularly slow, both of these oxidation states can coexist irrespective of the redox conditions [2]. The arsenic(III) species are 25-60 times more toxic than arsenate and are more mobile in the environment [3]. Adsorption on mineral surfaces is an important factor that controls the mobility and bioavailability of arsenic. Arsenate adsorption on clays and aluminum and iron oxides is greatest at low pH and decreases with increasing pH while arsenite has a maximum in adsorption to these materials at approximately pH 8.5 [4].

A large variety of materials have been tested for removal of arsenic from water including adsorbants such as phyllosilicates, silica, and hydrous oxides of iron and alumina [3]. The most successful and heavily investigated materials have been iron oxides, especially ferrihydrite [5-12]. Surprisingly, there has been no report to date of the application of zinc oxide for the removal of arsenic from aqueous solution despite the fact that it is a useful adsorbent for gaseous arsenic pentoxide in combustion off-gases. Furthermore, arsenic is often a common contaminant in zinc ores suggesting an affinity between the two elements. Recently, it was discovered that hematite nanoparticles showed a significant capacity for adsorption of arsenate despite the relatively low reactivity of bulk hematite towards arsenate[13]. This is another example of the well-established ability of nanoparticulate materials to display unusual reactivity towards chemical weapons and environmental contaminants (e.g. halocarbons) as compared to bulk materials. This prompted the investigation reported herein of the testing of zinc oxide nanoparticles for removal of arsenate from water and the development of spherical aggregates of nanoparticulate zinc oxide for this purpose.

MATERIALS AND METHODS

The commercial zinc oxide was a dry process zinc oxide from Fisher Chemicals and was sintered at 1200°C. All other reagents were commercial products (ACS Reagent grade or higher) and were used without further purification. Water was purified by reverse osmosis and was deionized before use. Thermogravimetric studies were performed using 10-20 mg samples on a Seiko ExStar 6500 TGA/DTA instrument under a 50 ml/min flow of dry air. The temperature was ramped from 25 to 600°C at a rate of 2°C/min. Bulk pyrolyses at various temperatures were performed in ambient air in a muffle furnace using, a ramp of 5°C/min and a hold time of 12 hr. X-ray powder diffraction (XRD) patterns were recorded on a Bruker AXS D-8 Advance X-ray powder diffractometer using copper K α radiation. The XRD peaks were profiled with a Pearson 7 model using the Topas P Vers. 1.01 software program [14]. The profiles of a highly crystalline zinc oxide standard and the samples were input into the Win-Crystallite Vers. 3.05 program [15] and the Warren-Averbach evaluation method was applied to determine crystallite size and strain broadening effects. Surface areas were measured by nitrogen adsorption isotherms on a Quantachrome Nova 10 instrument using the BET analysis method and six points in the range 0.05 to 0.3 P/P₀. Arsenic concentrations were determined using a water analysis test kit (EM Science, Gibbstown, NJ).

Synthesis of Zinc Oxide Nanoparticle Powder

A 100-ml, aqueous solution of ZnSO₄·7H₂O (14.375 g, 50 mmol) was combined with a 100-ml, aqueous solution of sodium pyruvic acid oxime, Na(PAO)·H₂O (14.30 g, 100 mmol). A white precipitate of Zn(PAO)₂·2H₂O resulted upon mixing of the reactants. The precipitate was filtered off and then dried under vacuum overnight to give 15.02 g (98.37 %) of product. Heating this material to 389°C for 8 hours (using a ramp rate of 1°C per minute to raise the temperature from room temperature) yielded nanoparticulate zinc oxide as a very fine pale yellow powder with a ceramic yield of 26.52%

Synthesis of Spherical Aggregates of Zinc Oxide Nanoparticles

Dowex 650C (H) form resin (20.0 g, 58.0 mmol of ion-exchange sites) was stirred for 12 hours with a solution of zinc sulfate (34.5 g, 120 mmol) in water (100 ml). The supernatant solution was poured off and the zinc sulfate treatment was repeated with fresh solution. After stirring for 12 hours, the resin was isolated by filtration, washed extensively with distilled water, and air-dried. Nanocrystalline zinc oxide was obtained by firing the resulting resin (15.0 g) at 560°C for 8 hours using a ramp rate of 4°C per minute to raise the temperature from room temperature. The zinc oxide (2.51 g) was obtained in a 16.7% ceramic yield as pale yellow spherical aggregates.

