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Synthesis of nano-composite surfaces via the co-deposition of metallic salts and nano particles

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ABSTRACT

A novel, low energy method for coating different nano-particles via electro-deposition to a recyclable carbon glass supporting structure is demonstrated. In the resulting composite, the nano-material is bound to the substrate surface, thereby removing the potential for causing harmful interactions with the environment. Nano-particles were suspended in a salt solution and deposited at low current densities (<0.1 A cm^{-2}) producing thin (<100 nm), uniform nano-faceted surfaces. A co-deposition mechanism of nano-particles and cations from the salt solution is proposed and explored. This has been successfully demonstrated for iron, sliver, titanium in the current work. Furthermore, the removal of the surface coatings can be achieved via a reversed current applied over the system, allowing for the recovery of surface bound metal contaminants. The demonstrated applicability of this coating method to different nano-particle types, is useful in many areas within the catalysis and water treatment industries. One such example, is demonstrated, for the treatment of BTEX contamination and show a greatly improved efficiency to current leading remediation agents.

1. Introduction

In recent years, nano-particles of varying compositions have been demonstrated as effective for the sterilisation of harmful bacterial [1,2] and removal of harmful pollutants from water [3–9]. However, whilst nano-materials may well provide an effective new tool for the clean-up of pollutants they will not be universally adopted until deployment methods can be developed that limit or remove these aforementioned risks relating to nanomaterial toxicity [10,11]. The fabrication of nano-composites is an obvious way of achieving this and forms the basis for the research presented here in.

Whilst the limited existing literature on this topic has demonstrated the general feasibility of nano-composites for water treatment purposes, there are numerous fundamental flaws in the design of the composites developed. These include: (i) lack of structural performance, (ii) reduction in nano-material reactivity, (iii) use of surfactants and (iv) limited sustainability [12–16]. The method presented in the current work specifically addresses these key design limitations to develop a new suite of nano-composite materials, whereby the support material imparts the mechanical properties of the composite and at the same time the desired physical coating of well-bound nano-material, imbues the composite with nano-reactivity.

The nano-composite fabrication method represents a simple but intuitive adaptation of standard electro-deposition techniques. Electro-deposition is a well established method [17], in which an electronic field is applied over a salt solution, with deposition occurring on the target electrode surface. In the automotive industry, this technique has been refined for high current (3 A cm^{-2}) deposition of galvanising coatings [18]. Whilst some previous studies have examined the use of electro-deposition and co-deposition of nano-scale material, their focus has been on forming coatings between 50 and 100 μm thick, with nano-particles embedded throughout the structure, without an overall nano-scale surface [13]. Furthermore, the applications have been focused around photonics, batteries and sensors [19–23] and seemingly little research has been directed at developing electro-deposited nano-structures for water remediation applications. Here we present a modification on the technique, using a significantly lower current density (0.09 A cm^{-2}) for the deposition and formation of nano-composites, using a colloidal suspension of nano-particles in a metal salt solution.

In this method the electrostatically bound nano-particles act to provide low energy sites for surface nucleation of nano-scale metallic crystallites induced by electrochemical reduction of the aqueous metallic salts [24]. The resulting process is one of co-deposition and heterogeneous crystal growth, all at the nano-scale. The demonstrated method is considered to provide a synthesis route that is greener, cleaner and more readily usable for multiple nano-composites with beneficial applications in water and air

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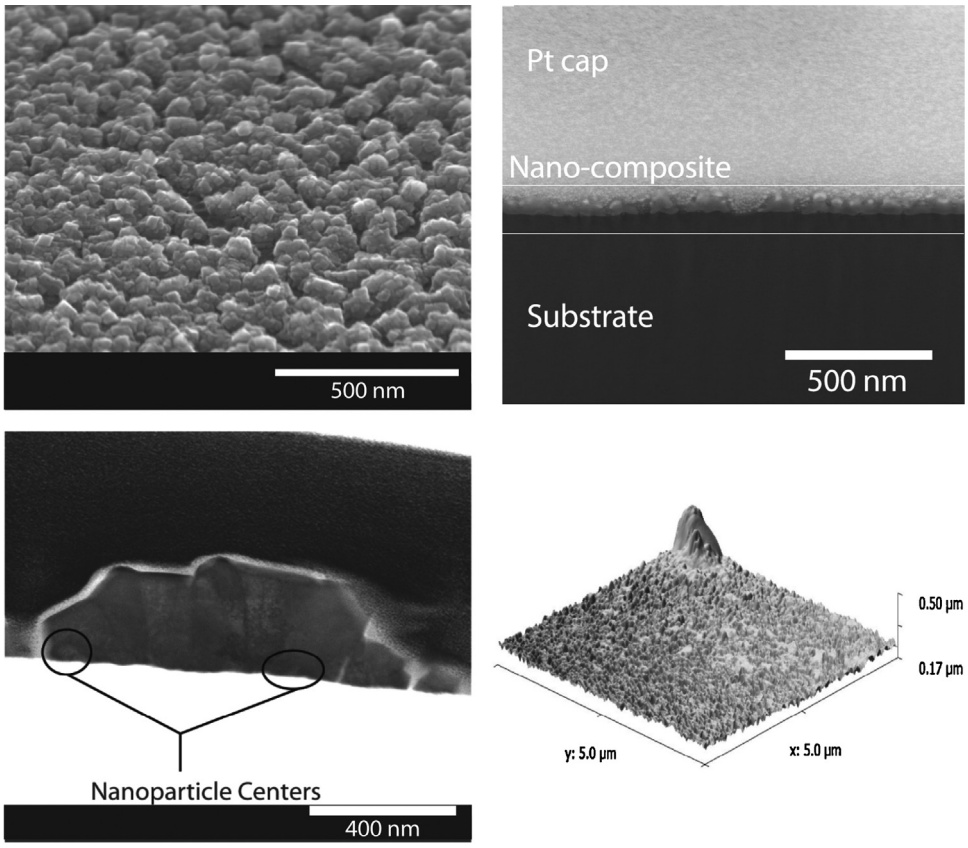

