

Research Article

Designing Zirconium Coated Polystyrene Colloids and Application

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A simple technique has been developed to prepare core colloids that are modified using zirconium oxychloride, based on heating a solution of core colloid composites, consisting of poly (ethylenimine) (PEI) and zirconium oxychloride. The interaction of zirconium oxychloride with the polystyrene (PS) core colloids has been investigated using Fourier transform-infrared spectroscopy (FT-IR), energy dispersive X-ray spectroscopy (EDX), and scanning electron microscopy (SEM) data. FT-IR studies confirm the occurrence of amine groups present in PEI which are oxidized to carboxyl groups after the reaction. The EDX data and the SEM images confirm the presence of zirconium particles immobilized on the polystyrene surfaces. Demeton, a highly toxic nerve agent, was used due to its ability to easily bind through its organophosphate group illustrating a practical application of the PS-PEI-Zr particles. Attenuated Total Reflection (ATR) Spectroscopy was used to assess the interactions between the toxic nerve agent demeton-S and the PS-PEI-Zr particles. The results show that the presented technique for coating polystyrene core colloids with zirconium was successfully accomplished, and the newly formed particles easily bond with demeton agents through the P=O functional group.

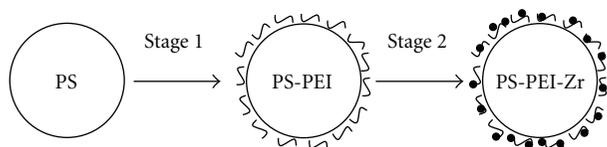
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1. Introduction

Recently, numerous synthetic mechanisms have been employed for surface adsorption of metal nanoparticles (NPs) onto colloidal inorganic and organic spheres [1–6]. A particularly successful method of depositing the metal NPs on the surface of the colloids involves the use of an intermediate linker poly (ethylenimine), PEI, which can bind both transition metal ions, such as zirconium, and negatively charged colloids [7–10]. Additionally, the PEI serves as the reducing agent in the conversion of the metal ions to the metal NPs [11]. In such a scheme, the core component, usually polystyrene (PS) or silicon dioxide (SiO₂), serves as a supporting structure, and the outer NPs predominantly exhibit the properties that are attributed to the metal NP-core colloid composites. The advantages derived from these hybrid materials can be seen in their remarkable attributes which include enhanced conductivity, temperature stability, optical, and catalytic activity [12–14].

Over the years, there has been considerable interest surrounding the fabrication of core-shell spheres that consist of templated cores coated with shells that have different chemical compositions. These core-shell spheres often exhibit properties that are substantially different from those of the templated core (increased stability, higher surface area, different magnetic, and optical properties), making them attractive from both a scientific and technological standpoint [15–17]. Furthermore, the properties of core-shell particles can also be tailored in a controlled fashion by independently altering the composition, dimension, and structure of the core or shell. Application for such core-shell spheres is diverse, including biosensors [18], chemical sensors [19], and so forth.

Organophosphates (OPs) are well-known neurotoxins; they disrupt the cholinesterase enzyme that regulates acetylcholine [20–22], a neurotransmitter needed for proper nervous system function. Because of their high neurotoxicity, OP compounds have been exploited for use as pesticides and as nerve agents with application as chemical and biological



SCHEME 1: Procedure for coating PS colloids with metal.

warfare agents. As a result of the high toxicity of OPs, fast and effective detection of these toxic agents in the environment, public places, or workplaces and the monitoring of individual exposures to chemical warfare agents have become increasingly important for national security and health protection purposes [23–25]. Early detection and detection of low concentrations of OPs still remain an extremely difficult challenge. Such information may give an indication of terrorist activity, allowing proper procedures to be followed to mitigate potential danger. Analysis of OPs in environmental and biological samples is routinely carried out using analytical techniques, such as gas or liquid chromatography and mass spectrometry [26].

For OP detection, enzyme-biosensors of inhibition and noninhibition systems are mostly based on the immobilization of acetylcholinesterase (AChE) [27], tyrosinase enzyme (Tyr) [28], alkaline phosphatase (ALP) [29], or organophosphorus hydrolase (OHP) [30, 31] onto various electrodes. Due to their high sensitivity and selectivity toward OPs, these have been proposed for field screening of OP neurotoxins [32]. However, while these specific antibodies against OP pesticides have been recently developed for enzyme-linked immunoassay and immunosensors [33, 34], acetylcholinesterase is commercially available but OP hydrolase and antibodies against OPs are still only produced in laboratories, which limits wide applications of biosensors. Demeton is also used as pesticide, which on most metal oxides, in our case zirconium and adsorbs through the P=O functional group. IR spectroscopy in combination with Attenuated Total Reflection (ATR) spectroscopy is one of the most widely used techniques for surface infrared analysis. ATR-IR has been used for studying processes at surfaces or in films, such as adsorption [35–37] and diffusion [38–40].

