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Gold Nanoparticle-Based Optical Probe for Screening Hexaconazole Rapidly

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Gold nanoparticles (Au NPs) were synthesized by reduction of hydrogen tetrachloroaurate and used as a facile and highly selective sensor for the visual detection of hexaconazole. The presence of hexaconazole could rapidly induce the aggregation of gold nanoparticles, thereby resulting in red-to-blue (or purple) colour change. The concentration of hexaconazole was determined by the naked eye visually and could further be monitored by an UV-VIS spectrometer with a limit of detection (LOD) about 0.7×10^{-6} mg/L. The highest selectivity was proved in comparison with other eleven pesticides and the sensitivity and dynamic range of the colorimetric signals could be adjusted by the addition of NaCl or changing pH in gold nanoparticles.

Key Words: Gold nanoparticles, Hexaconazole, Colormetric detection, Sensor.

INTRODUCTION

Although hexaconazole belongs to the triazole fungicide family and, like the imidazole fungicides, interferes with fungal sterol synthesis. It is registered agrochemicals that have been extensively used on crops world-wide[1]. Environmental and biological monitoring and quality control programs require the development of precise, specific and sensitive techniques for the rapid detection and identification of hexaconazole in crops, wood, water and soil. Since traditional GC, HPLC or enzyme-linked immunosorbent assay (ELISA)[2-4] are complex and time-consuming, there is increasing interest in developing some facile sensors for rapid detection. Colorimetric sensors possess some advantages such as requiring minimal instrumentations, low cost and realizing the detection on-site and real-time. Gold nanoparticles (Au-NPs) designed as a colorimetric sensor can provide an important method of detection, which allows a direct analysis of the target compound by the naked eye[5]. Although the high extinction coefficients and the wide variation of optical properties of gold nanoparticles enables construction of simple but sensitive colorimetric sensors for various analytes such as DNA, metal ions and amino acids [6-10] and few papers were published about the viusal detection the pesticides until now[11]. Dubas and Pimpan[12] synthesized silver nanoparticles (Ag NPs) by reduction of silver nitrate in the presence of humic acids which acted as the sensor of sulfurazon-ethyl herbicide. The solution of Ag NPs was found to changes from yellow colour to orange red and purple with increasing herbicide concentration, but to be with a low sensitivity in the range of 100-500 ppm. Lisha *et al.*[13] reported the method of visual detection for chlorpyrifos phosphorothioate and malathion using unmodified Au NPs and the sensitivity was obviously improved by the addition of NaCl.

In this letter, the unmodified AuNPs were successfully prepared and used for the colorimetric screening for hexaconazole and the molecular recognition abilities were comparatively investigated with other eleven pesticides.

EXPERIMENTAL

Hexaconazole with a purity of 99.2 % was purchased from DIMA Technology Inc (Lake Forest, USA). Hydrogen tetrachloroaurate (III) ($HAuCl_4 \cdot 4H_2O$, 99.99 %), trisodium citrate dehydrate and twelve pesticides dissolved in methanol were purchased from Beijing or Shanghai Chemical Factory, China and used without further purification. UV-VIS absorption spectra were performed on a UV-2100 spectrophotometer (Beijing Beifen-Ruili Analytical Instrument Co. Ltd.). Synthesis of aqueous suspensions of gold nanoparticles involves reduction of a gold salt solution by tri-sodium citrate to form gold crystals, which grow by Ostwald's ripening to form nanoparticles of gold. The excess citrate ions in the medium are adsorbed on the nanoparticles until there is sufficient electrostatic repulsion to keep them from agglomerating. In brief, 0.01-0.02 % solution (100 mL) of $HAuCl_4 \cdot 4H_2O$ was brought to boiling under stirring and 5 mL of 1 % trisodium citrate was rapidly injected into

the boiling solution of $HAuCl_4$ and the mixed solution was further boiled for another 15 min under stirring and a wine-red suspension was obtained. The suspension was gradually cooled to room temperature and then filtered through a 0.45 mm Millipore membrane. The filtrate was stored in a refrigerator at 4 °C for further use. Gold nanoparticles were imaged using a Hitachi H-600 transmission electron microscope operating at 80 kV. The samples for TEM characterization were prepared by placing a drop of colloidal solution on a carbon-coated copper grid and dried at room temperature.

