



Preparation of air stable nanoscale zero valent iron functionalized by ethylene glycol without inert condition



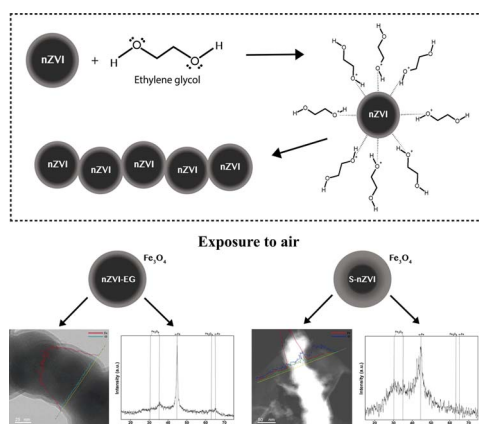
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GRAPHICAL ABSTRACT



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ABSTRACT

The use of nanoscale zero-valent iron has been widely studied in recent years for potential application in environmental engineering, due to its affinity for a large number of contaminants, which may be in aqueous or solid phase, and for its abundance, which makes it an attractive tool for environmental remediation. However, there exist some variables in the production of nZVI that complicate the generation of the material, such as the complex methodologies of synthesis and the cost of inert conditions like nitrogen or argon atmosphere, which have the purpose of preventing the oxidation and reducing the instability of the material under ambient conditions. As a simple and economical synthesis methodology, this work presents an optimized method to synthesize functionalized nanoscale zero-valent iron (nZVI) using ethylene glycol (EG) without need for inert conditions. The coordination of iron ions during the nZVI-EG synthesis and the functionalization mechanism of the nanoparticles were identified by UV-Vis absorption spectroscopy and Fourier transform infrared spectroscopy (FTIR). Functionalized nZVI showed increased dispersibility due to the effects of steric repulsion between the grafted polymers. Ethylene glycol functionalized nZVI showed stability against oxidation during dry atmospheric condition, while significant oxidation was observed in the case of unfunctionalized nZVI. This result

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was also correlated with actual capacity for contaminant reduction. Therefore, the possibility was verified of using ethylene glycol in an effective surface modification method to prepare air stable nZVI for environmental remediation.

1. Introduction

Environmental nanotechnology provides novel tools for remediation based on the synthesis and application of advanced materials that can be functionalized; the process of functionalization optimizes material environmental application, allowing material to act as a contaminant immobilizer in the environment or promoting contaminant degradation [1,2]. A good example is the use of zero-valent iron nanoparticles (nZVI). Because of their high surface area and standard redox potential ($E_0 = -0.44$ V), these materials allow a high rate of reactivity with contaminants via electron transfer during the oxidation of Fe^0 to Fe^{2+} and eventually Fe^{3+} ; this makes these materials efficient reducing and oxidizing agents [3,4] and provides them with specific affinity for toxic contaminants in aqueous systems [5]. Examples include chlorinated organic solvents, organochlorine pesticides, organic dyes [6–8], and metal ions such as Pb (II), Cu (II), Ni (II), and Cr (VI) [9–13].

Nevertheless, in the application of nZVI to environmental nanotechnology, the stability plays an important role due to high material tendency to react in response to large surface area; such materials are usually unstable when exposed to the air. Moreover, in the synthesis and handling of nZVI, this material is widely known to form an iron oxide thin layer around the particle called the core-shell; this layer is established by interaction of the metal core with oxygen present in the surrounding environment, creating a passivation of the surface, which can take different crystalline structures such as Wüstite (FeO), magnetite (Fe_3O_4), maghemite ($\gamma-Fe_2O_3$), or Goethite ($\alpha-FeOOH$) [14–17]. The main function of this layer is to prevent the additional particle oxidation [18].

However, most authors report that, in order to prevent oxidation as much as possible, the synthesis and application of nZVI must make use of nitrogen or argon atmosphere during the manipulation of the material. On the other hand, the implication of inert conditions in the synthesis process is a highly cost method, which hinders the development and application of this material in real cases. In relation to this highly relevant fact of nZVI production, it is extremely important to find new ways to stabilize and protect nZVI in the presence of air, where they are highly sensitive to oxygen. For this reason, nanomaterial surface modification has been a widely studied area and has great interest because it can provide tools to modify the interactions that materials may have with the surrounding environment [19]. Changes of stability, compatibility, and reactivity are some examples of modifications in materials via a coated surface; such modifications then lead to an increase in potential applications.