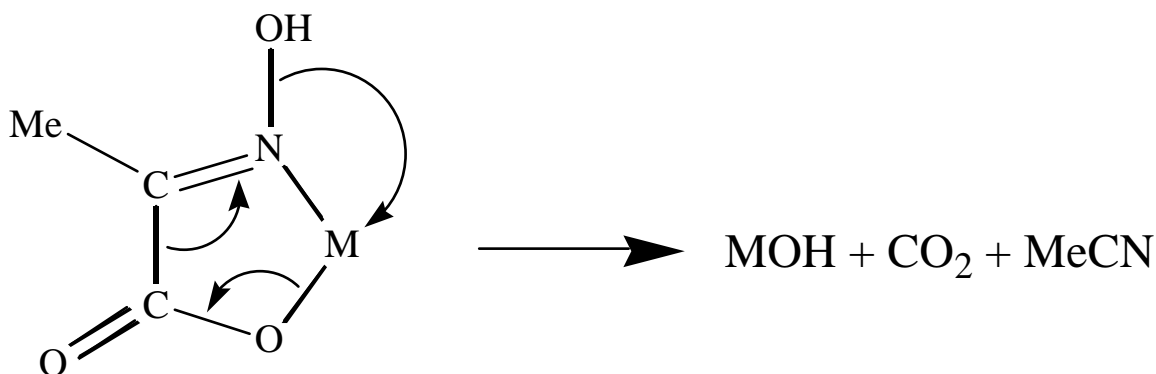
Adsorption of Arsenate

The various zinc oxides (1.10 g) were stirred with 110 ml of sodium dihydrogen arsenate (either 300, 1000, or 3000 ppb in arsenic) for one hour. At this point, the solution was separated from the adsorbent by filtration through a fine sintered glass filter.

The pH of the solutions were recorded before and after treatment with zinc oxide. Arsenic concentrations in the treated solution were determined using a colorimetric test kit.

RESULTS AND DISCUSSION

The desire to produce nanoparticles readily on a large scale has led to the design of metal carboxylate complexes that decompose at low temperature to yield the metal oxide and small, volatile organic fragments. For example the salts of 2-oximinopropionate (also call pyruvic acid oxime and designated as PAO in this paper) serve as useful nanoparticulate ceramic and catalyst precursors [16-20]. These salts decompose in the range of 85 to 170°C to yield carbon dioxide, acetonitrile, water and a metal oxide, hydroxide, or carbonate (Scheme 1). The metal-containing product is generally obtained as a high surface-area nanocrystalline material due to the extremely low deposition temperature and rapid volatilization of the organic decomposition products. Indeed, the great difficulty in using this approach to nanoparticle synthesis is keeping the nanoparticles from escaping the pyrolysis vessel.



Scheme 1. Pyrolysis of metal 2-oximinopropionate complexes.

The necessary zinc oxide precursor, $\text{Zn}(\text{PAO})_2 \cdot 2\text{H}_2\text{O}$ was readily prepared using a precipitation reaction between aqueous zinc sulfate and an aqueous solution of sodium pyruvic acid oxime. Thermal analysis showed an onset of decomposition at approximately 120°C. However, it was discovered that unlike the decomposition of other 2-oximinopropionates, the zinc salt lost the two PAO ligands in two separate stages necessitating a relatively high final temperature (389°C) before complete conversion to oxide. Nevertheless, the final product was nanocrystalline zincite (ZnO) with an average crystallite size of 25 nm and a surface area of m^2/g .

In order to test the resulting zinc oxide for adsorption of arsenic 10-ml solutions of arsenate with varying concentration were mixed with 0.1 g of the ZnO for 7 hours. The solutions were then filtered through a 0.20 μm , disposable membrane filter and the final arsenic concentration was determined using a test strip kit purchased from EM science. The data was analyzed using a, Langmuir sorption isotherms, $C/X = C/M + 1/KM$, in which C is the equilibrium concentration of arsenic expressed in mg/L (ppm), X is the

amount of arsenic sorbed in mg per kg of sorbant, M is the maximum amount of arsenic in mg sorbed by one kg of the sorbant, and K is a constant related to the affinity of the sorbant for the sorbate (arsenic in this situation). M and K are determined from the slope and the intercept, respectively, of plotting C/X against C (Figure 1). The zinc oxide prepared from the thermal decomposition of the zinc PAO complex at 389°C showed a fairly high arsenic adsorption capacity of 2081 mg/kg. This appears to be the first discovery that nanoparticulate zinc oxide is a good adsorbent for arsenic, a fact that is noteworthy, since bulk zincite displays no capacity for arsenic (see below).

