Electronic Supplementary Material (ESI) for Analytical Methods.

Supporting Information

Colorimetric Determination of Hydrogen Peroxide by Morphological Decomposition of Ag Nanoprisms Coupled With Chromaticity Analysis

Kritchapon Nitinaivinij,[a] Tewarak Parnklang,[a] Chuchaat Thammacharoen,[a]

Sanong Ekgasit [a] and Kanet Wongravee [†a]

[a]*Sensor Research Unit (SRU), Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok, Thailand 10330, Fax :+66 2218 7585; Tel : +66 2218 7589*

[†]Corresponding author (*Email : kanet.w@chula.ac.th*)

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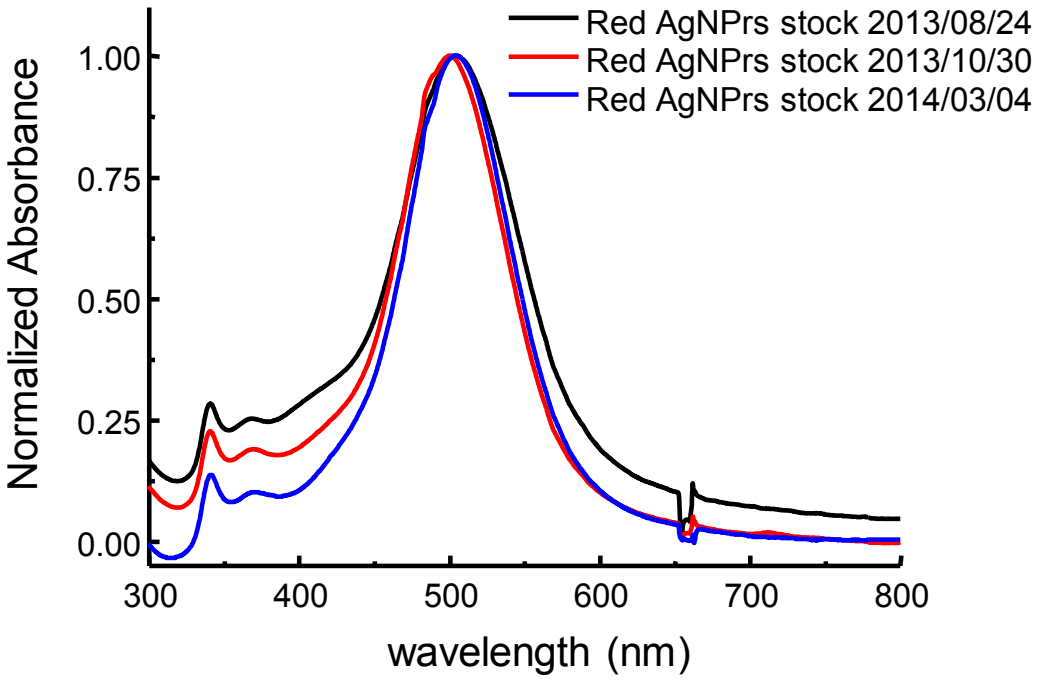


Figure S1. Normalized UV-visible spectra of red-AgNPrs for three repetitions.

