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Sensing of the uranyl ion based on its complexation with bisphosphonate-capped gold nanoparticles

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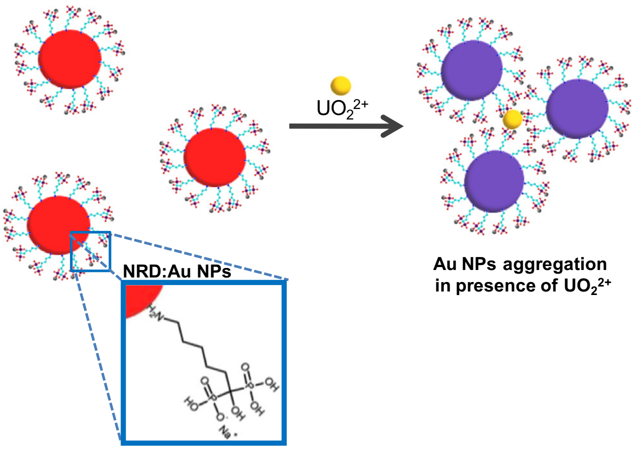
ABSTRACT

We describe a sensing system that relies upon the formation of specific complexes between uranyl ion and bisphosphonate-capped gold nanoparticles. The ensuing concentration-dependent red-shift of surface plasmon resonance absorption allows the determination of uranyl ion concentration within the 1.5–15 ppm range.

1. Introduction

The development of colorimetric sensors capable of selective recognition of cationic species is a research area of current interest [1–2]. More particularly, sensing of uranyl ion is an important challenge for nuclear companies and environmental groups. The management of uranium mines requires scheduled monitoring of surface and ground waters within the mining sites and in their surroundings. Determinations of uranium contents of water samples are usually obtained through time-demanding radionuclide estimations carried out in remote places. These tasks could largely benefit from the use of portable devices, preferably the ones based on colorimetric methods which are certainly the most handy when it comes to on-field analyses.

Techniques based on aggregation of gold nanoparticles (AuNPs) are currently knowing important advances [3] because they can lead to versatile applications dealing, for example, with sensing of oligonucleotides [4], metal cations [5–8], glucose [9], or the monitoring of enzyme activity [10]. These nanoparticles could also be used to develop miniaturized electronic and optical devices [11]. AuNPs stabilized in water by a capping agent avoiding their aggregation exhibit surface plasmon resonance properties, which are function of nanoparticle size. Such suspensions exhibit a wine red color when the particle diameter is comprised between 10 and 50 nm ($\lambda_{max} = 520$ nm) [12]. Analyte complexation by the capping molecules elicits nanoparticle aggregation, and induces a red-shift of the surface plasmon resonance absorption peak; the solution turns purple to blue, depending on analyte concentration. Bisphosphonates (BP) are known to form very stable and specific complexes such as tetra-, penta- or



Scheme 1. Schematic representation of the specific complexation of UO_2^{2+} by bisphosphonate-capped AuNPs.

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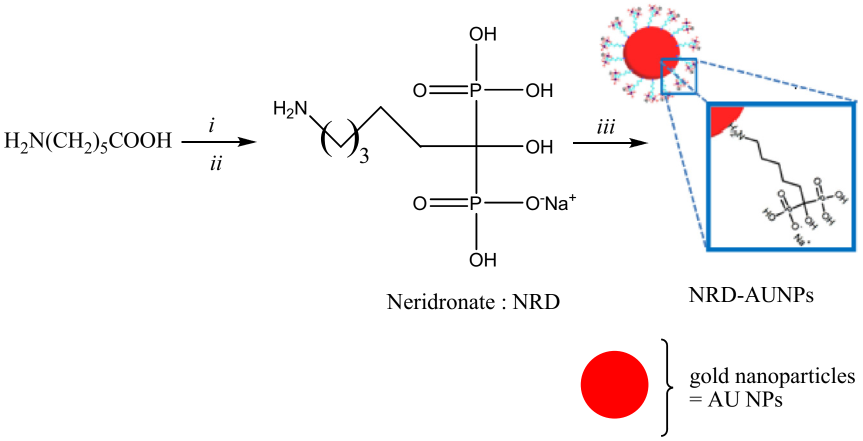
hexadentate complexes with uranyl ions (UO_2^+) [13–16]. So, in the light of the above, we have synthesized bisphosphonate-capped gold nanoparticles which lead to the formation of complexes with uranyl ions, allowing the determination of uranyl ion concentration in distilled water within the 1.5–15 ppm range by UV–visible detection (Scheme 1).

