



## Research article

## Facile synthesis of hierarchical nickel (III) oxide nanostructure: A synergistic remediating action towards water contaminants

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## ABSTRACT

Heavy metal ion removal from consumable water is an indispensable need to maintain healthy life. Therefore cost effective and highly efficient sorbents are strongly needed to pose threat to real water pollution. Nanomaterials are widely used to maintain clean aqueous system in a very cost effective way with high removal efficiency. In this present work, pure coral like Ni<sub>2</sub>O<sub>3</sub> nanostructures were prescribed for Cr(VI) remediation which were prepared by two step synthesis procedure at room temperature. The single hierarchical morphology as confirmed from HRTEM (size~200 nm) were subjected to toxic Cr(VI) ion removal experiments. They were found to remove ~65% Cr(VI) ions that was higher than that of pure Ni<sub>2</sub>O<sub>3</sub> nanoparticles of comparable size. The enhanced properties were explained on the basis of the defect states present within the nanostructure, investigated by positron annihilation lifetime spectroscopy (PALS). It was found that the hierarchical nanostructure had more number of di-vacancies and vacancy-clusters as compared to the particles. On performing isotherm fitting, it was found that the coral like morphology had a high heterogeneity factor that aided to a high adsorption rate when compared to the pure Ni<sub>2</sub>O<sub>3</sub> nanoparticles (which had a homogenous surface). The synthesized nanostructure was severely toxic to bacterial community having minimum inhibitory concentration (MIC) of ~300 µg/L. Also the nanostructure exhibited dual functionality towards Cr(VI) and bacteria contaminated water at 200 µg/ml. The maximum Cr(VI) removal efficiency for this dual system is found to be 39% whereas antibacterial activity was turned out to be 30% which was extensively higher than that of toxic Cr(VI) ions. A plausible mechanism for the dual functionality was also predicted.

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## 1. Introduction

Industrial effluents, produced as inorganic by products, are large source of toxic heavy metals to the environment and possess great threat to the aquatic ecosystem (Han et al., 2006). They are known to cause life threatening diseases if taken above a permissible concentration. Among various heavy metals, Cr ions, present abundantly in drinking water, are known to stimulate carcinogenic pathways in human body (Zhitkovich, 2011).

Out of two different form of chromium e.g. Cr(VI) and Cr(III) in aqueous medium, Cr(III) precipitates in its hydroxide and oxide forms, therefore they don't migrate in the solution and are easily separable. On the other hand, Cr(VI) being highly soluble in water and having high redox potential becomes highly toxic and causes cancer, kidney damage, gastrointestinal disorder etc (Zhang et al., 2014a,b; Gu et al., 2012). In this context, it may be stated that US Environmental Protection Agency (EPA) and World Health Organization (WHO) have set maximum allowed level of Cr(VI) concentration in drinking water 100 µgL<sup>-1</sup> and 50 µgL<sup>-1</sup> respectively (Qiu et al., 2014). The challenge of removing heavy metal ions from water using chemical precipitation, solvent extraction, membrane separation, ion exchange, adsorption etc. has been successfully formulated by researchers to carry out this process (St John et al., 2010; Wang et al., 2009; Prasad et al.,

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2010; Kabay et al., 1998; An et al., 2011; Akoz et al., 2012; Wang and Kuo, 2008; Wu and Tian, 2008; Sun et al., 2015). Among them, adsorption provides a simple, effective and user friendly way of Cr(VI) removal due to its simple procedure and reaction mechanism (Gan et al., 2013; Zhang et al., 2013a,b; Li et al., 2014a,b; Liu et al., 2014a,b). In this context, it has to be mentioned that several materials like magnetic carbon (Zhang et al., 2014a,b; Zhu et al., 2014), bimetallic nanoparticles (Zhou et al., 2014). Fe<sub>3</sub>O<sub>4</sub> nanoparticles (Cheng et al., 2012a,b), functionalized graphene oxide (Dinda et al., 2013) zinc–bio-nanocomposites (Gan et al., 2015) etc. are used to remove Cr(VI) from water. With the advancement of nanotechnology, several nanostructured materials such as carbon nanosphere (Gan et al., 2015; Gu et al., 2013), hierarchical TiO<sub>2</sub> (Qin et al., 2012), iron oxide submicron-wires (Yang et al., 2014; Liu et al., 2014a,b), multi-walled carbon nanotubes (Lu et al., 2017) have also been developed to achieve higher Cr(VI) removal efficiency.

Fouling is another major cause of concern for metallurgical industries to produce submerged metal parts. Underwater metal surfaces are often attacked and leached by micro-organisms that results damage of the submerged parts. Anti-fouling coatings are found to be indispensable for under water metallic surfaces and they are mainly prepared using antimicrobial materials. Metals and metal oxides like ZnO, TiO<sub>2</sub>, Ag etc. show considerable bactericidal property at their nano level (Zhang et al., 2013a,b; Ravi et al., 1998; Chen and Wu, 2000; Surhio et al., 2014). Several nanocomposites are commercially available in surgical accessories as antibacterial coatings in recent times (Ashraf et al., 2013).

