

Colorimetric Detection of ammonia and hydrogen peroxide in aqueous solutions using green synthesized silver nanoparticles from soapberry pericarps

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Research Article

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Abstract

The present study aims to investigate the sensing properties of silver nanoparticles synthesized via microwave assisted green method using *Sapindus mukorossi* (commonly known as soapberries) extract (SME) which acted as a reducing as well as stabilizing agent. AgNps on exposure to the analyte molecules ammonia (NH_3) and hydrogen peroxide (H_2O_2) resulted in decolourization of solution accompanied by a decrease in the SPR absorption band at 420 nm due to the complex formation and catalytic degradation of the sensor respectively. The results revealed precise detection of ammonia with a linear detection range of 0–1000 ppm and H_2O_2 with a linear detection range of 0–1300 μM . Further, spike/recovery measurements were done in various water samples which showed the percentage recovery values in the range of 99.10–99.87% for ammonia and 99.30–99.95% for hydrogen peroxide. Thus, the AgNps can act as a simple, cost effective and green nanosensor probe for colorimetric detection and quantitative determination of ammonia (NH_3) and hydrogen peroxide (H_2O_2) in real-time environmental analysis.

1. Introduction

Ammonia (NH_3), has extensive applications in the manufacture of fertilizers, plastics, papers, explosives, pharmaceuticals and animal feed ^{1,2}. There are various techniques such as electrochemical, pH sensors ion mobility spectrometry and near IR absorption reported for detection of ammonia in gas form ^{3,4} and optoelectronic, ratiometric fluorescence and luminescence for detection of ammonia in solution form ^{5–7}. Since, the dissolved ammonia imposes toxic effects to aquatic life and human health it is important to find efficient ways to detect its presence in solutions ⁸.

Hydrogen peroxide (H_2O_2), a strong oxidizing agent is an indispensable chemical widely used in a number of industries like food industry for sterilization ⁹ and in textile industry as bleaching agent ¹⁰. In dairy industry, H_2O_2 is used as an adulterant for the preservation of milk ¹¹. The presence of residual H_2O_2 after the above specified usage may cause severe cellular damage and serious health disorders ^{12,13}, hence the precise determination and monitoring of H_2O_2 even at low concentrations are practically important. For this, various analytical methods that include spectrometry, chromatography, voltammetry, electrochemical methods ¹⁴ are followed.

However the requirement of technical expertise, sophisticated instruments, prolonged time, toxic chemicals and high costs makes these methods undesirable for routine analysis ¹⁵. It is noteworthy that compared to several other available methods, colorimetric sensing based on the localized surface plasmon resonance is found to be user-friendly for detection of hydrogen peroxide and liquid ammonia owing to its simple, rapid and accurate analysis ¹⁶. In particular, exploration of noble metal nanoparticles for its colorimetric sensing properties have attracted much attention among researchers due to its simplicity, selectivity and sensitivity in detection. Compared with other noble nanoparticles, the localized surface plasmon resonance of silver nanoparticles makes it to be a precise colorimetric sensor probe with

interesting optical properties^{17,18}. Eco-friendly sustainable synthesis of nanoparticles using plant extracts has been the current trend as it is found to be highly simple and beneficial over other existing physical, chemical and biological methods¹⁹. *Sapindus mukorossi* belongs to the family *Sapindaceae* and are commonly acknowledged as soapnuts or soapberry²⁰. The pericarp of *Sapindus mukorossi* with potent bioactive contents was chosen for green synthesis of AgNps as they are abundantly available in India and are traditionally, being used as natural surfactants. In 2017, Dinda et al.²¹ reported the synthesis of colloidal AgNPs by using *Sapindus mukorossi* which took a significant amount of time, around 5 h, for complete reduction. In order to reduce the time taken for nanoparticle synthesis, microwave and ultrasound assistance will serve as a promising alternative²².

The present study has been carried out to evaluate the optical properties of synthesized AgNps towards colorimetric sensing of ammonia and hydrogen peroxide. This paper discusses the colorimetric detection results of AgNps synthesized in our previous works where we have incorporated the AgNps into biodegradable chitosan film²³ and eggshells²⁴ and highlighted its utilization towards microbial inhibition and degradation of several pollutants. As an extension, in this work we have successfully explored the sensing application of AgNps in real-time water samples.