Fig. 1. The deposition of nano-composite surfaces, formed from an Fe salt solution containing suspended INPs; top left nano-composites showing mixed cubic and spherical structures. Top right, focused ion beam (FIB) cross section demonstrating the deposited surface thickness The nano-composite is seen between the boxed region with a protective layer of Pt deposited above the surface and the substrate below. Bottom left, scanning transmission electron microscopy image of part of the nano-composite coating, illustrating the formation of cubic crystals over spherical nano-particle centres. Bottom right atomic force microscopy (AFM) data of a 5 μm^2 region.

filtration (industrial and domestic), and the potential for alternative uses in other areas of industry.

By applying the coating method to a substrate of reticulated vitreous carbon (RVC) foam, a highly porous nano-composite suitable for both in situ and ex situ water filtration is created. The current work demonstrates how a reactive and nano-structured coating may be created throughout the filter and investigates the physiochemical benefits for the iron nanoparticles (INPs) of post synthesis vacuum heat treatment, which has previously been shown to improve the structure, and hence reactivity, of free INPs [25,26,28,29]. Data presented here demonstrates the arising filter material to be highly effective for the remediation of a range of volatile aromatic organic pollutants at rates and magnitudes competitive with well-established remediation agents; organo-clay (OC) and granulated activated carbon (GAC).

2. Results and discussion

2.1. Deposition of nano-composite iron surfaces

Results are shown of a coating formed from an Fe salt solution containing suspended INPs (Fig. 1). Under empirically determined deposition variables nano-faceted surface coatings of metallic iron were successfully and repeatably deposited on vitreous carbon substrates, as shown in Fig. 1. The AFM and SEM data show the resulting nano-texture of the coatings to include both cubic and spherical structures.

Using focused ion beam (FIB) cross-sectioning (Fig. 1), the surface coating was determined to between 50 and 100 nm in thickness; approximately equivalent to the average diameter of the INP material. Approximate surface area was determined from the AFM data, using a surface area integration method [29], to be $3 \pm 0.5\ m^2\ g^{-1}$ of surface coating.

X-ray photo-electron spectrometry (XPS) was used to confirm the oxidation state of the formed nano-composite surfaces, the presence and chemistry of surface contaminants (Fig. 2). The analysis confirmed the presence of both metallic iron and iron oxide in the surface analysis volume. With an approximate maximum sample depth of 6 nm (for the XPS analysis conditions) the recorded oxide signal is ascribed to the formation of a (<2 nm, Fig. 1 TEM image) surface oxide layer (<2–3 nm) on the deposited metallic

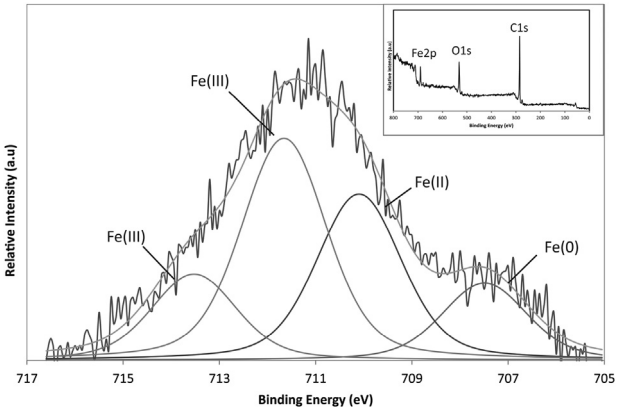

Fig. 2. XPS of Fe 2p3/2 peaks of the nanocomposite surface formed from an Fe salt solution containing suspended INPs.