The aim of this paper is to treat polystyrene colloids with zirconium oxychloride in order to create a hybrid material which may find utility as an organophosphate sensor. The composite colloids are obtained by coating PS with PEI followed by the addition of ZrO_2 (Figure 1). In this reaction scheme, PEI is relatively inert and thus does not have a significant effect, if any, on the ultimate formation of the NPs. The advantages of this method are simple operation, easy large scale production, and the generality for various core colloids. The zirconium acts as a selective probe targeting the phosphate group of the demeton which upon bonding shows a change in the ATR spectrum. Other inorganic ions have also found to have an affinity for P=O functional groups, such as Mg, thus paving the way for future research into different colloidal compositions for OP detection.

In this paper, we report a novel method for detecting OP chemical nerve agents by incorporating the enhanced properties of zirconium coated polystyrene core colloid composites with the strong affinity for chemical nerve agents. Polystyrene was utilized for the core component with the outer layer being comprised of zirconium NPs. We characterized the PS-PEI-Zr colloids by using SEM, EDX, and FT-IR spectroscopy. The prepared zirconium colloids were placed on the ATR ZnSe crystal forming a thin layer used for the detection of demeton-S.

2. Experimental Section

2.1. Materials. Poly (ethylenimine) (PEI), polystyrene (PS) colloids with an average size of 210 nm, sodium phosphate buffer, zirconium oxychloride, sodium citrate ($C_6H_5O_7Na_3 \cdot 2H_2O$), absolute ethanol, ammonium hydroxide solution (NH_4OH , 25%), formaldehyde (HCHO, 37%), and Demeton-S were all obtained from Sigma-Aldrich.

2.2. Modification of Core Colloids with PEI (PS-PEI). 1 g of PS colloids was dispersed in 50 mL of phosphate buffer solution with a pH of 6.5 (solution A). 0.1 g of PEI was then dissolved in 5 mL of phosphate buffer to produce solution B (mass ratio of PEI to PS was 1 : 10). Solution B was stirred at room temperature ($25^\circ C$) for 1 hour followed by three cycles of centrifugation (20 000 rpm) and washing with 10 mL of water.

2.3. Preparation of PS-PEI-Zr. PEI modified PS colloid solution was dispersed in 100 mL water, and 0.15 g of zirconium oxychloride was added and then heated for one hour at $100^\circ C$. After cooling to room temperature, the ammonia and sodium citrates were added into the dispersion solution. 12 mL of sodium citrate (1 M) was added to result in a 1 : 1 molar ratio of zirconium oxychloride to sodium citrate. Dropwise addition of NH_4OH (1 M) were used to bring the pH up to 10. Then, the HCHO diluted with ethanol was added. After completion, the solid was isolated by 3 cycles of centrifugation/washing.

2.4. Characterization. FTIR and ATR data were recorded with a *Perkin Elmer Spectrum BX FT-IR System*. The sample for the FTIR measurement was prepared by grinding a dry PS-PEI-Zr sample with KBr into fine powders which were then pressed at 20 000 psi into pellets. Scanning electron microscopy (SEM) was performed with a JSM-5900.

2.5. Demeton Adsorption on PS-PEI-Zr. 10 μL of the prepared PS-PEI-Zr colloids were placed on a Miracle Universal Plate composed of ZnSe crystal (PIKE Technologies, Single Reflection Horizontal ATR) and allowed to dry, forming a thin layer. 10 μL of 1 mM demeton-S solution were then added to the dry PS-PEI-Zr thin layer, and the ATR spectrum was obtained at a 4 cm^{-1} resolution with a spectral range of $750\text{--}4000\text{ cm}^{-1}$. Following this, an additional 10 μL of the

demeton-S solution were added to give a cumulative 20 μL , for which the ATR spectrum was obtained in each case.

3. Results and Discussion

In the present study, PEI-modified polystyrene colloids were used as the templates for the deposition of zirconium nanoparticles. Tian et al. [41, 42] have previously demonstrated that PEI acts as a reductant in the conversion of transition compounds into metallic particles. Moreover, through the use of TEM, XPS, and XRD they were able to identify the metallic particles whether it was Ag, Au, or another transition, and the exact oxidation state was thus obtained. In this study we use zirconium oxychloride which is reduced to metallic zirconium particles upon being adsorbed onto the PEI modified colloids. This chemistry is critical in the formation of the metal nanoparticles; otherwise, the PEI will simply be coated with a layer of oxychloride, changing the chemical properties we seek.

