

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

DA Ondigo^{1,4*}, B Mudabuka¹, B Pule¹, ZR Tshentu³ and N Torto^{1,2}

¹Department of Chemistry, Rhodes University, P.O. Box 94, Grahamstown, 6140, South Africa

²Botswana Institute for Technology Research and Innovation, P/Bag 0082, Gaborone, Botswana

³Department of Chemistry, Nelson Mandela Metropolitan University, P.O. Box 77000, Port Elizabeth, 6031, South Africa

⁴Department of Physical Sciences, Karatina University, P.O. Box 1957-10101, Karatina, Kenya

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 alkali 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 dehydrogenases, 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 (Kasprzak 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 spectrofluorimetry (Ressalan and Iyer, 2004), X-ray fluorescence spectrometry (Zawisza et al., 2012), atomic absorption spectrometry (Álvarez 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 Bhethanabotla, 2009).

In order to confer some special properties, organic and inorganic polymers have been used as solid supports for nanoparticles (Barbadillo 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,

* To whom all correspondence should be addressed.

☎ +254 107 590; e-mail: dondigo@karu.ac.ke

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response time and stability (Xavier et al., 1998). Furthermore, polymers could give rise to electrospinnable composites for transformation into nanofibre mats for solid-phase measurements. Electrospinning of polymeric materials into well-defined fibre mats has received significant interest in the recent past (Greiner and Wendorff, 2007; Teo and Ramakrishna, 2006; Reneker and Yarin, 2008). Specifically, the technique has been found to be a unique and cost-effective approach for fabricating large surface area mats for a variety of sensor applications (Wang et al., 2002; Reneker and Chun, 1996; He et al, 2009, Balaji et al., 2006; Shin and Jang, 2007; Gao et al., 2007).

Herein, we report the development and characterization of a simple, sensitive and selective colorimetric probe for the detection of Ni^{2+} ions in water based on Ag-Cu alloy nanoparticles hosted in electrospun nanofibres.

EXPERIMENTAL

Materials and reagents

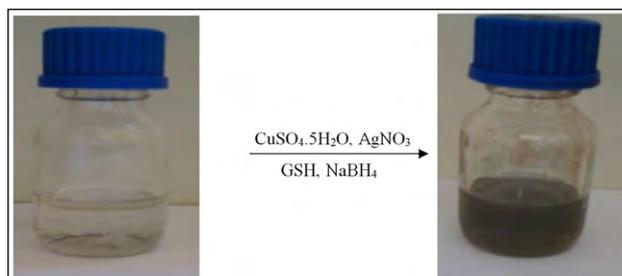
All chemicals used were of analytical grade. All solutions were prepared with double-distilled deionized water obtained from a Millipore system. Nylon 6 (Mw = 10 000), AgNO_3 (ACS reagent $\geq 99.0\%$), NaBH_4 , glutathione and salts of different cations studied ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, CaCl_2 , NaCl , $\text{Pb}(\text{NO}_3)_2$ and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) were obtained from Sigma Aldrich (St. Louis MO, USA). Formic acid (90%) and glacial acetic acid (100%) were purchased from Merck Chemicals (Wadeville, South Africa) and used as received. All glassware were cleaned with 3:1 HCl/HNO_3 and rinsed with double-distilled deionized water before use.

Instrumentation

Surface plasmon absorption spectra were acquired using a Perkin Elmer Lambda 25 UV/VIS double beam spectrophotometer equipped with a quartz cell (1 cm) at room temperature (Perkin Elmer, USA). Transmission electron micrographs (TEM) were evaluated on a JEOL JEM 2100 LaB6 working in STEM and HAADF (high angle annular dark field) mode (JEOL Ltd., Japan). The morphology of the nanofibre mat was studied by a JEOL JSM-7001F field emission scanning electron microscope operating at 2 kV after gold sputter coating (JEOL Ltd., Japan). The EDS spectrum of the Ag-Cu alloy nanoparticles hosted in electrospun nanofibres was recorded with Tescan (TS5136ML) scanning electron microscope (SEM) operating at an accelerated voltage of 20 kV after a gold sputter coating.