2. Experimental

2.1. Materials

Analytical grade silver nitrate (AgNO₃), 25% (w/v) ammonia solution (NH₃) and 30% (w/v) Hydrogen peroxide (H₂O₂) used in this study were purchased from Sigma Aldrich, India and used without further modification. Soapberries or soapnuts (*Sapindus mukorossi*) were purchased from a local grocery store at Chennai (India).

2.2. Methods

The green preparation of silver nanoparticles using pericarps of soapnuts as reducing as well as stabilizing agent was carried out as described in our previously reported work²⁴. The prepared AgNPs were used for the colorimetric detection of NH₃ and H₂O₂ in aqueous solution. A 10⁻² M stock solution of ammonia and hydrogen peroxide were prepared using 25% (w/v) NH₃ and 30% (w/v) H₂O₂ respectively which was further diluted to various concentrations using double distilled water. About 1mL of NH₃/H₂O₂ solution of different concentrations were added separately to 2 mL of AgNps and allowed to react for 0–25 mins and 0–30 min at room temperature respectively. The visual colour change in AgNp was sensed by naked eye and subsequently the change in SPR band was recorded at 420 nm using UV-Vis spectrophotometer. Further to examine the practical applicability of the method, real-time analysis was carried out by spiking different concentrations (100, 200 and 300 µM) of NH₃/H₂O₂ with drinking water, tap water and environmental water samples like river water¹³. The water samples were filtered before H₂O₂ was spiked into it and then the solutions were analyzed as described earlier.

3. Results and Discussion

In our previous work, AgNps was synthesized by microwave irradiation within 90s using soapnut pericarp extract as stabilizing agent. The characterization of AgNps has been discussed elsewhere.²⁴ As a follow-up to our previous research work, the present study aims to explore the potential application of prepared AgNps as colorimetric sensors for recognition of NH_3 and H_2O_2 in aqueous medium.

3.1. Colorimetric detection of ammonia

The synthesized AgNps was utilized for the determination of dissolved ammonia. It is known through literatures that the decrease in the SPR band intensity of AgNps could be attributed to the formation of $[\text{Ag}(\text{NH}_3)_2^+]$ complex between ammonia and unreacted silver ions present in the solution²⁵. As shown in the Fig. 1 (a), only decrease in adsorption spectra of AgNps could be witnessed in the presence of various concentrations of NH_3 and no significant shift in peak was observed. Also, the formation of $[\text{Ag}(\text{NH}_3)_2^+]$ complex is capable of affecting the surface plasmonic band depending upon the concentration of ammonia⁸. As the concentration of ammonia increases, more number of complex will be formed which results in the decrease of AgNps that in turn reflects in the decrease in SPR band at 420 nm observed through UV-vis spectrometer. The Fig. 1 (b) shows the linear range of responses that represents the change in SPR band intensity of AgNps as a function of different concentrations of NH_3 from 0-1000 ppm.

Also, the visual detection has been illustrated through digital photograph in the Fig. 1 (c), which shows the change in colour of AgNp solution on addition of different concentration of NH_3 from brown to clear colourless solution that was detectable by naked eye. As observed in Fig. 2, the time required to detect dissolved ammonia with the help of SME@AgNps was observed as the colour vanishes with increase in time and 30 mins was fixed as the optimum time necessary for detection. Additionally, as listed in Table 1, the accuracy of SME@AgNPs was comparable with other reported literature for detection of ammonia.

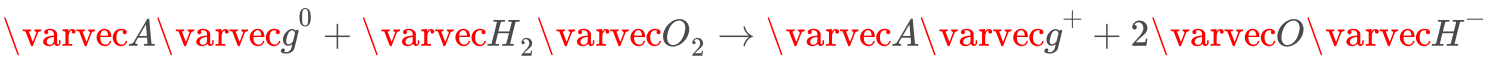
Table 1
Comparison of SME@AgNps for NH_3 detection with other reported methods

Materials	Linear range	Detection limit	Reference
Polymethacrylic acid -AgNps	1–50 ppm	1 ppm	26
D. <i>erecta</i> fruit extract@AgNps	5-100 ppm	0.5 ppm	27
SME@AgNps	100–1000 ppm	10 ppm	This work