RESULTS AND DISCUSSION

A great challenge of visual detection using it is to develop an effective method for the special target molecular with high sensitivity and selectivity[14]. In this work, a series of gold nanoparticles were first synthesized by the reduction of $HAuCl_4$ with trisodium citrate in aqueous solution. The particles with narrow size distribution and controllable size could be obtained by changing the ratio of $HAuCl_4$ and trisodium citrate. In order to examine the specific recognition for the target using the unmodified Au NPs, control experiments in Microlon ELISA Plates 96 were carried out using twelve pesticides including iprodione (a), isoprocarb (b), carboxin (c), metalaxyl (d), atrazine (e), carbendazim (f), buprofezin (g), indoxacarb (h), teiadimefon (i), tebuconazole (j), tebuconazole (k), hexaconazole (l). The comparative experiments were also carried out using 200 μL of Au NPs in the presence of 10 mg/L different pesticides with a total volume about 250 μL, respectively. No colour changes were observed after 10 min except hexaconazole in the selective concentration range of 1-20 mg/L, respectively (Fig. 1). Furthermore, the comparative experiments were also done in 12 glass vials with the addition of 2 mL Au NPs, the total volume of 2.50 mL in vial for colour metric detection was kept in the presence of 10 mg/L different pesticides, respectively. After several minutes, the solution containing hexaconazole changed from red to deep blue, while other pesticides had no effect on the red colour of Au NPs. It is clearly shown that only hexaconazole shows a significantly