Coating techniques can generally be divided into two large groups: first, coating of nanomaterials by use of inorganic materials such as precious metals (Ag, Au, Pt, Pd) [20–23] and silica [24]; second, the coating of nanomaterials by use of organic shields such as surfactants or polymers [25,26]. Researchers have emphasized the latter group in recent years, and advances in polymer nanotechnology have led to new and different methodologies to stabilize nanomaterials as protective agents [27,28]; these agents have been applied in the development of systems of organic-inorganic composites. Using nanoparticle functionalization to optimize material properties, it is possible to dramatically increase the applicability of nanomaterials, because polymers grafted on particles surface form a protective layer that imparts different properties to the material; as well, it has been reported that the presence of layers of different varieties of polymers, like coated agents, makes it possible to control the size and agglomeration of nanoparticles by varying the concentration, the geometry, and the terminal groups of

the polymers [29]; this is due to the effects of electrostatic repulsion or steric repulsion between the polymers grafted onto each particle. The main interest in the functionalization of nanomaterials based on iron and iron oxide is the stabilization and protection of nanoparticles from excessive oxidation under ambient conditions, which would greatly reduce material reactivity and applicability [30,31].

In general, because there exists a certain affinity of the functional groups contained in polymer molecules with inorganic surfaces, modification of the surface of nanomaterials by use of organic compounds can occur through chemical and electrostatic interactions among the molecules of the polymer and the nanomaterials; therefore, functionalization can be performed by various mechanisms such as physical adsorption, mono-, bi-, or tri-dentate coordination, bridging chemisorption, or chelating chemisorption [32,33]. In view of this, a higher affinity of certain binder groups to specific inorganic surfaces has been reported, an example of which is the use of oleic acid, which has been reported to have a high affinity for magnetic nanoparticles composed of iron and iron oxide; several reports show that functionalization occurs by interaction between O-atoms of the carboxylate and hydroxyl groups and Fe-atoms present in the nanoparticles surface, generating bi-dentate coordination of the particles [33–37]. The higher affinity presented by these types of terminal groups towards the particles compared to that toward different binding groups such as thiol or amine groups can be explained by the high affinity of oxygen for iron and the greater electronegativity of oxygen atoms in contrast to that of others atoms used in the functionalization of materials, increasing the probability of the interaction between the O-atom contained in the ligand group and the surface of the material for their bonding.

However, in metal nanoparticle functionalization, the affinity and solubility of the binding molecule are important aspects, such that the insolubility of oleic acid in aqueous systems produces a lower density of grafted organic molecules on the surfaces of the particles [38]. In relation to this, in some cases, the functionalization of materials is restricted to post-synthesis methods, which have reported a lower density of functionalization relative to the one-step functionalization methods [38,39]. Influenced by this, a greater solubility of the coated agent will have a better effect on the functionalization of the material.

On the other hand, due to the magnetic interaction between ZVI particles there exists a high aggregation rate between these nanomaterials, which implies a reduction in the surface area and in the reactivity of the particles [40,41]. In view of this, and of the fact described above, for a greater interaction with the surface of nanomaterial, it is necessary to functionalize with –OH ligand groups due to the high polarity and hydrophilic nature of this type of binder molecule, as well as to achieve less aggregation via reduction of the interfacial energy between the solvent and the particles and an increase of the dispersibility of the material [19,42,43]; these facts highlight the need to use these types of ligand molecules in contrast to various agents with functional groups such as –COOH, –NH₂, and –SH [38,44].

In relation to this, there have been numerous studies that have described successful mono-dentate functionalization of iron and iron oxide nanomaterials using polyethylene glycol (PEG), which contains a hydroxyl (–OH) ligand groups where, in the same way, free electron pairs of the O-atoms can interact with the surface of the nanoparticles for generation of coordinated covalent bonds, leaving grafted polymer chains [45–47]. However, a limitation in the use of dense polymers with a high degree of polymerization such as PEG, are the effects of steric repulsion due to volume exclusion to which the polymeric brushes are subjected, limiting the insertion of other chains at the surface of the particles, reducing the uniformity of the protective layer and

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