3.2. Colorimetric detection of hydrogen peroxide

The synthesized AgNps was utilized for the determination of H_2O_2 , the simplest peroxide. At pH 7, the oxidation of AgNps by H_2O_2 occurs since the standard reduction potential of Ag^+/Ag couple (0.8 V) is

found to be lower than the H₂O₂/H₂O couple (1.77 V)²⁸. According to Mohan *et al*,²⁹ the degradation of silver nanoparticles was initiated by the formation of free radicals upon addition of H₂O₂. Similarly, in our study, the observed significant decrease in the SPR band intensity of AgNps at 420 nm indicates the conversion of Ag⁰ to Ag⁺ on the addition of H₂O₂ as the oxidizing agent as given in the Eq. (2). Subsequently, the colour change in AgNps solution was visualized by naked eye or UV-vis spectrophotometric measurements which helps in the recognition of H₂O₂.



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As shown in the Fig. 3 (a), changes in adsorption spectra of AgNps could be witnessed in the presence of various concentrations of H₂O₂. The Fig. 3 (b) shows the calibration graph drawn with respect to the SPR peak changes of AgNps as a function of different concentrations of H₂O₂ and the Fig. 3 (c) displays the photographs of quantitative sensing of H₂O₂ using AgNps that depicts the apparent changes in the colour intensity upon addition of different concentrations (0-1300 µM) of H₂O₂. It could be seen that the colour of AgNps gradually fades on increasing the concentration of H₂O₂. The detection limit for H₂O₂ by measuring the decrease in the SPR peak of AgNps was found to be 10 µM and the correlation factor R² was found to be 0.9897. Further, the time required to sense the analyte was determined and from the Fig. 4, it could be seen that the colour of AgNps faded gradually and then levels off at 25 mins which was considered as the maximum incubation time needed for the measurement of H₂O₂.

Additionally, as listed in Table 2, SME@AgNPs was compared with other reported literature. The comparison results revealed a good linear detection range and detection limit. Based on the ability of AgNps to decompose H₂O₂, it could be made use of for the colorimetric determination of H₂O₂ in environmental samples.

Table 2
Comparison of SME@AgNps for H₂O₂ detection with other reported methods

Materials	Linear range	Detection limit	Reference
Cellulose nanowhiskers-AgNps	60–600 µM	112 µM	13
Agar-stabilized AgNPs	0.05–7.5 µM	0.032 µM	30
Chitosan-AgNPs	0–1.2 mM	10 µM	14
Peach gum polysaccharide-AgNps	10 ⁻⁷ -10 ⁻¹ M	0.035 µM	31
Cubic AgNps	200–500 µM	110 µM	18
SME@AgNps	100–1300 µM	10 µM	This work

3.3. Real sample analysis

The colorimetric sensing applicability of AgNps was evaluated in real samples like tap, drinking and river water spiked with different concentrations of H_2O_2 and NH_3 (100, 200 and 300 μM). As shown in the Table 3, the percentage recovery values were in the range of 99.10–99.87% for ammonia and 99.30–99.95% for hydrogen peroxide and 99.10–99.87% for ammonia from various environmental samples. Thus, the quantitative results were found satisfactory suggesting that this method could be facile for the detection of NH_3 and H_2O_2 in practical application with excellent accuracy.

Table 3

AgNps for the detection of ammonia and hydrogen peroxide spiked in environmental water samples

Sample	Ammonia			Hydrogen peroxide		
	Added (μM)	Found ^a (μM)	Recovery ^{a,b} (%)	Added (μM)	Found ^a (μM)	Recovery ^{a,b} (%)
Tap water	100	99.3	99.30	100	99.5	99.50
	200	199.1	99.55	200	198.9	99.45
	300	299.1	99.70	300	299.4	99.80
Drinking water	100	99.4	99.40	100	99.3	99.30
	200	199.3	99.65	200	199.6	99.80
	300	299.4	99.80	300	299.2	99.73
River water	100	99.1	99.10	100	99.7	99.70
	200	199.5	99.75	200	199.9	99.95
	300	299.6	99.87	300	299.3	99.76
a = mean, b = 100 X (found/added)						

4. Conclusion

In this work, we have developed a simple and facile colorimetric method for the detection of ammonia and hydrogen peroxide in aqueous solution. The detection was based on the changes observed in the colour of AgNps solution by naked eyes as well as through decrease in the surface plasmon resonance (SPR) peak by UV-vis spectrophotometric approach. The formation of $\text{Ag}(\text{NH}_3)_2^+$ complex with ammonia and oxidation phenomenon occurring with H_2O_2 resulted in the conversion of Ag^0 to Ag^+ which was suggested as the fundamental mechanism behind the detection technique. This method was able to detect ammonia and hydrogen peroxide in the linear range of 100–1000 ppm and 100–1300 μM respectively. Moreover, the proposed sensor was validated for sensing the target analytes (NH_3 and H_2O_2) in real water samples to enable practical applications.