In-situ synthesis of glutathione-stabilized Ag-Cu alloy nanoparticles

Nylon 6, AgNO_3 , CuSO_4 , NaBH_4 and glutathione were used as electrospinnable polymer, Ag precursor, Cu precursor, reducing agent and stabilizer, respectively. Nylon 6 pellets were dissolved in a mixture of acetic acid and formic acid in the ratio of 1:1 to make a solution with a concentration of 15 wt/wt%. The mixture was stirred for 1 h until the lumps of the nylon 6 pellets were dissolved and well dispersed. 10.5% of AgNO_3 and CuSO_4 in the molar ratio of 1:1.96 were then added to the nylon 6 solution. The mixture was allowed to stir for further 1 h after which 1.5×10^{-1} moles of NaBH_4 was added to the mixture. The colour of the solution changed to black (Scheme 1). After stirring for about 5 min, 22.8% of GSH was added. The percentage weight of the salts and the capping agent were calculated based on the weight of nylon 6.



Scheme 1

In-situ synthesis of glutathione-stabilized Ag/Cu alloy nanoparticles

Fabrication of electrospun nanocomposite fibres

The homogenous nanocomposite solution was loaded into a 10 mL plastic syringe. The syringe was then mounted on a programmable syringe pump (New Era, NE-1000). The solution was delivered at a flow rate of $0.3 \text{ mL} \cdot \text{h}^{-1}$ through a steel needle of 0.584 mm internal diameter. Nanofibres were collected on an aluminium foil, the distance between the needle tip and the collector was 12 cm and the applied voltage at the needle tip was 22.5 kV. The electrospun fibre mats were cut into uniform strips and without any further treatment the strips were placed in the various test solutions.

Performance testing of the probe

To investigate the metal ions recognition ability of GSH-Ag/Cu NPs, metal ions (Ni^{2+} , Mn^{2+} , Fe^{2+} , Co^{2+} , Cd^{2+} and Pb^{2+} , Na^+ , Cr^{3+}) of the same concentration ($0.1 \text{ mol} \cdot \text{L}^{-1}$) were prepared. Aliquots (5 mL) of the standard solutions were measured out in a sample vial and the strips of electrospun fibre mats were placed in the solutions. Deionized ultrapure water obtained from a Millipore system was used as control in the study.

RESULTS AND DISCUSSION

Optical properties of synthesized Ag-Cu alloy NPs

UV-vis spectroscopy is one of the widely used techniques for structural characterization of nanoparticles. The absorption spectrum (Fig. 1) of the black Ag-Cu alloy colloids showed a surface plasmon absorption band with a maximum at 424 nm. If Ag and Cu ions are reduced simultaneously in the same solution, Ag-Cu alloy nanoparticles are expected to form. The alloy formation could be concluded from the fact that the optical absorption spectrum showed only one plasmon band, in agreement with literature reports (Mulvaney, 1996; Papavassiliou, 1976; Torigoe et al., 1993). Two bands would be expected if there was a mixture of Ag and Cu nanoparticles. Further, the appearance of an SPR absorption band at 424 nm confirmed the narrow size distribution and the well dispersed state of the alloy nanoparticles that were formed.