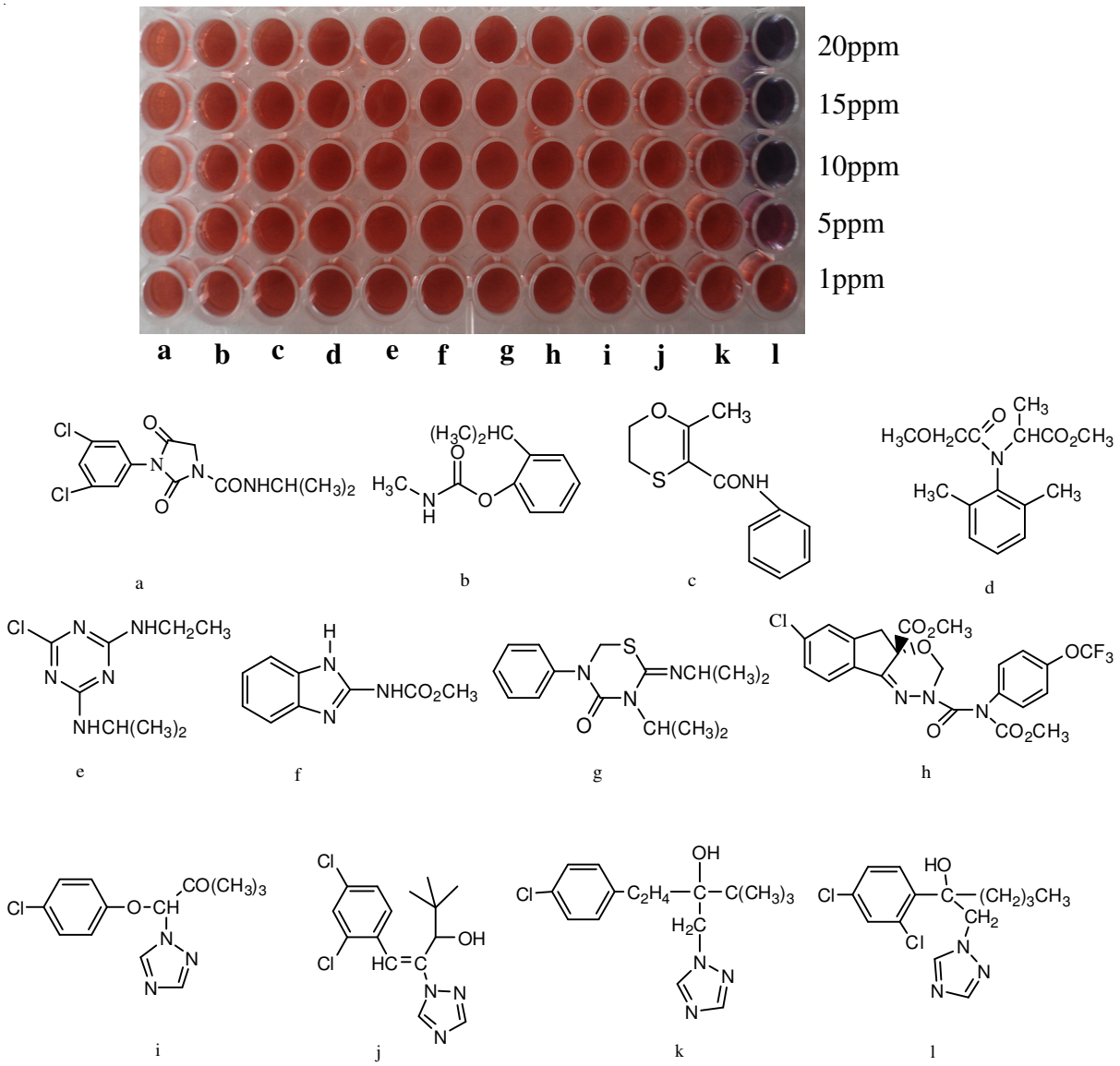

Fig. 1. (A) The Au NPs suspension (in Microlon ELISA Plates) after the addition of twelve pesticides with different concentrations, respectively. The structures of twelve pesticides were plotted below, respectively

higher absorption ratio (A_{640}/A_{520}) more than 1.4 and a deep blue colour (Fig. 2). Other pesticides can not interfere the detection of hexaconazole with an original red colour and lower absorption ratio less than 0.5. All mentioned above indicates that the unmodified Au NPs have a selective response towards hexaconazole.

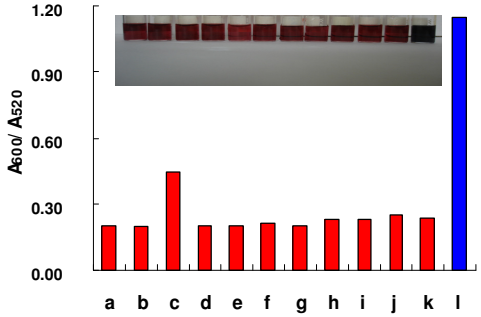

Fig. 2. The corresponding A600/A520 ratios of Au NPs suspension with the addition of 10 mg/L different pesticides, respectively. Inset: visual colour changes of Au NPs with the relative pesticides.

In order to quantitatively detect hexaconazole using Au NPs colorimetric sensor, UV-visible absorption spectra of Au NPs in the absence and presence of different concentrations of hexaconazole were recorded at a wavelength of 400-790 nm. The original absorbance of Au NPs at 520 nm decreased gradually while a new absorbance (centered at 640 nm) from their resulting aggregates increased obviously. With the addition of different concentration of hexaconazole from 0 to 20 mg/L, the colours of Au NPs changed from wine red, purple (5-9 ppm), blue (10-20 ppm) progressively. The absorption ratio *versus* the target concentration was also plotted and some typical spectra were given in Figs. 3A and 3B. It exhibited a linear correlation (R=0.9891) between the absorption ratio and hexaconazole concentration in the range of 2×10^{-6} mg/L to 20×10^{-6} mg/L. The linear equation is as follows: Abs = 0.0036 $\times C^2$-0.0042 $\times$ C+0.0734. The detection limit which is taken to be three times the standard derivation in blank solution is found to be 0.7×10^{-6} mg/L. This colour change from red to blue indicates that more and more Au NPs were consumed to form more and more aggregates, which was further confirmed by the TEM observations. The monodisperse nanoparticles with a size about 13 nm in the absence of hexaconazole and the significant aggregation of the Au NPs in the presence of 10 ppm hexaconazole (Figs. 3C and 3D, respectively).