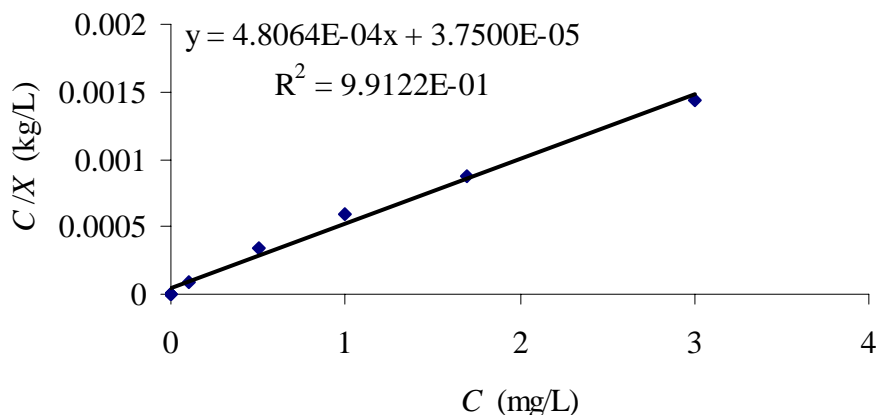


Figure 1. Langmuir adsorption isotherm for arsenate by zinc oxide derived from $Zn(PAO)_2$.

In the above arsenic adsorption experiments, a key step was the filtration using a fairly expensive 0.20 μm membrane filter. The fine nature of the nanoparticulate zinc oxide required this since the particles readily pass through normal sintered glass frits and also suspend too readily for decanting. Therefore, nanoparticulate zinc oxide was synthesized as ceramic replicas of ion-exchange beads that are normally used for water treatment. In this fashion aggregates are obtained that are an ideal size and shape for water treatment. The resin used was Dowex 650C, a sulfonated styrene/divinyl benzene copolymer with an ion-exchange capacity of 5.37 mmol/g of anhydrous resin (or 2.90 mmol of exchangeable protons per gram of the as-received, hydrated resin). This resin can be purchased as reasonably monodisperse spherical beads. The resin was used in its proton form and was reacted with a four-fold excess of zinc ions in two aliquots of 1.2 M solutions. This treatment lead to complete replacement of the protons of the sulfonate groups for Zn^{2+} ions in a stoichiometry of one zinc ion per every two sulfonic acid residues. Thermal gravimetric analysis demonstrated that this material loses approximately 25% by weight of water between room temperature and 300°C. At 360°C gradual decomposition of the ion exchange resin occurs until 490°C when a sharp decrease in mass starts to occur that eventually that culminates in formation of zinc oxide

at 560°C. During the latter step, extensive evolution of sulfur dioxide occurs so care must be taken to vent the fumes to a hood.

Pyrolysis of the zinc-loaded resin at 560°C yields spherical pale yellow particles that were determined to be zincite by X-ray powder diffraction (Figure 2). The off-gasses of the pyrolysis consist mainly of combustion products (water and carbon dioxide) and sulfur dioxide. The observed X-ray reflections were broadened compared to a highly crystalline sample of zincite so the crystallite size of the particles was analyzed. The result of this analysis, was an average crystallite size of 12.3 nm with a somewhat broad distribution (12.9 nm full width at half-height). The maximum in relative frequency of crystallite size was 7.6 nm. Interestingly, hematite (Fe_2O_3) prepared in a similar manner had an almost identical distribution of crystallite sizes (an average crystallite size of 12.0 nm, 16.9 nm full width at half-height and maximum at 6.9 nm) [13] suggesting that domains within the ion-exchange resin exert a strong control over the size of the particles generated upon pyrolysis. If so, the size of the oxide particles might be controllable by variation of the cross-linking of the polymer by changing the divinylbenzene content. The degree of sulfonation might also be a parameter that controls particle size.