A physical mixture of synthesized Ag and Cu nanoparticles showed two absorption bands corresponding to the individual metal nanoparticles (Fig. 2 inset). Silver NPs alone in the polymeric solution had a strong surface plasmon resonance peak at 408 nm, while that of the Ag-Cu alloy NPs was broad and red-shifted to 424 nm (Mulvaney, 1996). In addition, the plasmon resonance absorption band of Ag NPs was stronger and sharper in comparison with that of Cu nanoparticles (at 551 nm), and occurred at longer wavelengths (Fig. 2). The collective plasmon

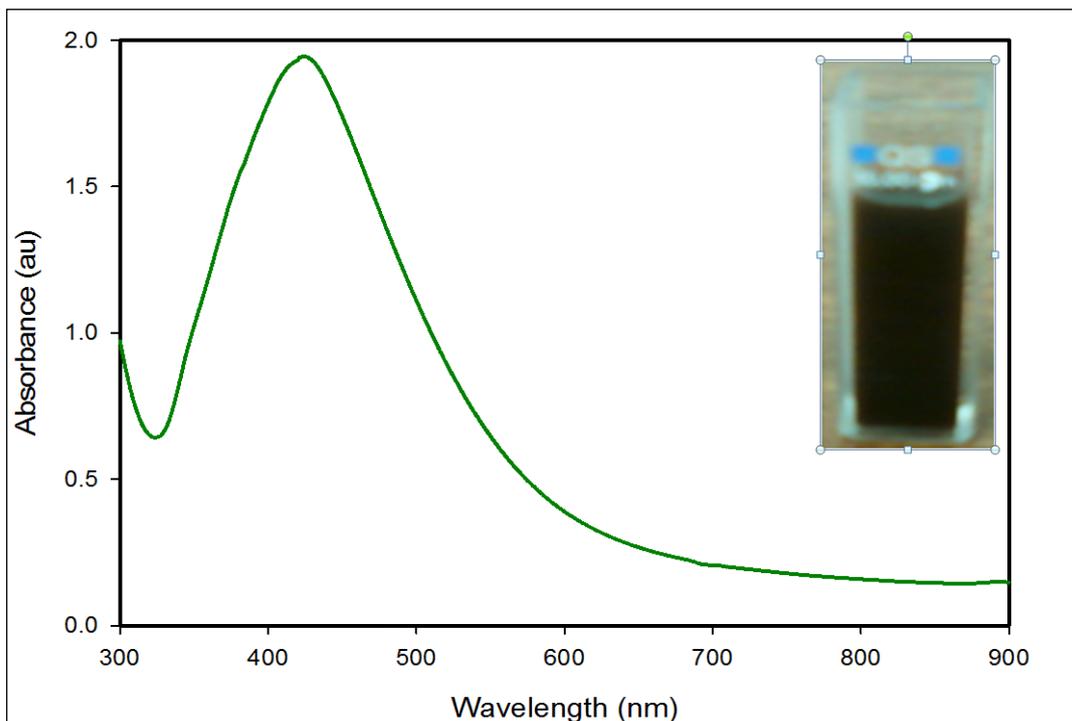


Figure 1

UV-vis spectrum of Ag-Cu/nylon 6 nanocomposite solution before electrospinning

resonance absorption band of Ag-Cu alloy differed dramatically from that of Ag or Cu, and could easily be tuned in the UV-vis region by changing the Cu/Ag mole ratio. The notable change in the absorption spectra could primarily be attributed to a change in the dielectric function when different metal atoms were mixed. Silver has been reported to display approximately free electron behaviour in the visible range, which gives rise to a sharp absorption band. Other metals, including Cu and Au, have less free-electrons, which gives rise to broad absorption bands (Chimentão et al., 2006).

Reducing agent

The general chemical reduction reactions involve reducing agents that are reacted with a salt of the metal (M) according to Eq. 1.



where: M is the metal ion, n^+ is the charge on the metal ion, n is the moles of the reducing agent, Red is the reducing agent and O is the oxidized form of the reducing agent.

In a study of metal ion reduction by a borohydride system, it was reported that BH_4^- ions function not only as a reducing agent but also as a stabilizer that prevents the nanoparticles from aggregating (Jae-Seok et al., 2009). Adsorption of borohydride onto the surface plays a key role in stabilizing growing nanoparticles by providing particle surface charge leading to electrostatic repulsion that keeps them from agglomerating (Scheme 2). Therefore, there has to be enough borohydride in solution to reduce the metal ions as well as to stabilize the particles as the reaction proceeds.