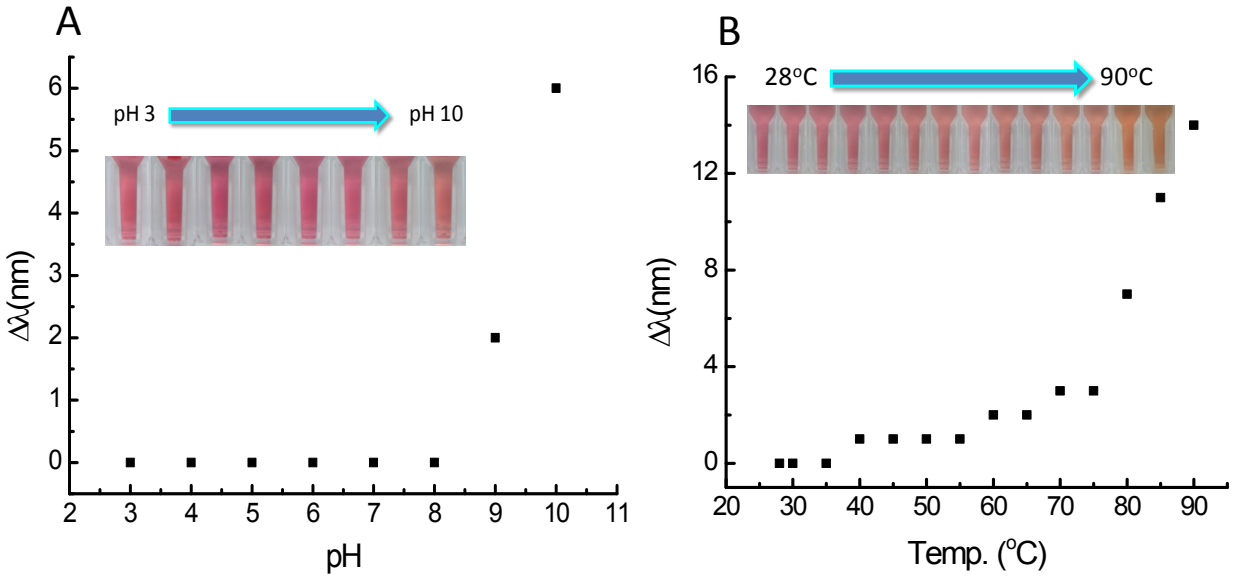


Figure S2. The influences of (A) pH and (B) temperature on the AgNPrs with the insets of AgNPr solution color at various pH and temperatures.

The effect of pH and temperature on the synthesized of AgNPrs was monitored by using UV-visible spectroscopy. A pH of AgNPr solution was adjusted to pH 3-10 using either 20% acetic acid or 10% NH_4OH. A temperature of AgNPr solution was adjusted in the range of 28°C – 90°C using water bath. The $\Delta\lambda$ of AgNPrs and corresponding solution color at various pH and temperature are depicted in Figure 1A and 1B, respectively. The results reveal that no significant changes in LSPR of AgNPrs ($\Delta\lambda = 0$) in the range of pH 3-8. In addition, no considerable changes in LSPR of AgNPrs is observed in the temperature range of 28-40°C. The $\Delta\lambda$ increase and the color of the AgNPr solution became pale orange only when pH > 9 or temperature > 45 ºC.

To gain an insight into understanding the decomposition profile and the evaluation of the optical characteristics of the AgNPr solution as a LSPR-based hydrogen peroxide sensor, 100 μM of H_2O_2 was introduced to 10 ppm of AgNPr solution in a quartz cuvette. The time-resolved LSPR band of AgNPrs incubated with the imposed H_2O_2 from 0 to 15 min was monitored by UV-visible spectroscopy (Figure S1). The in-plane dipole LSPR of AgNPrs (λ_{max} = 502 nm) gradually blue-shifted after the addition of H_2O_2, while the out-of-plane quadrupole LSPR (λ_{max} = 340 nm) remained unchanged. These results indicate that the lateral size of AgNPr decreased, while the aspect ratio of the morphology remained the same, i.e. the thickness of AgNPr constantly decreased along with the lateral size.

