Chronochromic smart tag to replace expiry date in packed perishable food items

C. Srinivasan and R. Saraswathi

We live in a world where colour is an inevitable part of our life. While certain colour or combination of some colours brings joy and peace, some colours convey important signals to the observer. For example, in the traffic signals that we see daily red signifies stop, green go and amber to be cautious to the observer[1]. Chronochromism means the change of colour with time for a process[2]. One well-known chemical example for chronochromism is the reaction between dilute aqueous solutions of sodium thiosulphate and silver nitrate. During the addition of silver nitrate the colourless solution of thiosulphate initially gives a white precipitate and then the colour changes to yellow, brown and finally to black – one will observe a 'play of colours' and this experiment would have been carried out in an elementary course in chemistry by many.

When we purchase milk, other dairy products, perishable materials and medicine, we immediately look at the expiry date which is printed at one corner in small fonts outside the container to know whether the product is in a good or bad condition. The life of the product in the container has been estimated on the basis of several assumptions including that the perishable item (particularly for food) is kept at 4°C. But in practice when the product is sent from the production centre to the retailer, it is exposed to different temperatures. Therefore the expiry date given in the container may not always be correct. It will be convenient and desirable for a customer to know the state of the perishable product without opening the container using an indicator affixed on the container that changes colour according to the status of the milk or other perishable product. Though some electronic indicators have been developed taking into account the perishability of the product with change of temperature, they are expensive[3]. There are other proposed chemical indicators based on physico-chemical reactions, but they are not programmable for the change of temperature as the electronics one[4–6].

Due to plasmon resonance the colour of bimetallic nanocrystals depends on their size and shape. Zhang *et al.*[7] suggest that the growth of bimetallic nanocrystals may be used as an indicator to keep track of the status of the perishable products. For the growth they added to an aqueous solution of cetyltrimethylammonium chloride, silver nitrate solution, ascorbic acid solution (AA) and Au nanorod solution yielding a colloidal dispersion. In the course of time AA reduced silver nitrate and Ag was epitaxially deposited on Au nanorods. Transmission electron microscopy images of the Au and Au/Ag nanorods are shown in Figure 1 *a* and *b* respectively. Initially the solution was red due to Au nanorods, but the colour gradually changed from red to orange, yellow, greenish-yellow, and further to green (Figure 1 *d*) due to the deposition of Ag nanoparticles on Au nanorods. Au nanorods exhibit two plasmon bands at 510 and 880 nm. During the deposition of Ag on Au nanorods the 880 nm band is shifted to the blue region and that is the cause for the observed chromic effect. It is important to note that this behaviour of the above solution can be retained when the above mentioned colloidal solution is solidified as agar hydrogels. The hydrogels can be used as indicator by affixing a small amount of this gel on the container of milk or other perishable material. Figure 2 shows the chronochromism of the hydrogel cubes. The gel has red colour, but changes colour over time as its ingredients react with each other. However, it must be mentioned here that the duration of colour change can be controlled at a constant temperature with change of concentration of various ingredients in the colloidal solution and pH.

Perishable products like milk and other dairy foodstuffs are easily spoiled by bacterial growth. The growth of *Escherichia coli* in milk is largely responsible for the deterioration of its quality. Temperature has a marked influence on