Following synthesis, the prepared composites were characterized by FT-IR spectroscopy, scanning electron microscopy (SEM), and EDX. Figure 1 shows SEM images of the prepared composites at different magnifications, showing the deposition of zirconium onto the core polystyrene colloids. A larger central PS core can be observed, and on the superficial surface, small protrusions of the Zr metal are visually attached which are shown by a porous network on the surface of the colloids as opposed to bare PS which shows a smooth consistent surface. Scanning electron microscopy images were obtained on a JSM-5900 which was operated at 30 kV. The SEM analysis was consistent and reproducible with a representative area shown in Figure 2. The synthesized PS-PEI-Zr composites were suspended in water, dispersed then on glass, and coated with approximately 10 nm of AuPd. The lighter edges is an edge effect, that is, secondary electrons can be collected from the top and bottom surfaces of the sphere edges, leading to an enhanced secondary electron signal. Figure 2 displays an EDX spectrum which quantitatively detects the constituent elements. The spectrum showed Zr LA1, Zr LB1, Zr LB3, Zr L1, Zr KA1, and Zr KB1 peaks, indicating the presence of the third layer of zirconium oxychloride on the polystyrene colloids. Other peaks detected in the EDX spectrum included Cl KA1, Cl KB1, and O KA1, exposing elements such as chlorine and oxygen, a result of the deposition of zirconium oxychloride on the polystyrene colloids.

In Figure 3, the IR spectra of PS, PS-PEI, and PS-PEI-Zr composites detect a peak at 2916 cm^{-1} which corresponds to the stretching vibration of C–H, also indicating the presence of PEI on the PS colloids. At around 1700 cm^{-1} , the presence of the C=O stretching of carboxyl is detected. Analyzing the PS-PEI curve, it is noticeable that the C=O bond is not present anymore due to the consummation of the carboxyl group of PS with PEI and Zr nanoparticles in the colloidal modifications. There are two more prominent peaks present at 1492 and 1452 cm^{-1} which are a result of the antisymmetric and symmetric stretching of O–C–O. These two are easily detectable in the PS curve, however,

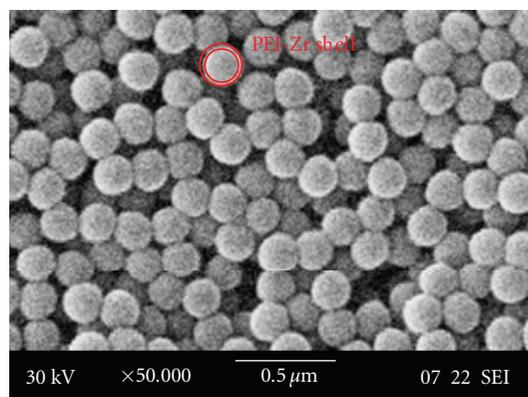


FIGURE 1: SEM image of PS-PEI-Zr spheres.

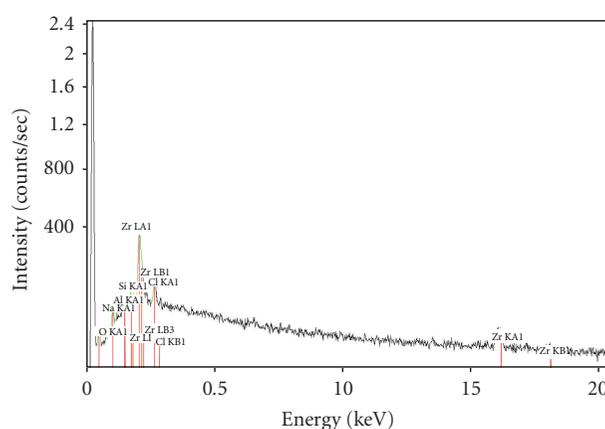


FIGURE 2: EDX of PS-PEI-Zr.

it diminishes in the PS-PEI curve and disappears almost completely in the PS-PEI-Zr curve. This is again due to the expenditure of the functional group in the formation of PS-PEI and PS-PEI-Zr colloids. The peak around 3500 cm^{-1} is characteristic of the N–H stretching vibration from the PEI, thus it is not present in the PS curve and does not considerably reduce in the PS-PEI-Zr curve. Analysis of the reaction mechanism occurring between PEI and Zr has previously been studied and reported by IR spectroscopy [43]. It was shown that two new IR bands involving interactions between Zr(IV) (Lewis Acid) and the nitrogen of the amine group (Lewis base) in PEI were present in the IR spectrum. A broad band in the 1580–1560 cm^{-1} region is observed both for aromatic amines (polyvinyl imidazole) and for aliphatic amines (polyethyleneimine), which can be easily assigned to the NH_2 asymmetric bending mode for the latter. A second band is observed in the 1450–1350 cm^{-1} range, depending on the nature of the amine group.