Declarations

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Ethical Approval

Not applicable

Competing interests

Not applicable

Authors' contributions

Study conception and design: D. Kalaivani, S.E.Noorjahan

Acquisition of data: D. Kalaivani, S.E.Noorjahan, V.Porchezhiyan, J.Shobana

Analysis and interpretation of data: D. Kalaivani, S.E.Noorjahan, V.Porchezhiyan.

Drafting of manuscript: D. Kalaivani, S.E.Noorjahan

Critical revision: D. Kalaivani, S.E.Noorjahan

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Availability of data and materials

Not applicable

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Figures

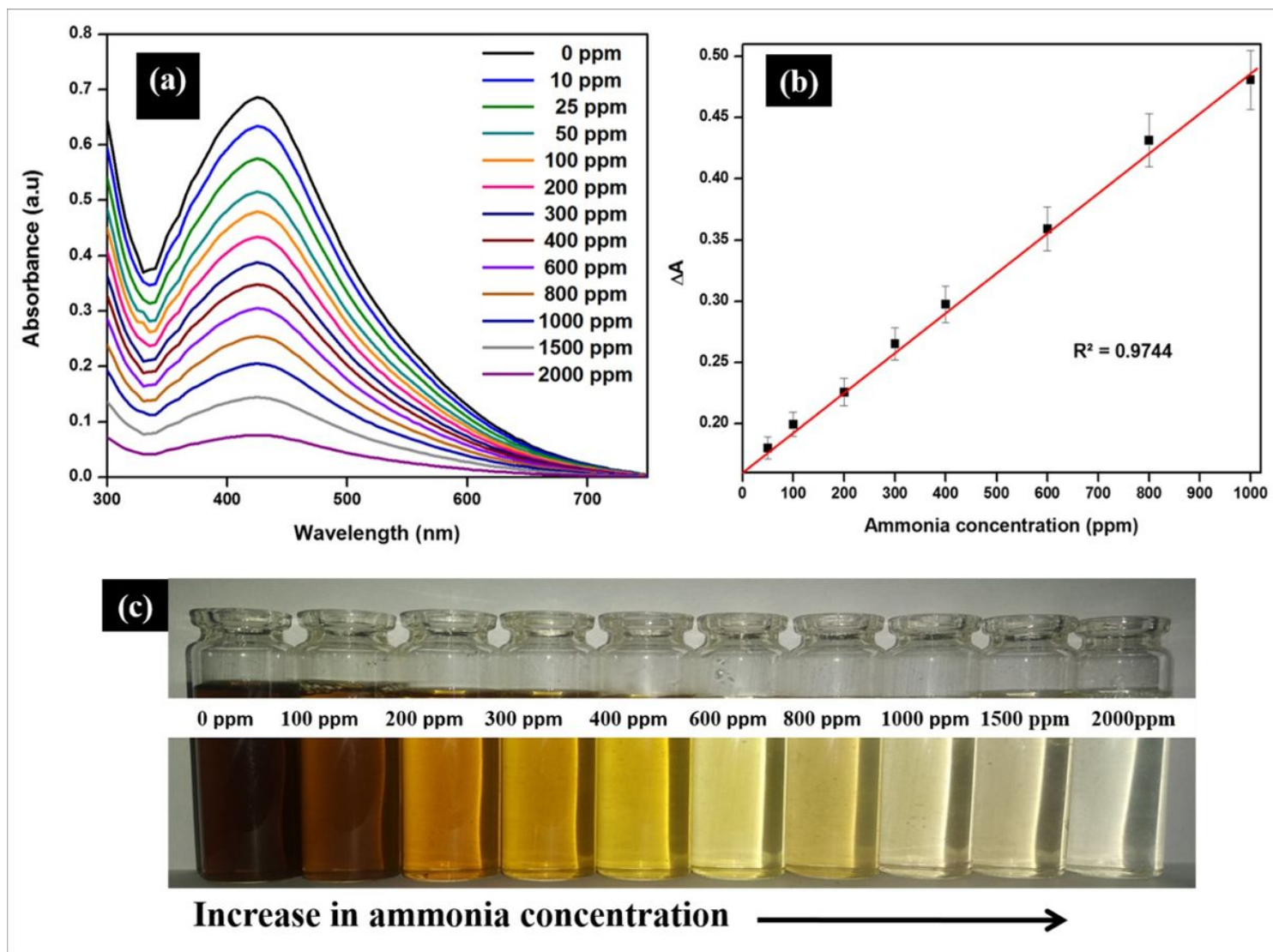


Figure 1

(a) UV-Vis absorption spectra (b) Calibration graph and (c) photographs of AgNps with different concentrations of ammonia (0-1000 ppm)

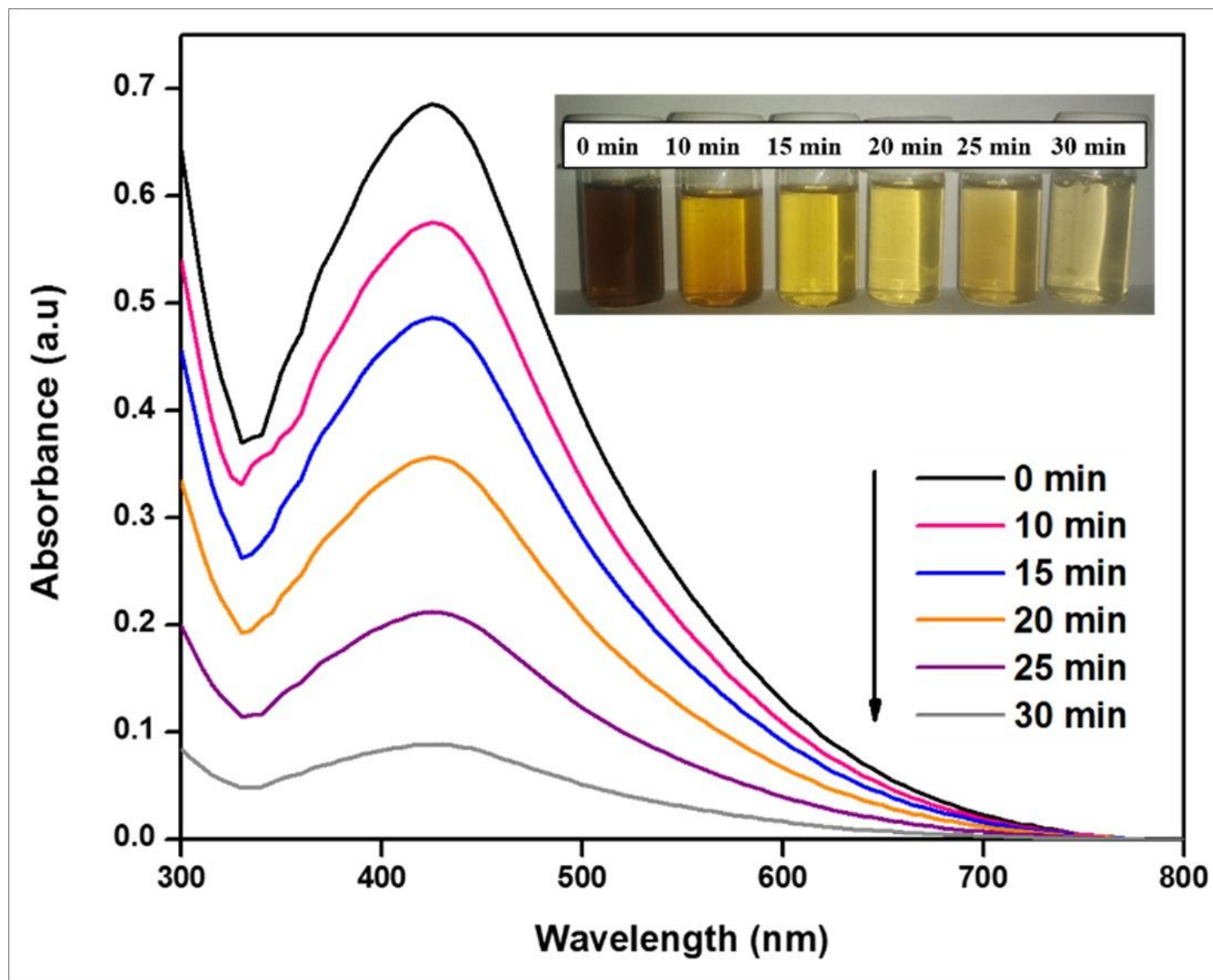


Figure 2

Effect of time in the degradation of AgNps upon ammonia addition (inset: colour degradation of AgNps)