The method developed here is much simpler than the existing method, without the requirement of expensive instrumentation. These excellent properties substantially enable the practical application for on-the-spot detection of hexaconazole at a low level (ppm). Moreover, it was possible to adjust the detection sensitivity and dynamic range to a desired concentration range by the addition of NaCl or the pH adjustment in Au NPs colloids[15,16]. For example, a significant colour change (from red to blue) occurred about 0.5 ppm for Au NPs with 10-40 mM NaCl whereas a colour change occurred over 3.5 ppm for Au NPs without NaCl. Here, with NaCl as an example, we demonstrated that it was possible to adjust the detection sensitivity and dynamic range to a desired concentration range by the addition of Au NP destabilizing/stabilizing reagents

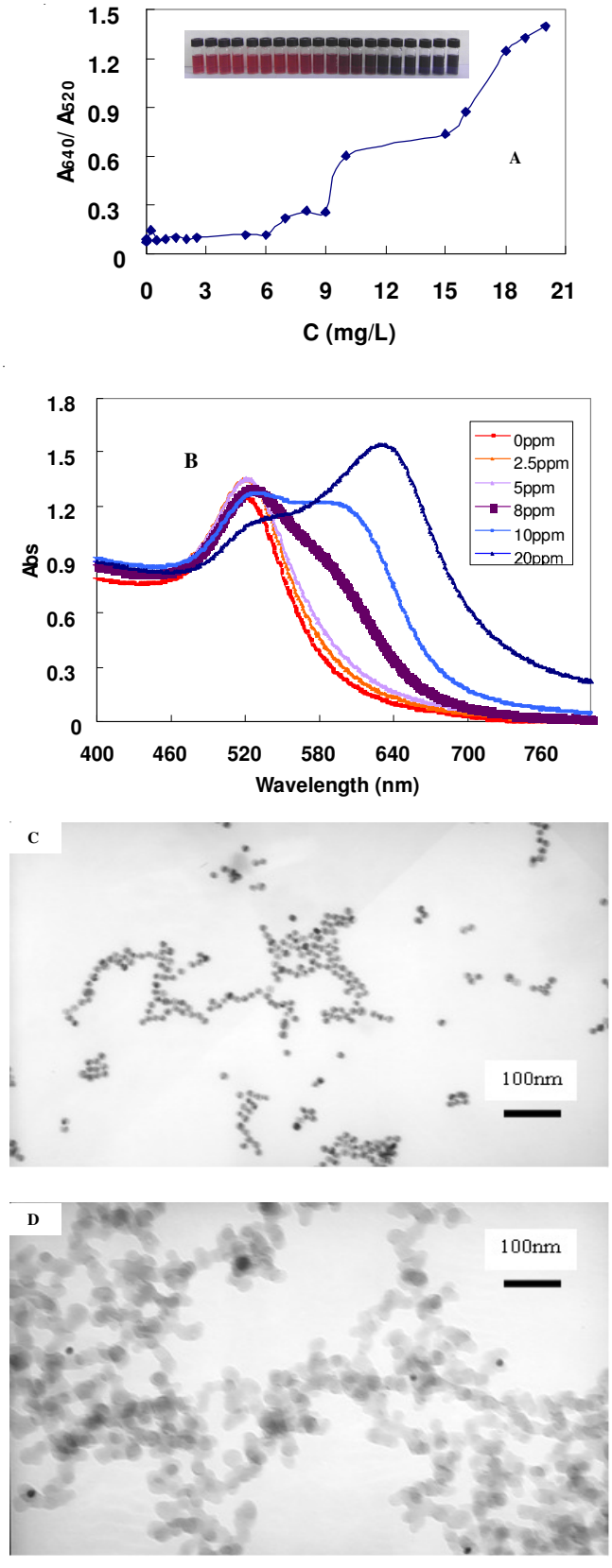

Fig. 3. (A) The corresponding plot of A640/A520 versus hexaconazole concentration from 0, 0.01, 0.1, 0.25, 0.5, 1, 1.5, 2.0, 2.5, 5.0, 6, 7, 8, 9,10, 15,16,18, 19, 20 ppm. Inset: visual colour change of Au NPs with the different concentration hexaconazole. (B) The evolution of UV-vis absorbance spectra of Au NPs suspension with the hexaconazole concentration from 0, 2.5, 5, 8and10 ppm. (C) TEM images of Au NPs in the absence of hexaconazole. (D) TEM images of Au NPs in the presence of 10 ppm hexaconazole.

(Fig. 4A). Conversely, pH dependence was also observed for the detection process. Low pH generally resulted in high sensitivity for visualization (Fig. 4B). For instance, a significant colour change occurred about 1.5 ppm for AuNPs in pH 3-4 whereas a colour change occurred over 3.5 ppm for Au NPs in pH 5-6. When the pH levels were in the range of 7-8 and no colour change occurred over 10 ppm due to the poor sensitivity of Au NPs. The adjustability in sensitivity and dynamic range is very important toward practical applications. For example, to determine whether a sample contains hexaconazole above a certain safety level, Au NPs can be preconditioned so that a significant colour change occurs around the safety level and is added to the sample as a prescreen.