Later in the reaction however, it was observed that when the mole ratio of the salts to $NaBH_4$ was greater than 1:2.8, aggregation of the nanoparticles was evident. This could be due to the fact that $NaBH_4$ increased the overall ionic strength of the

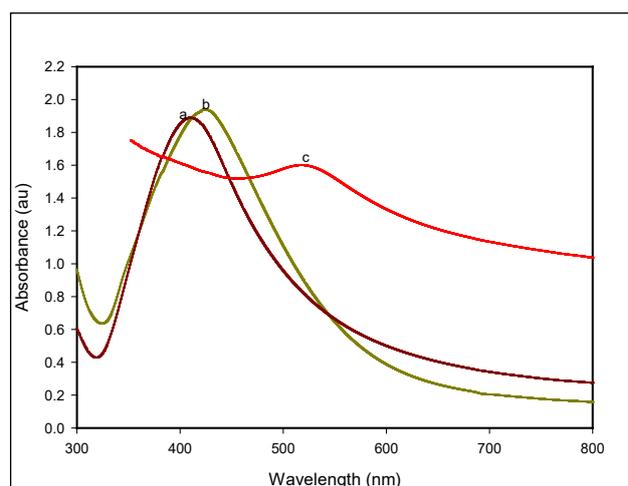
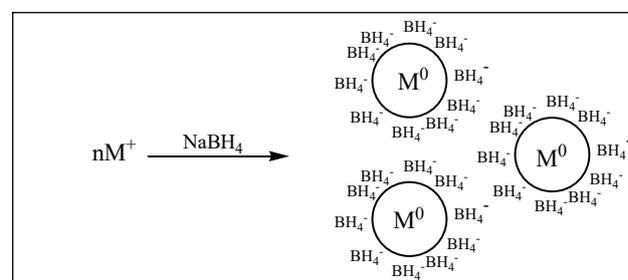


Figure 2

Surface plasmon absorption for Ag NPs (a), Ag-Cu alloy NPs (b), Cu NPs only (c), inset is for the physical mixture of Ag and Cu NPs



Scheme 2

Separation of nanoparticles by repulsive forces induced by adsorbed borohydride

solution leading to aggregation of the nanoparticles. Therefore, the quantities of NaBH_4 had to be optimized. The optimal mole ratio of the total salts to sodium borohydride was found to be; 1:2.8. Below and above the optimal mole ratio, there appeared more than one broad peak (Fig. 3). The broad nature of the peaks could be attributed to large size nanoparticle distribution and probably aggregation as a result of the concentration levels of the reducing agent.

Upon introduction of the stabilizing agent (GSH), the rather loose shell of borohydride ions on the Ag-Cu NP surface could easily be displaced by other desired ligands with valuable functionalities (for example, N and -SH groups). Molecules with electron-rich N or S atoms are easily bound onto the surface of metal nanoparticles through the coordinating interactions between S or N atoms with the electron-deficient surface of metal nanoparticles. In particular, the S atom of GSH exhibited much stronger binding ability/affinity to NPs than the borohydride ions. A stabilizing agent would normally rely on electrostatic repulsion forces caused by either surface charge or steric stabilization, or both, to prevent nanoparticles from aggregating.

Characterization of GSH-Ag-Cu alloy NP nanofibres

The morphology of the GSH-Ag-Cu alloy nanofibres was observed using a transmission electron microscope (TEM). As shown in Fig. 4a, glutathione-stabilized Ag-Cu alloy nanoparticles having sizes between 3 and 6 nm were well dispersed in the electrospun nanofibres. Glutathione was used as a stabilizing agent to prevent the nanoparticles from aggregating, since glutathione contains the -SH group which could be easily adsorbed onto the surface of metal nanoparticles resulting in a well-dispersed state. For environmental applications, surface functionalization of nanoparticles is essential to enable their application for the selective detection of specific analytes. Therefore, apart from stabilizing nanoparticles formed, GSH also served as a ligand that could selectively bind Ni^{2+} ions in aqueous media.