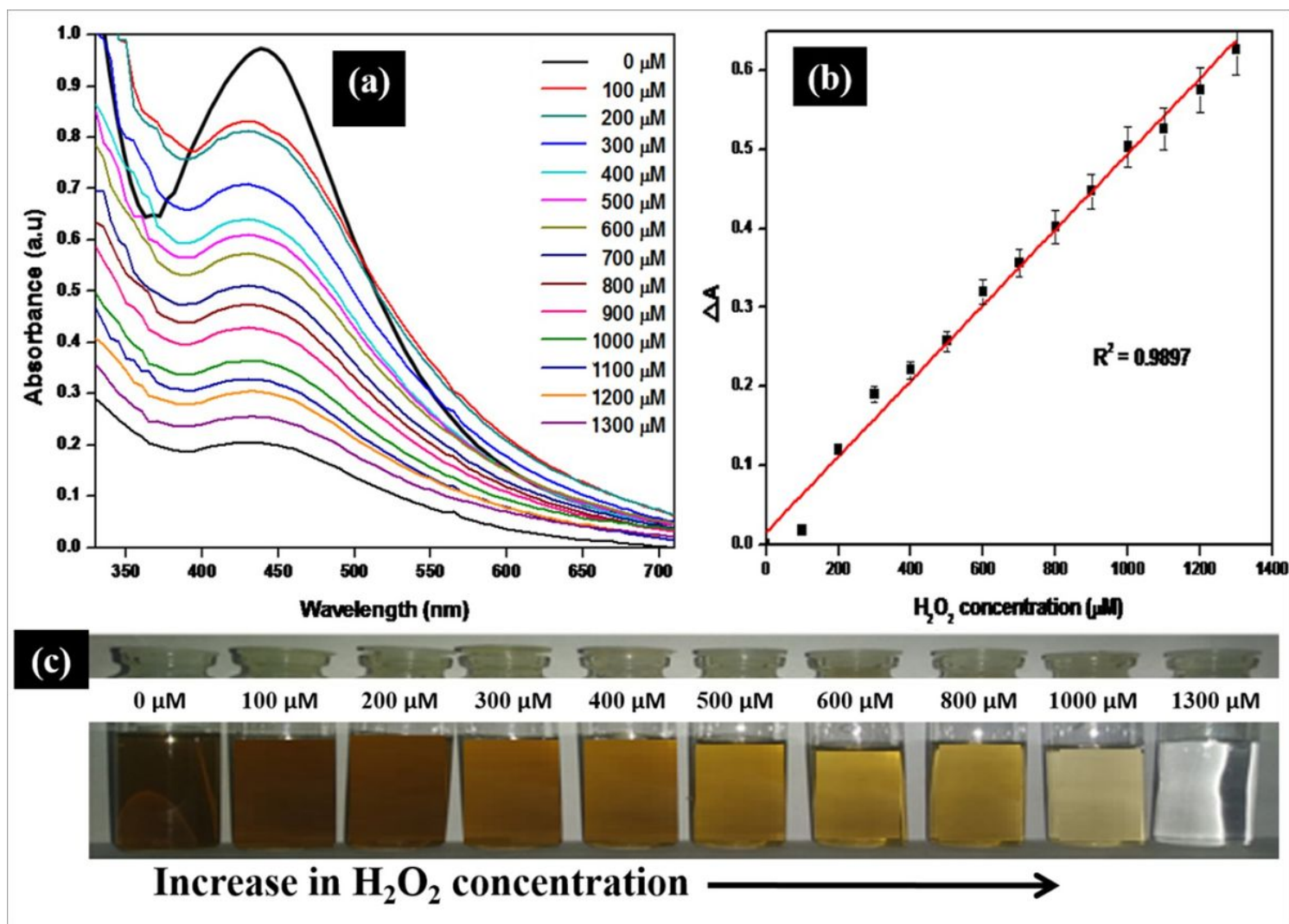


Figure 3

(a) UV-Vis absorption spectra (b) Calibration graph and (c) photographs of AgNps with different concentrations of H_2O_2 (0-1300 μM)