2. Experimental

Chemicals and equipment: All solvents and reagents were purchased from Aldrich, Prolabo or Acros. Analytical thin layer chromatography (TLC) was performed on Merck 60F254 silica gel. ^{1}H and ^{13}C NMR spectroscopies were performed with a Brüker



Scheme 2. Synthesis of neridronate-capped gold nanopaticles (NRD-AUNPs). (i) H_3PO_3, methanesulfonic acid, 65 °C, (ii) PCl_3, 20 h then NaOH aqueous solution; and (iii) $NaAuCl_4$, H_2O, 50 °C then dialysis against distilled water during 24 h.

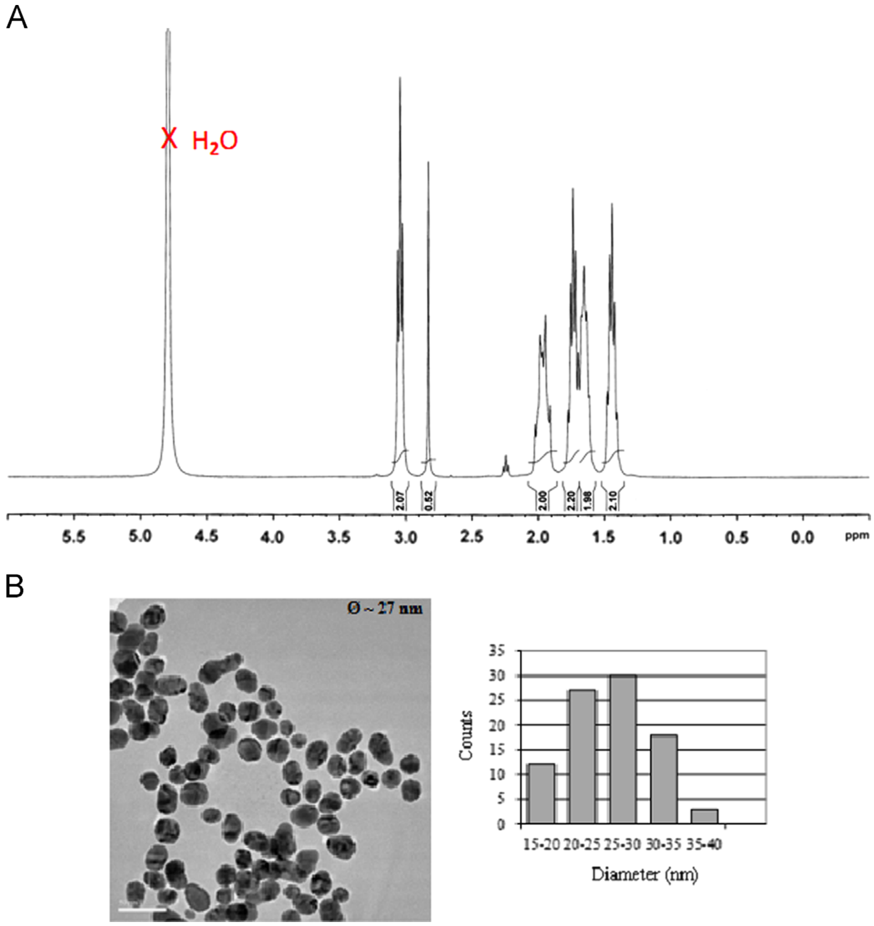


Fig. 1. (A) ^{1}H NMR spectrum of the synthesized neridronate in D_2O and (B) TEM image of NRD:AuNPs with an average diameter of about 27 nm (white bar=50 nm).