The EDS spectra obtained from SEM images (Fig. 4b) also confirmed the presence of Ag-Cu nanoparticles observed in Fig. 4a. The content of Ag NPs was found to be 15.52 wt% while that of Cu NPs was found to be 1.77 wt%. The presence of O and N peaks in the spectrum were attributed to the nylon polymer.

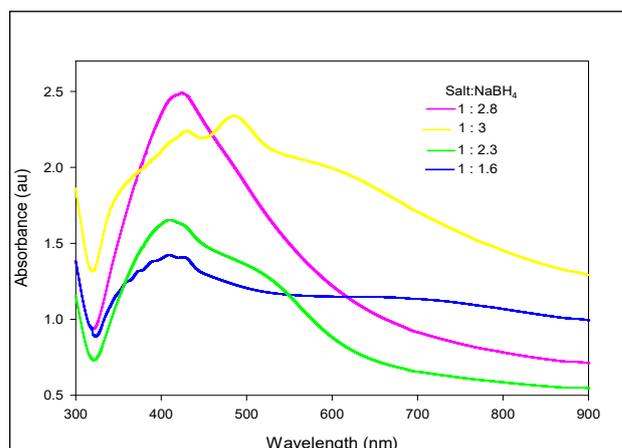


Figure 3

UV-vis spectra of Ag-Cu alloy nanoparticles with varying mole ratios of reducing agent

Metal ion recognition ability of Ag-Cu alloy nanoparticles

Upon interaction with various metal ions, as could be seen from Fig. 5, the fibre mat placed in solution containing Ni^{2+} was discoloured, while other metal ions did not discolour the fibre strips.

Glutathione, a tripeptide containing cysteine, has two carboxylic acid groups. Marco and Thomas (2005) reported that at least one of the carboxylic acid groups forms an additional anchor to the metal nanoparticle surface when it is used as a stabilizer. Upon interaction with the surface, the carboxylic acid group also deprotonates. Ni^{2+} is known to bind well to groups or ligands containing lone pair electrons, such as $-\text{NH}_2$ and $-\text{COOH}$, via the coordination bond (Jones and Vaughn, 1978). Both the terminal carboxylate groups of the glycine moiety and the free $-\text{NH}_2$ groups from the glutamate moiety were believed to be responsible in binding the Ni^{2+} centre. The nanoparticles are expected to aggregate upon interaction with Ni^{2+} due to strong coordination bonds between Ni^{2+} and $-\text{NH}_2$ and $-\text{COOH}$ of the functionalized glutathione modifier. We therefore concluded that: the carboxylic acid groups that may have been bound to the surface of the nanoparticles were detached and in the process the nanoparticle surface became exposed and this led to agglomeration and subsequent loss of their surface properties. Agglomeration is mainly caused by excess surface energy

