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Silver based nanomaterial, as a selective colorimetric sensor for visual detection of post harvest spoilage in onion

Divya Sachdev [a,*], Vinay Kumar [a], Priyanka H. Maheshwari [b], Renu Pasricha [c], Deepthi [c], Neeraj Baghel [a]

[a] Department of Agriculture and Environmental Sciences, National Institute of Food Technology Entrepreneurship and Management, Sonepat, India
[b] National Physical Laboratory, CSIR, New Delhi 110012, India
[c] National Centre for Biological Sciences, Bengaluru, India

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ABSTRACT

Onion being a semi-perishable horticultural bulb crop gets subjected to deterioration during the storage, which ultimately leads to huge monetary losses every year. Specific detection tools for onion spoilage will be an asset in relieving losses during post-harvest storage. In this context silver based yellow colored colloidal nanoparticle (AgY-NPs) solution was synthesized and evaluated as a visual sensor for the organo-sulfur compound released during the spoilage of onions. The visual changes during the spoilage was monitored for ten days wherein the yellow color of the AgY colloidal solution changed to orange, pink and finally turned transparent. Simultaneous analysis carried out by UV–Vis spectroscopy and colorimeteric analysis corroborates our investigation of AgY-NPs as a visual sensor displaying selectivity and specificity for volatile sulphur compound responsible for spoilage of onions. Furthermore, analysis of AgY-NPs in presence of healthy onions showed distinct visual results which were complemented by probable mechanism. Besides this the structural changes in AgY-NPs due to incorporation of sulphur compounds were supported by Powder X-ray diffraction (PXRD), Raman Analysis, Fourier Transform-Infrared Spectroscopy (FT-IR), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) which clearly indicated the capacity of these AgY-NPs as a powerful detection tool for onion spoilage.

1. Introduction

Onion (*Allium cepa* L.) is a widely grown crop with world production of 75 million metric ton annually (FAO 2012) [1]. Onion being a good source of minerals, vitamins, polyphenol and phytonutrients (organosulfur compounds) displays varied health benefits in preventing high blood pressures, diabetes and cancer [2]. Although onion possess a good nutritive value, but a high-quality check over its nutritive consistency relies mostly on the adequate storage conditions. Once these crops are harvested they are threatened by the post harvest diseases mostly caused by bacterial and fungal pathogens that may serve as a vehicle for disease propagation which in turn reduces their shelf life [3–6]. Microbial infection and mechanical aberration during transportation also leads to 20–30% post harvest loss [7–9]. Although many bactericides and fungicides are employed to mitigate the post harvest infection of onion, however there is a strong need to alter the prevalent methodologies that have deteriorating effects in a long run [10,11]. There is an important saying "prevention is better than cure" and therefore it is important to control the decay and infection at an early stage of storage for reducing the post harvest losses. Many physiological and biological changes accompanied during the initial infection needs to be sensed; therefore a specific, sensitive sensor is very much required that can address the above issues. So far, different methodologies for analysing the quantitative difference of the volatiles between healthy and infected onions were analysed by Gas Chromatography/Mass Spectoscopy [12], and compared to this an alternative approach such as gas sensor arrays or E-nose technology [13–15] have been developed. Although the uniqueness of the E-nose technology depends on the presence of the type of material used (metal oxide, conducting polymers) to predict the changes in the voltage signals via the volatiles released, however the complex calculations and preparation of customized gas chambers may have operational problems which may result in erroneous output. Hence, the need of an hour is to develop a simplified, cost-effective compact way to detect and sense the onset of infection in onions (even when the deterioration symptoms are not visible). In this regard, we synthesized yellow colored stabilized silver nanoparticles (AgY-

* Corresponding author.
E-mail address: divya19sachdev@gmail.com (D. Sachdev).

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NPs) that behaved as a visual sensor for onion spoilage and to best of our knowledge this is the first report that visually distinguished (supported by UV–Vis spectroscopy and colorimeter) healthy and the infected onions.

Recent studies have shown large contribution of nanoscience technology in the field of agriculture and food sciences [16–18]. The current genesis of the detection/sensing lies in the change of optical behaviour of novel silver nano-colloid due to the incorporation of volatile sulphur. During spoilage, the unstable organosulfur compounds, present in the onion gets ruptured and further rearranges to form a stable complex with AgY-NPs which ultimately leads to color changes. Moreover, the tendency of silver nanoparticles displaying credibility in terms of protection against microbes [19] will surely make them a better tool in food safety. And therefore our study has a commercial scope in detection and distinguishing post harvest spoilage of onions from healthy ones without any interference from moisture, atmospheric oxygen or carbon dioxide.