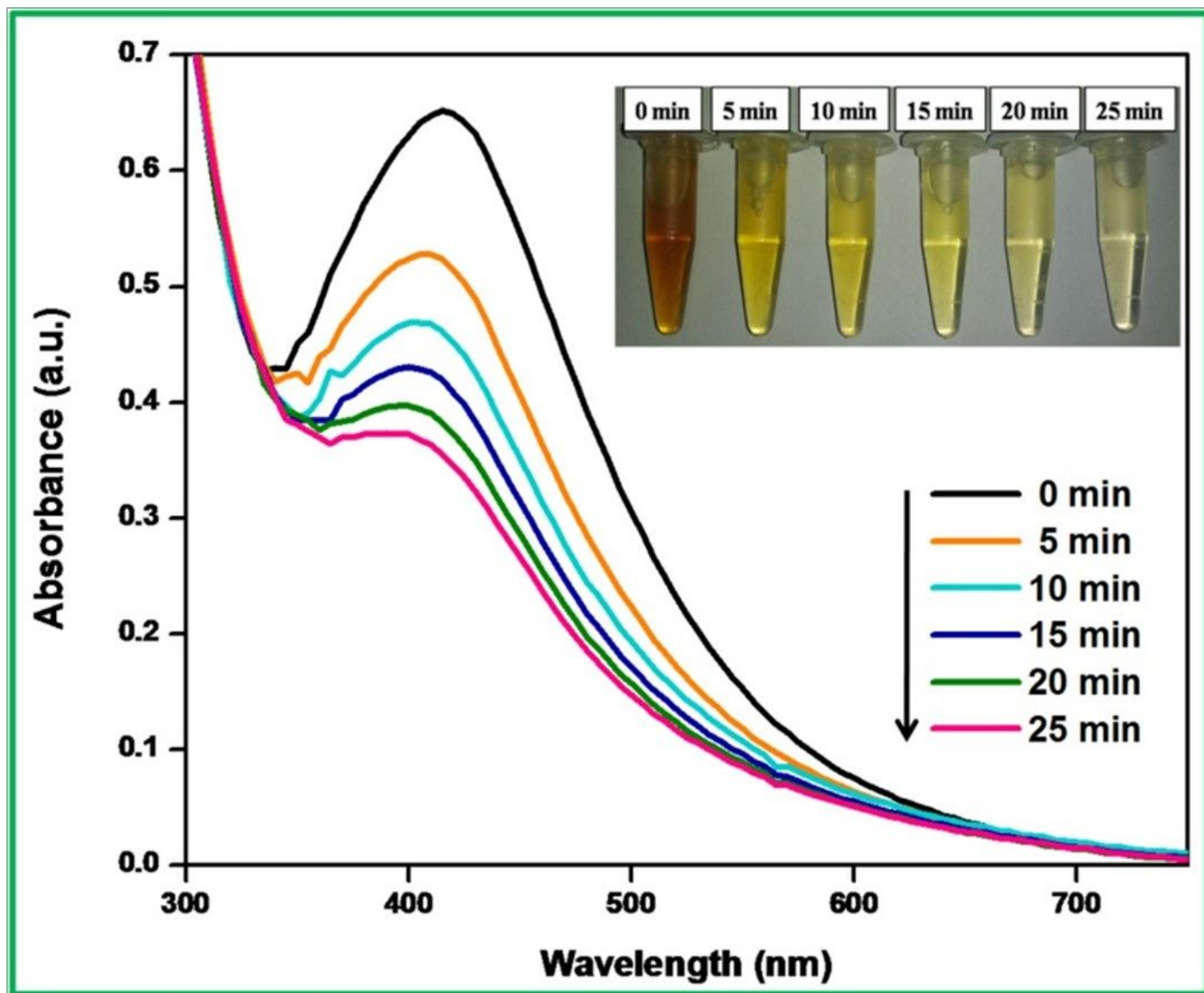


Figure 4

Effect of time in the degradation of AgNps upon H_2O_2 addition (inset: colour degradation of AgNps)

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