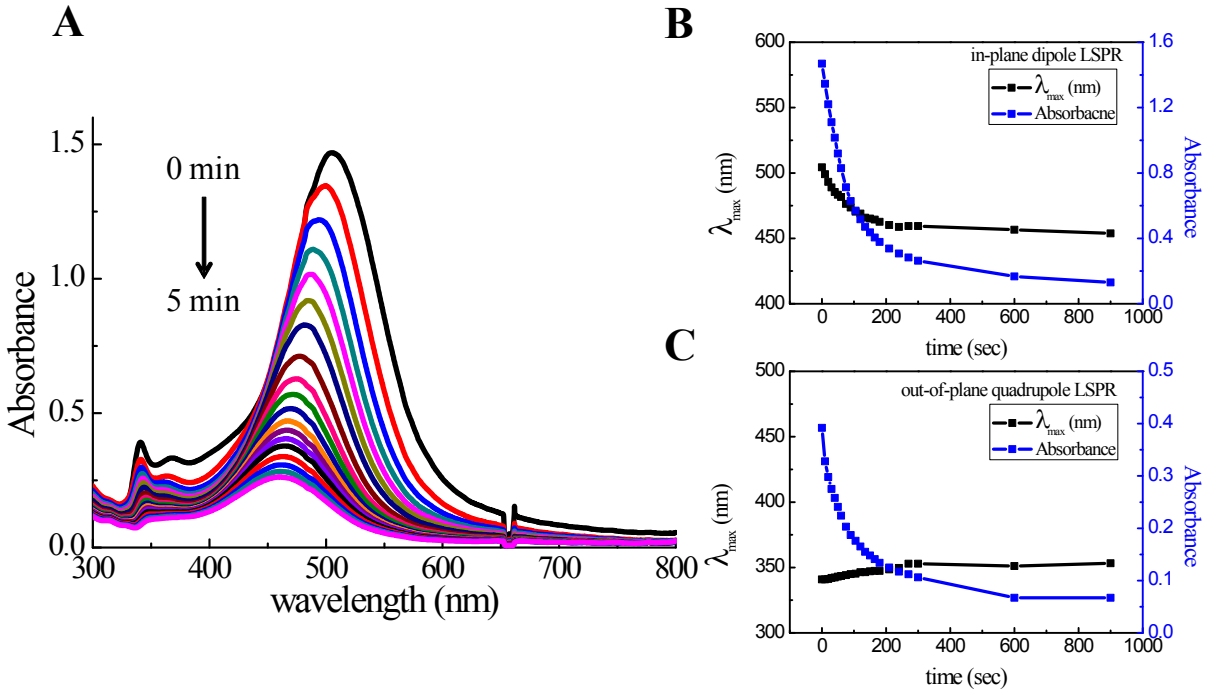


Figure S3. (A) Time-resolved LSPR spectra of AgNPrs after addition of 100 μM H_2O_2 from 0 to 15 min of incubation time. (B) Variations of absorbance and peak position of the in-plane dipole LSPR with incubation time. (C) Variations of absorbance and peak position of the out-of-plane quadrupole LSPR with incubation time.