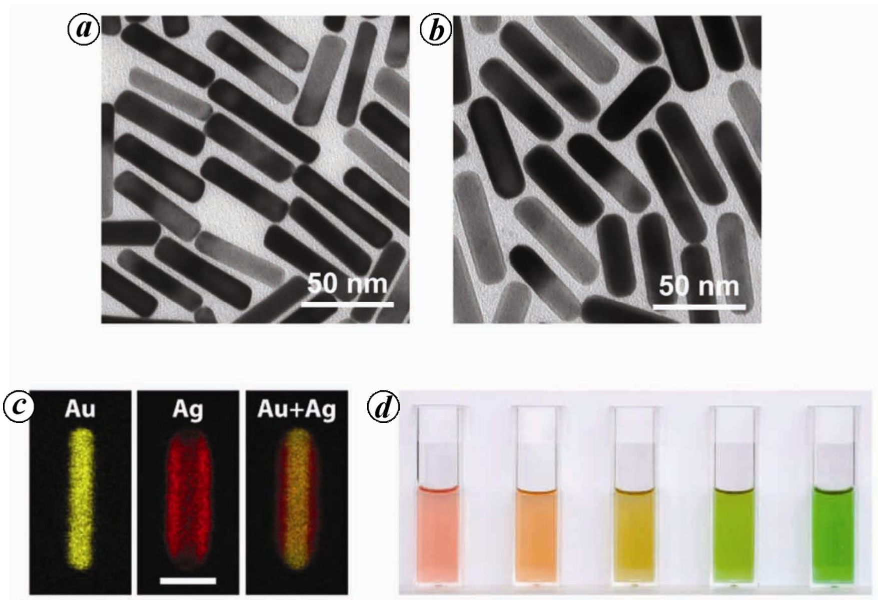

Figure 1. Chronochromic evolution from Au nanorods to Au/Ag nanorods. ***a***, ***b***, Transmission electron microscopy images of the Au and Au/Ag nanorods, respectively. ***c***, Energy-dispersive X-ray elemental mapping images for a typical Au/Ag nanorod. The scale bar represents 20 nm. ***d***, Photograph showing the colour change of the self-evolving colloidal solution during the reaction process (from left to right). The temporal intervals between the neighbouring samples are dependent on temperature and other parameters. Reprinted with ACS permission from Zhang *et al.*[7]. Copyright (2014) from the American Chemical Society.

the rate of growth of *E. coli* and the growth rate is enhanced with temperature. If bimetallic nanorods are to be used as indicators to know the status of the quality of the packed product, it is necessary that the red to green chronochromic rate should be the same as the growth rate of *E. coli* at a given temperature. Zhang *et al.*[7] achieved synchronization of rate of the self-evolution of different colours of the indicator and the rate of growth process of *E. coli* at a given temperature by manipulating the concentrations of various ingredients.

Another major issue is the synchronization of the chronochromic rate with the growth rate of *E. coli* at different temperatures because the perishable material packed in a carton is exposed to different temperatures during the transport from the place of production to the end user. Zhang *et al.*[7] accomplished this by the addition of acetic acid (HAc) to the colloidal solution during the preparation of the indicator and found an effective way for tuning the kinetics. These authors realized that the kinetics of colour change can be controlled by varying the concentrations of AA and HAc and by trial and error approach an optimized recipe has been obtained. Thus Zhang *et al.* magnificently synchronized, at multiple temperatures, the chemical evolution process displaying different colours in the smart tag with microbial growth processes in the milk. A red colour exhibited by the indicator tag in the carton of the milk indicates that the milk is fresh and fit for consumption. If the indicator tag turns green, it conveys that the bacteria have grown enough for the milk to be discarded.

Figure 2. Photograph of the hydrogel cubes (~$5 \times 5 \times 3$ mm^3) arranged in a manner resembling a clock in a petri dish, illustrating the red-to-green chronochromic performance. Reprinted with ACS permission from Zhang *et al.*[7]. Copyright (2014) from the American Chemical Society.

There are several advantages in using this smart tag. One need not open the milk carton to discern the quality of the milk. As the noble metals (Au and Ag) dosage is of the order of 10 μg ml^{-1} and the other chemicals used are cheap, the cost of the indicator is unbelievably low. A single hydrogel cube, shown in Figure 2, with a volume of ~70 μl is estimated to cost roughly US$ 0.002. Apart from the low cost, the materials used in the indicator are nontoxic and eco-friendly. Another notable feature of the proposed indicator is its compliance of the ASSURED (Affordable, Sensitive, Specific, User-friendly, Robust and rapid, Equipment-free, and Deliverable to end-users)[8] criteria proposed by WHO.

1. Bamfield, P. and Hutchings, M. G., *Chromic Phenomena: Technological Applications of Colour Chemistry*, RSC Publishing, Cambridge, 2010, 2nd edn, pp. 114–116.
2. Christie, R. M., *Colour Chemistry*, RSC Publishing, Cambridge, 2001.
3. Tao, H. *et al.*, *Adv. Mater.*, 2012, **24**, 1067–1072.
4. Robertson, G. L., *Food Packaging: Principles and Practice*, CRC Press, Boca Raton, FL, 2013, 3rd edn, pp. 415–418.
5. Tijskens, L. M. M., Hertog, M. L. A. T. M. and Nicolaï, B. M., *Food Process Modelling*, CRC Press–Woodhead Publishing, Cambridge, 2001, pp. 402–431.
6. Zeng, J., Robers, S. and Xia, Y. N., *Chem. Eur. J.*, 2010, **16**, 12559–12563.
7. Zhang, C. *et al.*, *ACS Nano*, 2013, **7**, 4561–4568.
8. Peeling, P. W., Holmes, K. K., Mabey, D. and Ronold, A., *Sex. Transm. Infect.*, 2006, **82**, v1–v6.

C. Srinivasan lives at 2/249 (Old No. 2/172), 7th Street, Kalvinagar, Rajambadi, Madurai 625 021, India; R. Saraswathi is in the Department of Materials Science, Madurai Kamaraj University, Madurai 625 021, India.*
**e-mail: ceesri@yahoo.com*