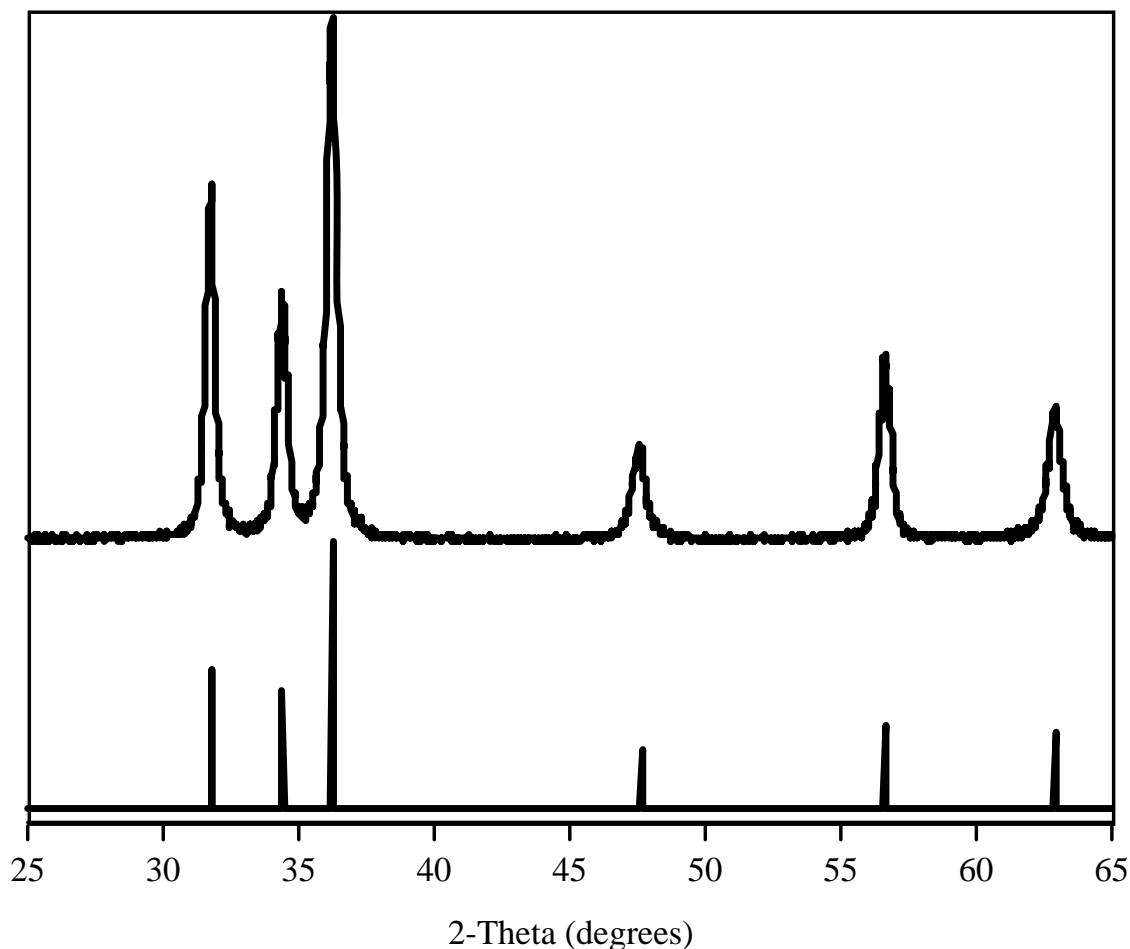


Figure 2. X-ray powder Pattern for Nanocrystalline Zinc Oxide Spherical Aggregates. The lower stick figure is the ICDD pattern for zincite (# 36-1451)

Scanning electron microscopy demonstrated that the agglomerates are spherical with an average diameter of 170 μm and are porous aggregates of smaller particles (Figure 3). The spheres consist of condensed ZnO throughout and are composed of aggregates of nanoparticles that are further fused together to yield the larger spherical particles. The spheres. They are fairly mechanically robust and do not break into smaller particles when shaken violently within a glass vial in a simulation of a fluidized bed. However, they can be easily crushed with an agate mortar and pestle to a fine powder. During the synthesis of the zinc oxide spheres, shrinkage from the initial size of the Dowex 650C resin beads was approximately 20% and occurred mainly during the dehydration step. The final product has a relatively high surface area of 30.7 m^2/g as determined by nitrogen absorption isotherms (BET analysis). By comparison, a commercial sample of sintered zinc oxide had a surface area of 0.13 m^2/g .