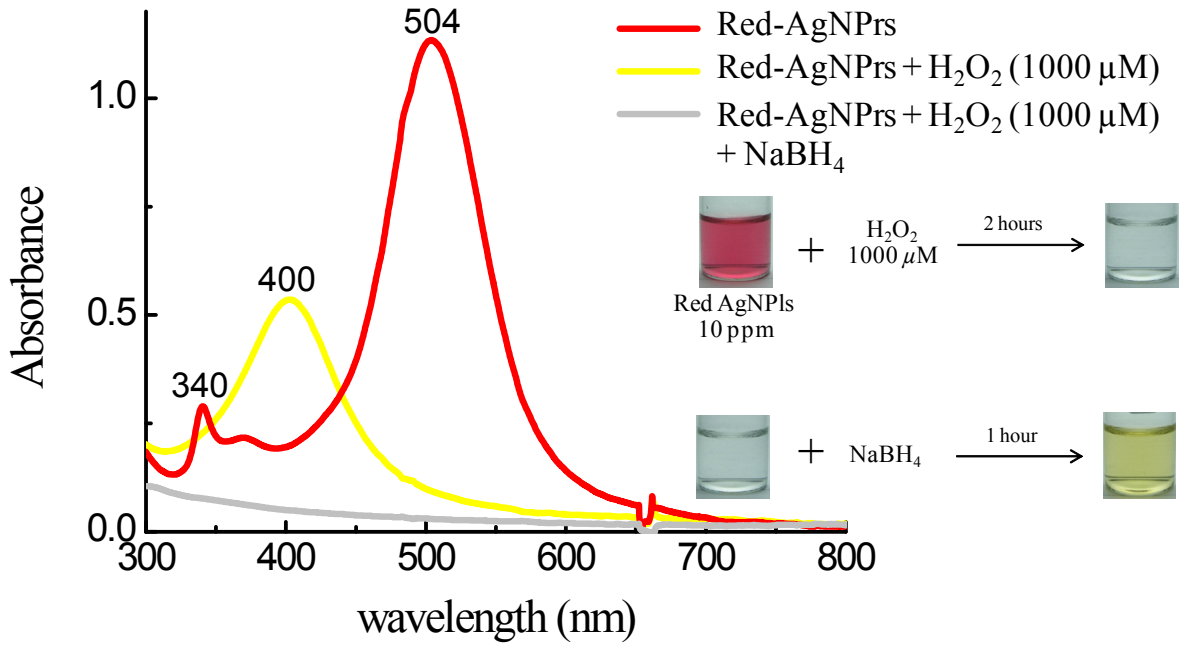


Figure S4. Extinction spectra of the original red-AgNPrs, red-AgNPrs interacting with hydrogen peroxide, and the solution after the conversion of silver ions to silver nanospheres by the addition of a reducing agent ($NaBH_4$).

The original AgNPr solution employed in the study exhibited the red-wine color with an in-plane dipole LSPR peak centered at 504 nm. The complete degradation of AgNPrs was observed when a high concentration of H_2O_2 (1000 μM) was introduced. From inset of Figure S3, it can be seen that the solution color changed from red to colorless. This observation confirms the etching phenomenon on AgNPrs after interacting with H_2O_2 as expressed by the following chemical equations [1-5]:

$Ag^+ + e^- \rightarrow Ag$ $\quad E^0 = 0.7996$ V

$H_2O_2 + 2e^- \rightarrow 2HO^-$ $\quad E^0 = 0.8670$ V

$2Ag + H_2O_2 \rightarrow 2Ag^+ + 2HO^-$ $\quad E^0 = 0.0680$ V

The formation of silver ions as the reaction products from the decomposition of AgNPrs by H_2O_2 was verified by the addition of a strong reducing agent ($NaBH_4$) into the degraded AgNPr solution. The result in Figure S3 shows that a new plasmon absorption peak at 400 nm emerges in the extinction spectrum, in correspondence with the change of the solution color from colorless to yellow after the addition of sodium borohydride. The plasmon absorption peak at 400 nm is a characteristic plasmon band of silver nanospheres. The silver nanospheres are formed by the following chemical reaction:

$$Ag^{+} + BH_4^{-} \rightarrow Ag^{0} + \tfrac{1}{2}H_2 + \tfrac{1}{2}B_2H_6$$

Therefore, it can be confirmed that the etching reaction of H_2O_2 on AgNPrs induces the degradation of silver atoms on AgNPrs to silver ions, and leads to the morphological transformation of AgNPrs.