2. Experimental

2.1. Synthesis of stable silver nanoparticles (AgY-NPs)

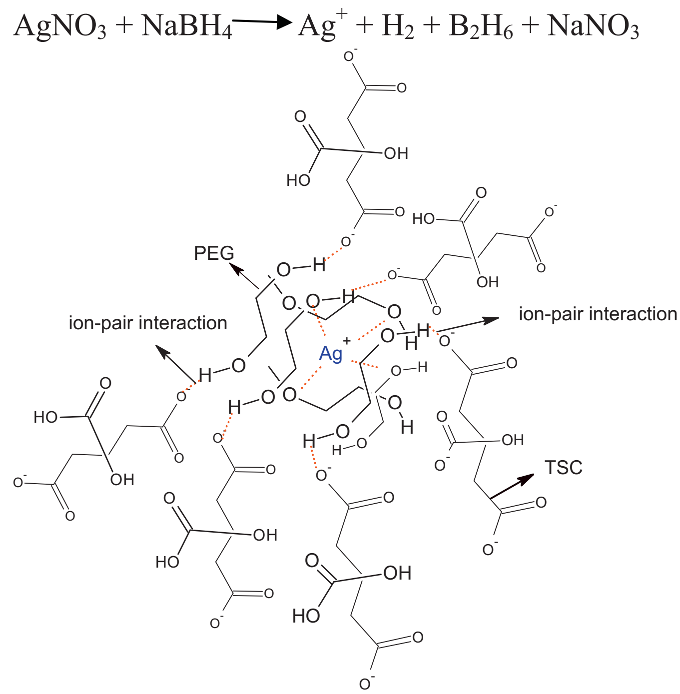
All the reagents used were of analytical grade. Synthesis of yellow colored stable silver nanoparticles were obtained by reduction of Ag^+ ions using $NaBH_4$ as a reducing agent in a combined matrix of polyethylene glycol (PEG) and trisodium citrate (TSC) [21] acting as a stabilizing and capping agent respectively. All the solutions employed during the synthesis were freshly prepared. In a typical synthesis, $AgNO_3$ (10 ml, 30 mM) was mixed to a solution containing PEG (5 ml, 5 mM) and TSC (5 ml, 30 mM) in a round bottom flask that was previously stirred for half an hour at room temperature. To this suspension, freshly prepared cold solution of $NaBH_4$ (5 ml, 26 mM) was added drop wise, the solution initially turned to faint yellow and gradually the yellow color deepened. The yellow colored colloidal NPs solution of silver nanoparticles was named as AgY-NPs and was stored in a dark colored closed container for further use. AgY-NPs colloidal solution was characterized via PXRD, UV–Vis spectroscopy and SEM analysis.

2.2. Monitoring the onion spoilage using AgY-NPs as a visual sensor

In the present study the onion spoilage was monitored by detecting the release of volatile metabolites evolved during the spoilage via the stable yellow colored silver colloidal solution. Two months stored variety of Pusa nasik after curing were purchased from local storage house. Set of onions at an initial stage of spoilage were carefully chosen and were placed in a sealed desiccator fitted with a tube containing AgY-NPs solution, to act as a visual sensor (as a gas analysing set up) during spoilage. The whole assembly was placed at a fixed place and ambient conditions were maintained for the period of investigation. The changed color of AgY-NPs during spoilage was examined through UV–Vis spectrophotometer and colorimetric response. Furthermore the changes in the AgY-NPs solution were evaluated via PXRD, FT-IR spectroscopy, Raman and TEM and finally mechanism of color change was also suggested.

2.3. Characterization

Photographs were acquired by Samsung digital camera. UV–vis spectra were measured using Schimadzu-2600 spectrophotometer. CHNS analysis for determining sulfur content in healthy onion was done on EuroVector model no. Euro3000 instruments. Inductively Coupled Plasma Spectroscopy for finding the amount of volatile sulfur in nanoparticle solution was done on PerkinElmer model Optima 7000DV. The X-ray diffraction examination of the samples was performed on Rikagu Powder X-ray diffractometer (PXRD) model: XRG 2KW using Cu Kα radiation. Raman spectroscopy was carried out using a Renishaw InVia Reflex Micro Raman Spectrometer equipped with the CCD detector at room temperature and in air. Argon ion laser (excitation line 514 nm) was used to excite the samples. One scan per sample was recorded wherein the sample was exposed to the laser power of 25 mW for 30 s. Infrared sepectroscopy (ATR-IR) spectra of the samples was recorded on Bruker–Alpha for evaluating the differences in functional groups on AgY-NPs solution via infected and the healthy onions. Morphology of the sample was analysed by Scanning Electron Microscopy (SEM), Zeiss. Colorimeter of the samples was conducted on Chromameter CR-400 (Konica Minolta). Particle size was analysed on Tecnai G2 Spirit Bio-TWIN Transmission Electron Microscope



Scheme 1. Schematic Illustration of stable silver nanoparticle; formed by interactions of PEG and TSC.

3. Results and discussions

3.1. Structural analysis of AgY-NPs

Synthesis of silver nanoparticle was done in the presence of two stabilizing agents polyethylene glycol (PEG) and tri-sodium citrate [21]; sodium borohydride was used as a reducing agent [21,22]. The addition of two stabilizers inhibits the aggregation of reduced silver nanoparticles for many days while keeping them dispersed in the solution. Moreover the methodology employed induced uniformity in the shape and size while forming an ultrafine silver nanoparticle. This may be due to the ion-pair interactions present between the polyethylene glycol and sodium citrate ion which forms a protective shell around the silver ions during the reduction and stabilize them in solution for months as shown in Scheme 1.

UV–Vis spectroscopy is the most prominent technique used for the structural characterization of Ag-NPs. The absorption spectra of initially made stable yellow colored AgY-NPs colloidal solution shows the Surface Plasmon Resonance SPR at 404 nm [21] (Fig. 1(A)) which slightly shifted to 425 nm on diluting with water [23], this may be due to the presence of the water (Scheme 1) ligands near