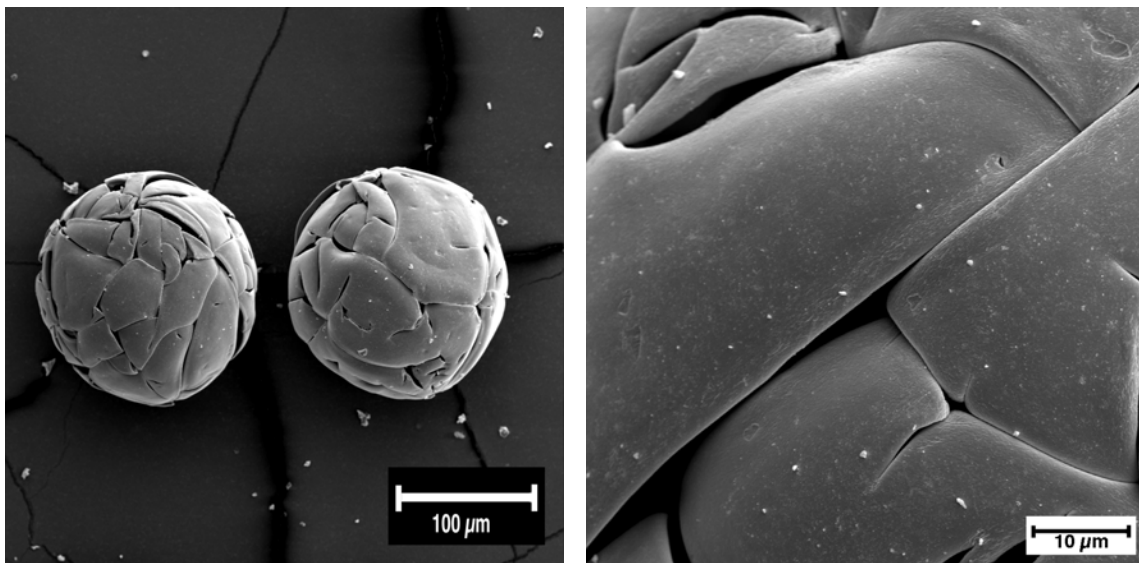


Figure 3. SEM Micrographs of Nanocrystalline Zinc Oxide Spherical Aggregates

The spherical zinc oxide particles were used to treat increasing concentrations of arsenic from 300 up to 10,000 ppm until significant arsenic remained in solution. For comparison, a commercial sintered zinc oxide was also used to treat a 300 ppb solution. The results are given in Table 1. The current United States Environmental Protection Agency's limit for arsenic in drinking is 50 ppb but it is scheduled to be lowered to 10 ppb in 2006. When challenged with 110 ml of 300 ppb solution of arsenate, 1.1 g of the nanoparticulate zinc oxide reduced the arsenic concentration to the proposed lower limit. Even at concentrations of arsenic as high as 3000 ppb (3 ppm), the spherical zinc oxide reduced the concentration to 40 ppb, less than the current drinking water standard. By contrast, sintered microcrystalline zinc oxide did not remove a detectable amount of arsenic from solution. The capacity of the zincite spheres for arsenate adsorption was 985 $\mu\text{g As/g adsorbent}$, exceeding the adsorption capacity of iron-oxide-coated sand, ferrihydrite, and spherical nanoparticles that are established as 18.3, 285, and 303 $\mu\text{g/g}$.

respectively [11-13]. Note that formation of nanoparticles into aggregates does reduce the capacity for arsenic as compared to the unaggregated powder discussed above. Nevertheless, the ease of use in water treatment is likely worth this cost.

Table 1. Results of Arsenic Adsorption Studies

ZnO Sample	Surface Area (m²/g)	Initial [As] (ppb)	Final As (ppb)
Commercial	0.13	300	300
Spherical	30.7	300	10
Spherical	30.7	3,000	40
Spherical	30.7	10,000	150

The success of the spherical iron oxide powders is likely due to their composition of nanocrystalline primary particles. This is another example of the ability of nanoparticulate materials display unusual reactivity towards environmental contaminants as compared to bulk materials. The spherical nature of the ion-exchanger derived zincite particles are well suited for "at-the-tap" remediation of arsenic because they would pack together efficiently but allow a decent flow of water as opposed to loose, fine powders. They could also be readily combined with ion exchange resins typically used in water treatment.

Numerous other metal oxides and sulfides can be prepared by a similar process to the spherical nanocrystalline zinc oxide aggregates. Therefore, the NANOSPHERE compounds form a family of materials that can be very effective for removal of lead and arsenic from water, destruction of halocarbons, neutralization of acidic gases, and adsorption of heavy metals and actinides. It is also possible to adapt the technology to create reactive membranes and materials for permeable reactive barriers.

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