References for Figure S4

1. C. M. Ho, S. King-Woon Yau, C. N. Lok, M. H. So and C. M. Che, *Chem-Asian J.*, **2010**, *5*, 285–293.

2. J. Weiss, *Trans. Faraday Soc.*, **1935**, *31*, 1547–1557.

3. F. T. Maggs and D. Sutton, *Trans. Faraday Soc.*, **1958**, *54*, 1861–1870.

4. F. T. Maggs and D. Sutton, *Trans. Faraday Soc.*, **1959**, *55*, 974–980.

5. Q. Zhang, C. M. Cobley, J. Zeng, L. P. Wen, J. Chen and Y. Xia, *J. Phys. Chem. C*, **2010**, *114*, 6396–6400.

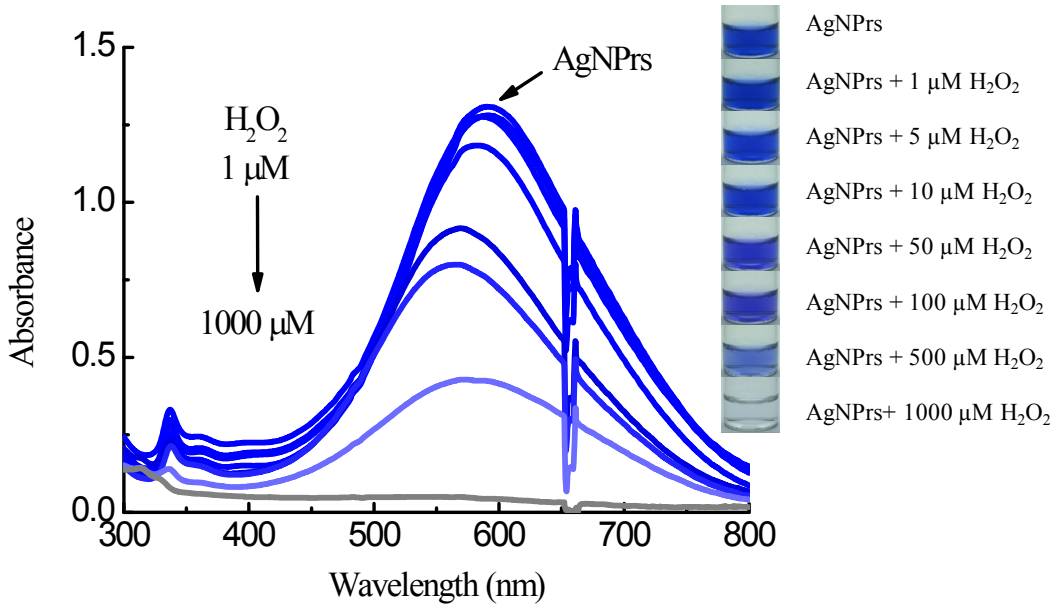
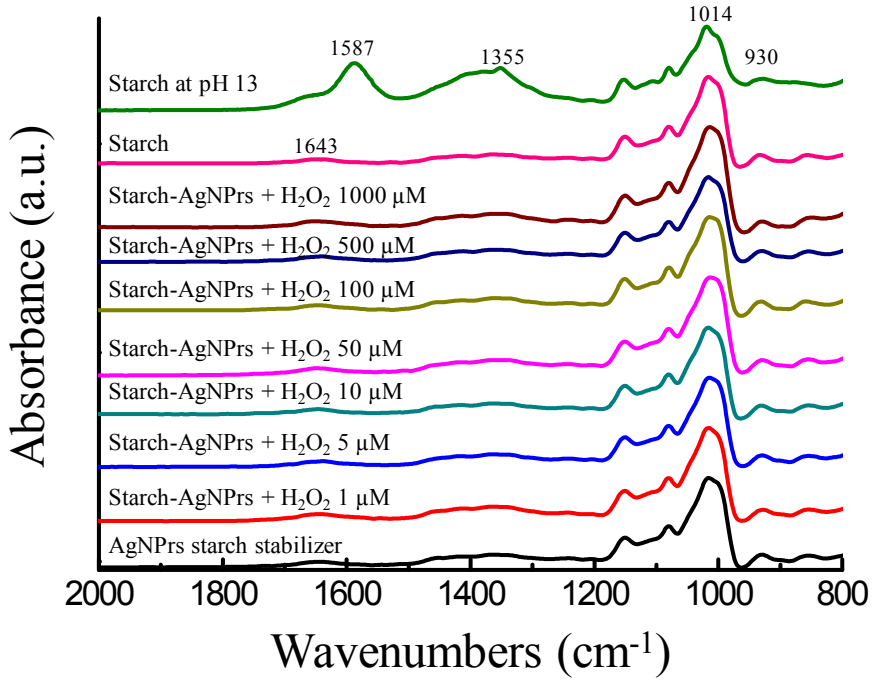


Figure S5. Extinction spectra of blue-AgNPrs when exposed to H_2O_2 at various concentrations ranging from 1 to 1,000 µM, with the corresponding inset photographs showing the color of the colloidal AgNPr solution after incubation with H_2O_2 for 60 min.



Infrared band (cm^{-1})	Infrared band assignment
860	CH_2 deformation
930	Skeleton mode vibration of α-1,4 glycosidic linkage (C-O-C)
1200-900	Bridge β C^1-O-C^4
1500-1300	Vibration band related to the carbon and hydrogen atoms
1610-1500/1420-1300	COO^- stretching vibration (carboxylic acid salt)
1642	Water adsorbed in the amorphous region of starch
1765	C=O stretching vibration of carboxylic acid

Figure S6. Normalized ATR FT-IR spectra of virgin starch, starch on AgNPrs, and starch on AgNPrs after incubation with H_2O_2 at various concentrations ranging from 1 to 1000 µM for 60 min. The infrared band assignment table is also included.