Figure 4 shows the ATR spectra for consecutive additions of 10 μL aliquots of a 0.06 M demeton solution to a thin layer of the PS-PEI-Zr colloids. Analysis of the ATR data and the relevant peaks shows that the binding of the PS-PEI-Zr colloids to demeton has been successfully achieved. All four peaks at 2350 cm^{-1} are designated peaks for the

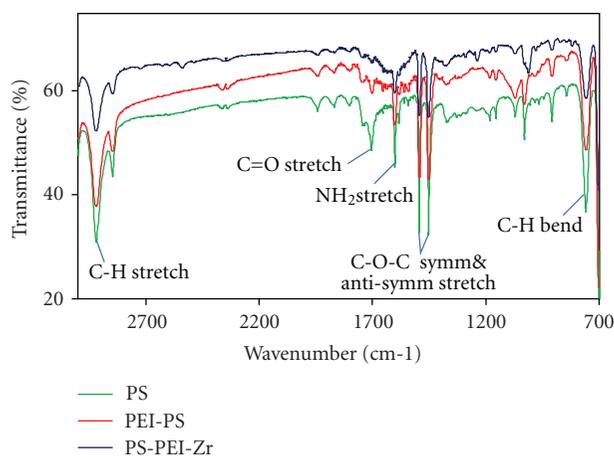


FIGURE 3: FT-IR spectra of PS, PS-PEI, and PS-PEI-Zr.

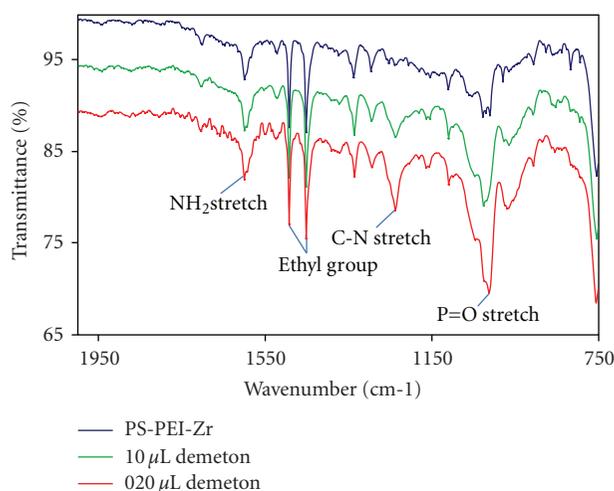


FIGURE 4: ATR spectrum PS-PEI-Zr with 10 and 20 μL of 0.06 M demeton.

presence of zirconium. Zirconium is not only present in the Ps-PEI-Zr compound form, but also in its binding to demeton. At 1010 cm^{-1} there is a strong presence of P=O bond for PS-PEI-Zr bonded to $20\ \mu\text{L}$ of demeton; while there is a considerable reduction of those bonds with $10\ \mu\text{L}$ of demeton and even disappearance for the actual compound not bonded to the nerve agent. Zirconium is an ideal candidate for immobilization of molecules with oxygen groups as contained in phosphates [44]. Because of zirconium's affinity for phosphoric groups, by treating the PEI modified colloids with zirconium we are able to amplify the interaction of the colloids with demeton's P=O bond and thus see a significant change in the corresponding ATR spectrum. Thus, a similar sensor can be developed to sense other nerve agents with the organophosphate structure such as paraoxon. In contrast, if only PEI modified colloids were employed we would not expect to see a dramatic change in the ATR spectrum as there is no known specificity of PEI for the P=O group of demeton. The ethyl group is

distinguished at 1452 and 1492 cm^{-1} as a result of PS-PEI-Zr bonding with demeton, explaining why it is absent in the curve of PS-PEI-Zr without demeton. These peaks strongly increase in intensity with increasing amounts of demeton solution. As the concentration of demeton decreased, it was observed that no strong peak of demeton is noticeable due to the weak signal, leading to much more prominent peaks when 10 and $20\ \mu\text{L}$ of demeton are present. Based on the response of the PS-PEI-Zr nanocomposites to the experimental parameters of the concentration of demeton in 1 liter of solution, the minimum sensitivity limit of this platform for the detection of demeton is approximately 2.0 ± 0.2 PPB. This can be considered the effective dose which would result in a detectable change in the ATR spectrum. The above result allows us to propose a model for the development of chemical nerve agents through the use of ATR.

4. Conclusion

A simple method was developed to coat polystyrene colloids with zirconium particles. The zirconium nanoparticles were able to attach to polystyrene due to its modification with PEI, which increased the speed of the reaction and it had no appreciable effect on the formation of the core colloids. The detection of OPs has become important because many nerve agents and pesticides are organophosphates. The ability to detect small quantities and/or low concentrations of these compounds is critical. The strong bond formed between Zr and demeton allows for facile detection of the demeton peaks by using various characterization techniques. PS-PEI-Zr is simple to synthesize and utilize, and its use to detect OPs is useful for applications such as pesticide analysis. The developed method is an efficient strategy due to its simple operation, easy large-scale production, and generality for various core colloids.

Acknowledgments

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