A colorimetric probe for the detection of Ni²⁺ in water based on Ag-Cu alloy nanoparticles hosted in electrospun nanofibres

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ABSTRACT
A Ni²⁺ based colorimetric probe based on glutathione-stabilized silver/copper nanoparticles (GSH-Ag-Cu alloy NPs) in an electrospun polymer matrix is reported. Glutathione-Ag-Cu alloy NPs were characterized by ultraviolet-visible spectroscopy (UV-vis), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The freshly synthesized GSH-Ag-Cu alloy NPs in a polymer matrix were black in colour due to an intense surface plasmon absorption band at 424 nm. However the electrospun nanocomposite fibres were green in colour and in the presence of Ni²⁺ the green GSH-Ag-Cu alloy NP fibres were discoloured. The sensitivity of the GSH-Ag-Cu alloy NPs towards other representative transition, alkali and alkalai earth metal ions was negligible. The effect of the concentration of Ni²⁺ on the nanocomposite fibres was evaluated and the ‘eye-ball’ limit of detection was found to be 5.8 μg/mL.

Keywords: colorimetric probes, alloy nanoparticles, electrospun nanofibres, heavy metal determination

INTRODUCTION
Nickel is an essential trace element for plants and animals where it participates in a variety of cellular processes. It plays important roles for various enzymes such as hydrogenases, superoxide dismutase, acetyl-coenzyme, carbon monoxide dehydrases, and in catalytic processes (Mulrooney and Hausinger, 2003). However, overexposure to Ni can cause acute pneumonitis, dermatitis, asthma, disorders of central nervous system and cancer of the nasal cavity and lungs (Kaspzak et al., 2003). The International Agency for Research on Cancer (IARC) has classified nickel compounds as Group 1 carcinogens to humans (Denkhaus and Salnikow, 2002). Group 1 carcinogens are described by the IARC as substances which are carcinogenic to humans (IARC, 2015). Therefore detection of Ni²⁺ ions in industrial, environmental and food samples has become very important.

Like many transition metals, the determination of Ni by photometric methods is well established. Many sensitive instrumental methods, such as spectrophotometry (Ressalan and Iyer, 2004), X-ray fluorescence spectrometry (Zawisza et al., 2012), atomic absorption spectrometry (Alvarez and Carrillo, 2012), and chemiluminescence (Li et al., 2006), have been widely applied for the determination of nickel. While these techniques are capable of accurately detecting low levels of transition metals, they require high-cost analytical instruments or at the very least electricity. Consequently, the current instrumental methods are insufficient for online and field monitoring, especially for resource-poor settings. Hence, there is a need to develop simple, reliable methods that are cheap, sensitive, selective as well as capable of use by non-skilled personnel, preferably in the field. Recently, colorimetric sensing of metal ions has been shown to be a less labour-intensive alternative to techniques based on fluorescence (Nazeeruddin et al., 2006). It is well known that solid materials that change colour upon recognition of macromolecules are widely accepted for fingerprinting and for conducting pregnancy tests at home (Prabhakaran et al., 2007). The throughput of the testing process has been profoundly advanced as a result of the elimination of instrumentation and the use of organic solvents. This idea could be extended towards developing simple visual detection methods for trace environmental toxins such as transition metal ions.

Metal nanoparticles with well controlled size have recently been the focus of great interest because of the colour changes associated with their surface plasmon absorption. The surface plasmon absorption is dependent on a number of parameters such as the size and shape of the particle, the adsorbed species and the distance between particles (Aslan et al., 2004). Among the metals, gold, silver and copper are known to display plasmon resonances in the visible region of the electromagnetic spectrum (Kreibig and Vollmer, 1995). These nanoparticles have been used with great success for the detection of a range of analytes such as metal ions (Reynolds et al., 2006). For colour signal generation, metal nanoparticles are particularly attractive as they possess much higher extinction coefficients compared to organic dyes, enabling sensitive colorimetric detections with minimal material consumption (He et al., 2005; Rosi and Mirkin, 2005). Metal alloy nanoparticles, on the other hand, have mainly been studied because of their catalytic effects (Dutta et al., 2011, Shifeng et al., 2010). They have been reported to offer additional degrees of freedom for tuning their optical properties by altering atomic composition and atomic arrangement (Chowdhury and Bhatlanabota, 2009).

In order to confer some special properties, organic and inorganic polymers have been used as solid supports for nanoparticles (Barbudello et al., 2009). The choice of solid support and immobilization of the indicator onto the support have significant impact on the performance of the probes in terms of selectivity (Brook and Narayanaswamy, 1998), sensitivity,