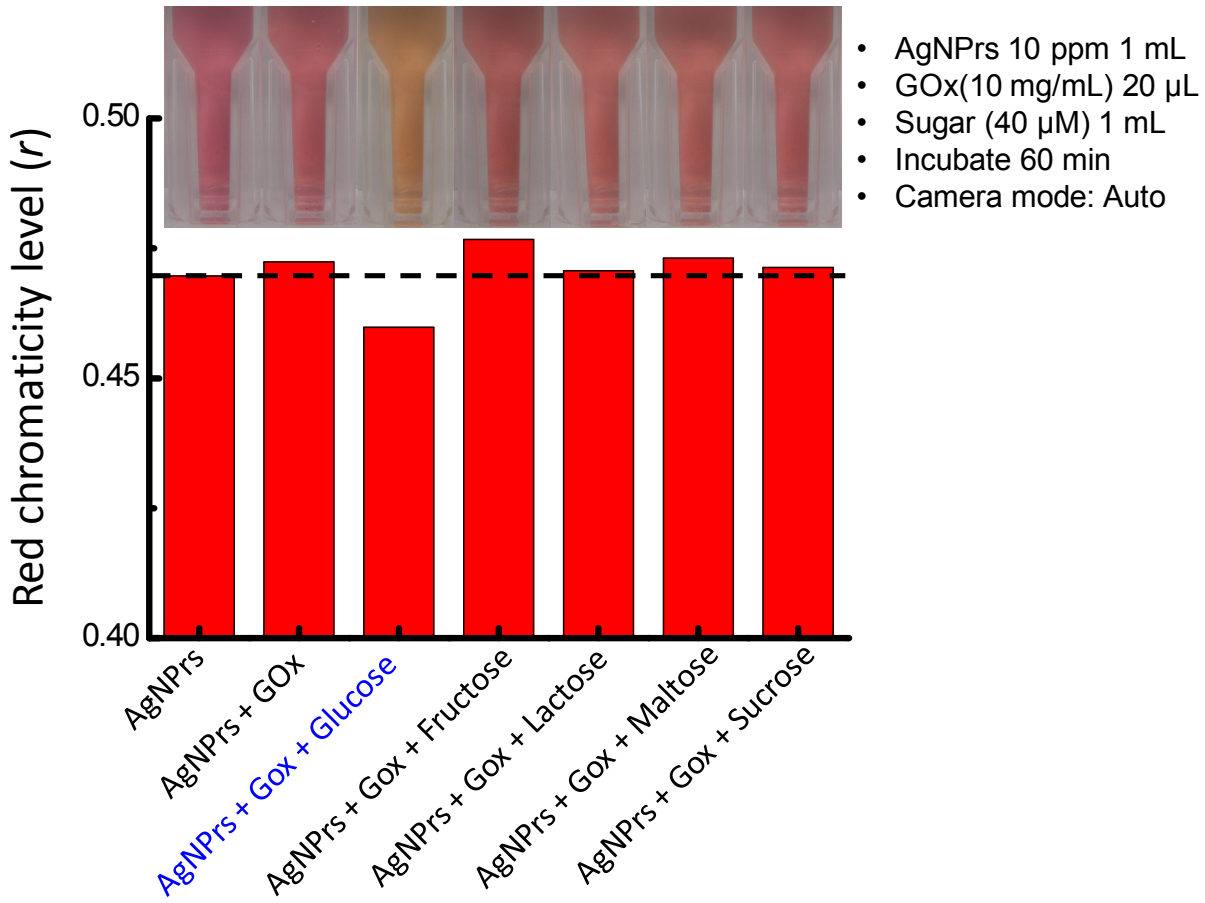


Figure S7. Red chromaticity level of the AgNPrs with glucose oxidase enzyme (GOx) after incubating with glucose and various potential sugar species. Inset photo shows the corresponding digital images of the AgNPrs solutions.