Though various hierarchical nickel oxide (NiO) nanostructures like coral, flower, rod etc, synthesized using co-precipitation, hydrothermal, solvothermal etc., have proved their candidature in different fields like optics, magnetic, catalysis etc., but they were not tested to remove Cr(VI) or possess antibacterial activity. Moreover, to the best of our knowledge, the possible synergistic effect of using any transition metal oxide with a contaminant to eradicate another contaminant effectively have not been studied till date. Higher oxides of nickel like Ni<sub>2</sub>O<sub>3</sub>, NiO<sub>2</sub>, Ni<sub>3</sub>O<sub>4</sub> hierarchical nanostructures were not found to be stable at room temperature and have a tendency of forming pseudo hydrates. However, anhydrous forms of these oxides are not possible as on heating, since they decompose into more stable nickel (II) oxide (Li et al., 2006).

In this paper, we have proposed a room temperature chemical method of synthesizing hierarchical coral like pure anhydrous Ni<sub>2</sub>O<sub>3</sub> nanostructures from hydrothermally prepared Ni(OH)<sub>2</sub>. The prepared nanostructures are subjected to Cr(VI) ion removal from aqueous solution in presence of *Pseudomonas putida* (in situ bio composite formation) to gain enhanced Cr(VI) ion removal compared to its non-composite counter parts (i.e. pure Ni<sub>2</sub>O<sub>3</sub> coral like nanostructure) as well as to study the adsorbent-contaminant synergistic effect in efficient water remediation. The anti-bacterial activity of the synthesized nanostructure has also been examined in presence of Cr(VI) ions in aqueous solution (in situ inorganic composite formation with Cr(VI) ions) and compared with the activity of Ni<sub>2</sub>O<sub>3</sub> coral like nanostructure for understanding possible synergistic effect. We also highlighted the comparative study of Cr(VI) removal and antibacterial activity of as synthesized Ni<sub>2</sub>O<sub>3</sub> coral like structure with that of Ni<sub>2</sub>O<sub>3</sub> nanoparticle synthesized at 70 °C which was the optimal sample for Cr(VI) removal as already published in our previous work (Dey et al., 2015). The plausible mechanism for the synergistic effect and in situ dual system (composite) formation has also been suggested.

## 2. Experimental

### 2.1. Preparation of coral like Ni<sub>2</sub>O<sub>3</sub> nanostructure and nanoparticle

All chemicals were procured from MERCK India Pvt. Ltd. and were used without further purification. Ni<sub>2</sub>O<sub>3</sub> coral – like nanostructure had been prepared by sustained oxidation of the hydrothermally synthesized Ni(OH)<sub>2</sub>. In a typical experiment, 1.57 g of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 1.57 g of urea (NH<sub>2</sub>CONH<sub>2</sub>) and 1.3 ml poly ethylene glycol (PEG-600) were taken in a beaker containing 60 ml double distilled water and stirred to form a clear greenish solution. Solution was then transferred to a steel lined autoclave and was kept in a hot air oven at 90 °C for 10 h. The resultant product was allowed to cool to room temperature and a pale green precipitate of Ni(OH)<sub>2</sub> was filtered out. The powder, so obtained, was subjected to sustained oxidation with the help of concentrated sodium hypochlorite (NaOCl) solution containing 4% active chlorine. 15 ml of NaOCl solution was taken in a beaker and Ni(OH)<sub>2</sub> was added to it under mild stirring. The reaction was continued till the effervescence ceases and a black precipitate of Ni<sub>2</sub>O<sub>3</sub> was formed. Finally, the precipitate was centrifuged, dried and collected for further analysis. The detailed synthesis procedure for Ni<sub>2</sub>O<sub>3</sub> nanoparticle is described in Dey et al. (2015).

### 2.2. Characterization

Crystallinity and phase purity of the synthesized samples were investigated by Ultima-III, Rigaku, Japan x-ray diffractometer (Cu K<sub>α</sub> radiation, λ = 1.5404 Å). Field emission scanning electron microscope (FESEM, S – 4800, Hitachi) and transmission electron microscope (TEM, JEM – 2100, JEOL) were employed to investigate microstructure and morphology of the synthesized samples. Positron annihilation spectroscopy has been employed to investigate defect structure of the synthesized samples. Positron, the antiparticles of electron, after escaping from the radioactive active neutron deficient nuclides enters into the investigating material where they suffer a series of free annihilation with electrons within the material before achieving thermal equilibrium. Annihilation rate, in general, is dependent on electron density of within the material and indicates the presence of defects. In this study, <sup>22</sup>Na positron source having strength ~7 μCi was used here and the source got sandwiched between the radiation-exposed parts of the two pieces of the material. Dimension of the each of the two pieces of pellets was 10 mm in diameter. Positron lifetime measurements were taken using fast-fast coincidence technique having a system resolution of 293 ps with <sup>60</sup>Co prompt spectrum at positron window settings. All the measurements were taken at room temperature. Analysis of each positron lifetime spectrum, after proper source and background corrections, was computed using standard PATFIT program (Kirkegaard and Eldrup, 1972) in accordance to the positron trapping model.

### 2.3. Adsorption of Cr(VI) by Ni<sub>2</sub>O<sub>3</sub> nanostructure and nanoparticles

A batch adsorption procedure was applied to study the sorption of Cr(VI) ions by Ni<sub>2</sub>O<sub>3</sub> nanostructure and nanoparticles using methods as carried out by us (Dey et al., 2015). Details of the experiment are furnished in Scheme S1 of ESI. All experiments were performed in triplets and volumetric measurements done in volumetric flasks to minimize error. After determining initial and final concentrations of the solution from absorption spectra obtained from UV–Vis spectrophotometer, adsorption (in %) and adsorption capacity (Q<sub>e</sub>) are calculated using the following relations (1) and (2) (Yilleng et al., 2013):

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