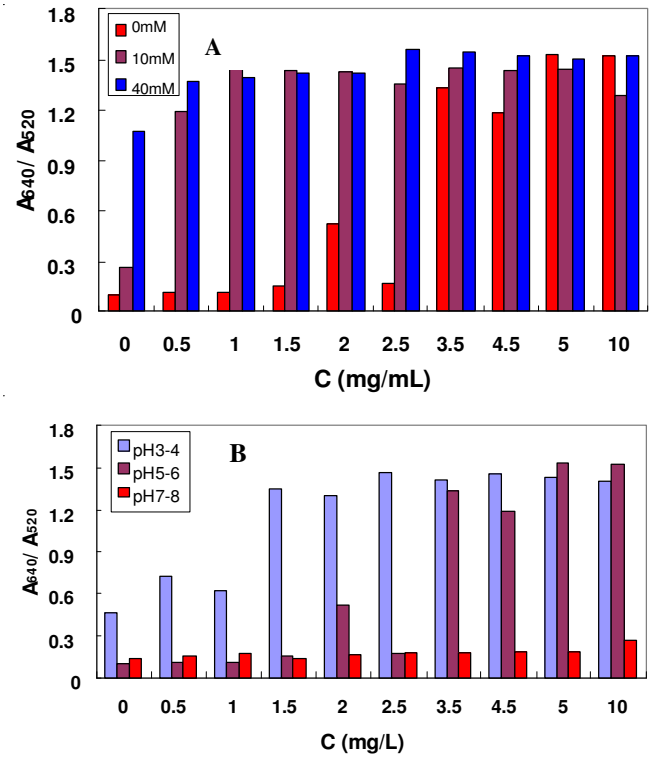

Fig. 4. (A) NaCl (sodium chloride)-dependent colorimetric analysis of hexaconazole detection using unmodified Au NPs colloids. (B) pH-dependent colorimetric analysis of hexaconazole detection using unmodified Au NPs colloids.

Previous studies have shown that there is a strong interaction between Au NPs and melamine with three exocyclic amino groups and three-nitrogen hybrid ring and the exocyclic amines could play an important role in the melamine-induced colorimetric visualization[15, 16]. Here, hexaconazole with one triazole-ring and one hydroxyl group contains multiple binding sites including two-nitrogen hybrid ring, the hydrongen-bonding recognition and the possible π-π stacking interaction between triazole or benzene ring. The above binding sites may interact with Au NPs and induce the relative aggregation. Therefore, the colloidal stability is drastically reduced to result in the fast/prompt occurrence of particle aggregation. The reason that teiadimefon (i), tebuconazole (j), tebuconazole (k) with similar structures, respectively cannot induce the colour change is possibly attributed to the fewer binding sites for coordinating interactions or the weaker π-π stacking interaction between them and benzene ring/triazole, respectively. The above weak interaction is obviously different from that of covalent bond between molecules. The relative mechanism for the target was investigated with the simultaneous addition of tiopronin (TIO) and glutathione (GSH) in the Au NPs collides with hexaconzaole, respectively. Herein, TIO/GSH solution was first mixed with hexaconzaole in equal molar ratio, respectively, followed by the addition of AuNPs solution and allowed to interact for several minutes. The thiol group of TIO or GSH with intriguing reactivity could bind onto the unmodified gold. No colour change was observed due to the interaction of covalent bond (Au-S) superior to the van der Waals attractive forces between the target (hexaconzaole) and AuNPs. So that such similar compounds generated strong interaction with Au NPs like TIO/GSH should be avoided in the application of colorimetric detection of hexaconazole.

In this letter, the use of Au NPs for colorimetric detection of hexaconazole was demonstrated and UV-VIS spectroscopy, TEM analysis were used for understanding the mechanism. The prepared sensor possesses some advantages including high selectivity over other pesticides, rapid detection speed (several minutes), high sensitivity (1 ppb if pH or ion strength is adjusted) and provide a promising approach for the on-site pesticide monitoring in water stream.

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