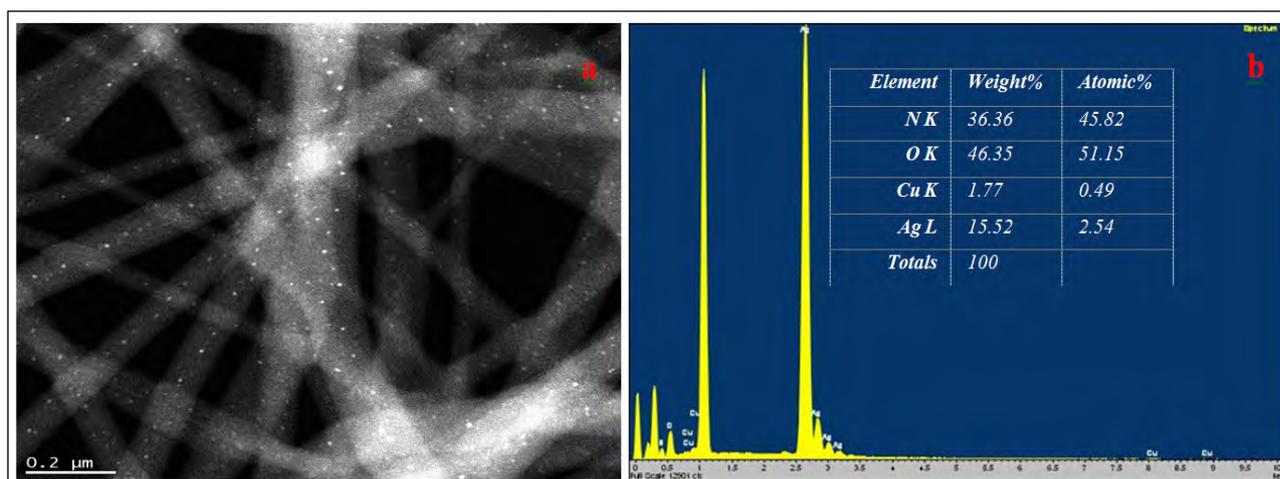


Figure 4

Transmission electron micrograph (a) and EDS spectrum of Ag-Cu alloy nanoparticles in the electrospun nanofibres (b)



Figure 5

Colorimetric responses of the fibre strips to various solutions from left: H_2O (a), Pb^{2+} (b), Ni^{2+} (c), Fe^{2+} (d), Na^+ (e), Cr^{3+} (f), Ca^{2+} (g), Mn^{2+} (h) and Co^{2+} (i)

and high thermodynamic instability of the nanoparticle surface (Tolaymat et al., 2010).

It must be noted that in the presence of Ni^{2+} ions, Ag-Cu alloy nanoparticles were aggregated and subsequently oxidized to Ag and Cu ions, most likely because GSH no longer surrounded the alloy nanoparticles. The observations were consistent with the SEM results obtained. The SEM images of alloy nanoparticles before and after the addition of Ni^{2+} ions are shown in Fig. 6. Aggregated nanoparticles were observed in nanofibres treated with Ni^{2+} solution, but it was not possible to see the nanoparticles, using SEM, before the nanofibres were treated with the analyte. This may have been because the nanoparticles were encapsulated within the nanofibres (see the TEM image in Fig. 4). The discolouration was probably related to the oxidation of the aggregated nanoparticles which we believe were then no longer stabilized and the consequent formation of a colourless complex between glutathione and Ni^{2+} ions.

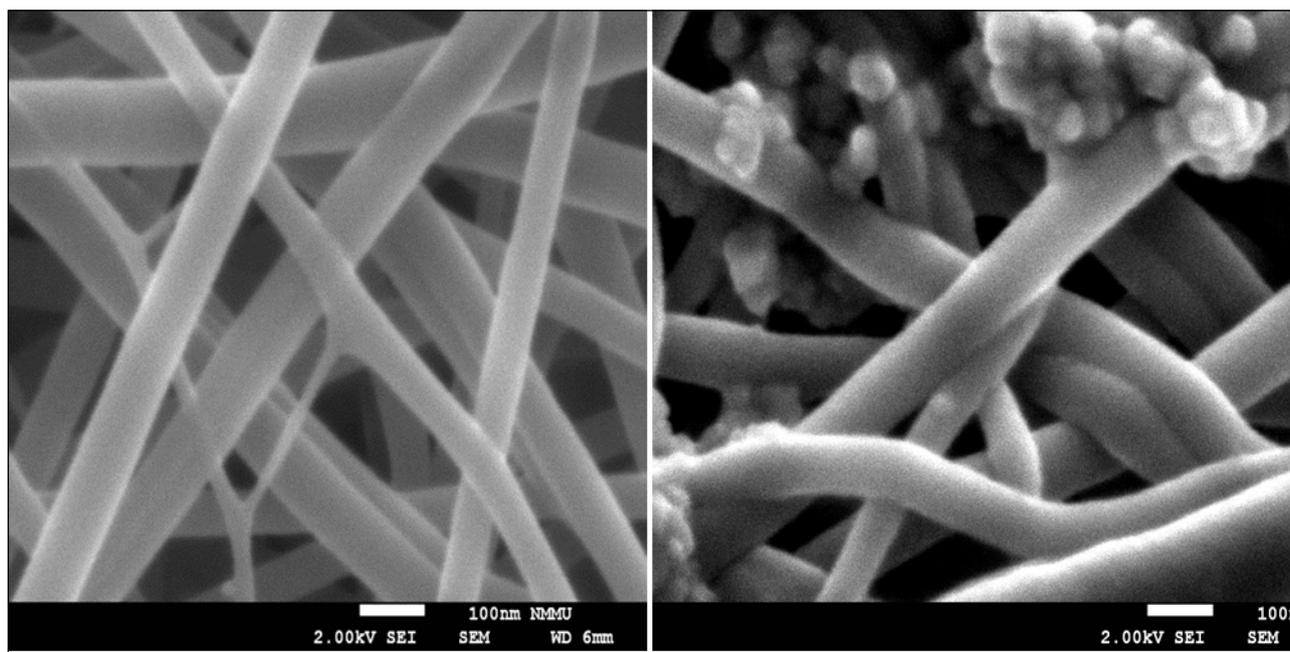


Figure 6

Scanning electron micrograph of Ag-Cu alloy/nylon 6 nanocomposite fibres (a) before and (b) after treatment with Ni^{2+}

To further confirm that the nanoparticles had actually been oxidized, some crystals of $NiCl_2$ salt were dissolved in the nanocomposite solution before electrospinning and a colour change from black to blue was observed (Fig. 7 inset). The blue colour showed the presence of Cu^{2+} ions in the mixture given that Ag^+ ions are colourless. The oxidation was further confirmed by UV-vis spectroscopy (Fig. 7). It could be seen that the SPR absorbance had been significantly decreased by the presence of Ni in the nanocomposite solution and that designated a considerable decrease in the concentration of Ag-Cu alloy NPs.

Calibration curve

The linearity studies were carried out using the polymeric nanocomposite prior to electrospinning. A series of Ni^{2+} standard solutions were prepared in the concentration range of $20\text{ mg}\cdot\text{L}^{-1}$ to $80\text{ mg}\cdot\text{L}^{-1}$. $25\ \mu\text{L}$ of the nanocomposite were added to 3 mL of Ni^{2+} solutions of different concentrations. Colour change was observed at 4 min and maximum absorbance was realized in 7 min. Therefore, all nanocomposite absorbance was carried out at 424 nm after 7 min. The limit of detection (LOD) was calculated using Eq. 2; where δ is the standard deviation and s is the slope of the calibration curve (Busaranon et al., 2006) (Fig. 8).

$$LOD = \frac{3.3\delta}{s} \quad (2)$$

The standard deviation was calculated from the slope of the calibration curve. The LOD of the proposed method was found to be $0.037\ \mu\text{g}\cdot\text{mL}^{-1}$.

In an attempt to gain insight into the effect of concentration of Ni^{2+} on the colour change of the nanocomposite fibre, a series of solutions of Ni^{2+} with different concentrations ranging from $0.058\ \mu\text{g}\cdot\text{mL}^{-1}$ to $5.8\text{ mg}\cdot\text{mL}^{-1}$ were prepared and the fibre immersed in the solutions. Colour changes were observed on the fibres in solutions having concentrations of $5.8\ \mu\text{g}\cdot\text{mL}^{-1}$ to $5.8\text{ mg}\cdot\text{mL}^{-1}$ within 30 min, the rate of which was proportional to the concentration. Below $5.8\ \mu\text{g}\cdot\text{mL}^{-1}$, the fibres changed colour after an overnight stay in the Ni^{2+} solutions down to a concentration of $0.058\ \mu\text{g}\cdot\text{mL}^{-1}$.

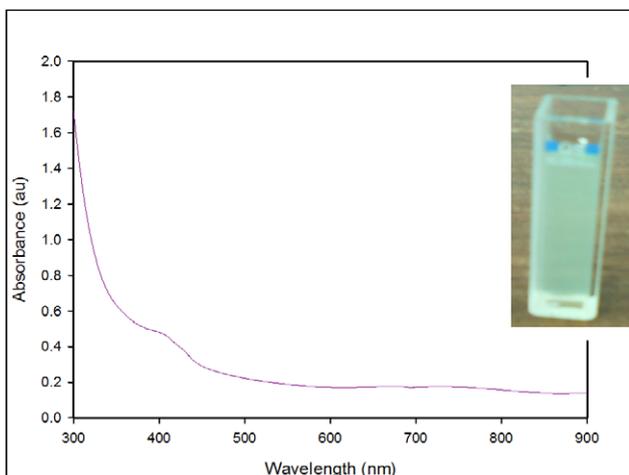


Figure 7

UV-vis spectra of Ag-Cu alloy nanocomposite solution incubated with Ni²⁺ ions. The insert shows a photograph of the mixture in a cuvette.

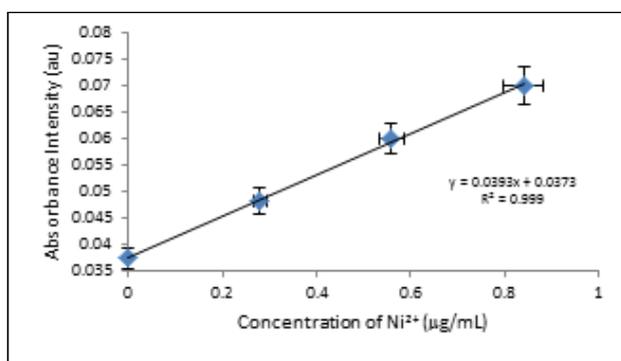


Figure 8

Calibration curve for the determination of Ni(II) concentration

Real sample analysis

The proposed method was applied in the determination of the concentration of Ni²⁺ ions in a water sample; tap water from the F12 research lab at Rhodes University was used. For this purpose, the fibre strip was put in a vial containing 5 mL of a tap water sample. No change in the colour of the fibre strip was observed thus confirming that the concentration of Ni²⁺ in the sample was less than the limit of detection of the proposed method. The tap water was then spiked with 5.8 µg·mL⁻¹ of Ni²⁺ solution and the fibre mats were discoloured. This result demonstrated the applicability of the colorimetric probe for detection of Ni²⁺ ion in real water samples.

CONCLUSIONS

Nylon 6 nanofibres containing glutathione-stabilized Ag-Cu alloy nanoparticles were prepared by electrospinning. The nanocomposite was characterized by UV-vis, SEM and TEM. Metal-sensing ability of the probe was evaluated and it was found to be selective to Ni²⁺. The approach relied on the simple oxidation of the formed nanoparticles in the presence of the analyte. The presence of Ni²⁺ eliminated the SPR band of the nanoparticles at 424 nm at room temperature. In contrast to other nanoparticle-based colorimetric assays, this system did not imply the use of complex nanoparticle modification

(i.e., using biological material). The method is user-friendly and is field-portable; it is inexpensive, very simple, rapid, and a reliable alternative in comparison to other techniques. By functionalizing nanoparticles with ligands and other specific heavy-metal receptors, the possibility exists to further improve the sensitivity of the method achieving much more efficient screening tests for metal toxicity in general, in addition to single metal detection.

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