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"Less Blue, More Clean": Cu_2O nano-cubic functionalized hydrogel for the energy transformation of light-emitting screens†

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Cubic Cu_2O nanoparticle modified hydrogel (CMHG) was synthesized to address two major problems (harmful irradiation and high density pathogens) of the current light-emitting screens simultaneously. The as-prepared hydrogel could conveniently form an adjustable semitransparent film over various shaped screens to provide enhanced antibacterial activity and longer Cu_2O service life. More importantly, with the aid of cubic Cu_2O nanoparticles, the energy of the harmful blue light irradiation could be effectively transformed into a photocatalysed power source to sterilize the surface of the screen. This low toxic CMHG showed no significant influence on the touch control experience, and had obvious eye protective effects, which thus offered a convenient manner to protect vision and sterilize touch screens at the same time.

Introduction

As the core components of mobile phones, tablet computers and automobile navigation, various light emitting screens have been intensively used in our daily life.[1,2] Despite considerable progress being made, two common and serious problems still threaten the safety use of these devices. One is the formation of pathogenic biofilm on the surfaces of these frequently touched screens.[3–5] The other is the harmful irradiation, especially blue color ranged light (between 400 nm to 500 nm), which had been demonstrated to cause some skin diseases and eye diseases.[6–9]

Aiming at above problems, a low toxic antibacterial material coupled with blue light attenuation property urgently needs to be developed for screens. Although numerous antibacterial agents have been developed, such as Ag_2S/Ag heterodimers,[10,11] silver nanoparticles (NPs),[12–14] copper NPs.[15–17] Although these NPs had been used in the fields of drug delivery, antibacterium and photocatalysis.[18–21] Unfortunately, very few research explored their applications in the area of touch screen. However, these Cu_2O powders were difficult to cover the surface of the screen directly. Besides, exposed Cu_2O powders were also easy to be oxidated, which has greatly limited their practical applications.[22,23]

Results and discussion

In order to solve this problem, pure Cu_2O nano-cubic was first synthesized through a facile hydrothermal process. The obtained Cu_2O NPs were then coated by specialized hydrogel (HG) which was formed of hyaluronic acid (HA) crosslinked polyvinyl alcohol (PVA). The as-prepared hydrogel was a viscous and transparent materials, it was thus suitable as the coating membrane of various shaped screen. Meanwhile, hydrogel also prevented Cu_2O NPs from being oxidized (ESI Fig. S1†). On the other hand, with the aid of Cu_2O NPs, most of the harmful blue light irradiation could be absorbed and transform to the photocatalysed power source to sterilize the surface of screen. One feature should be mentioned was that, after drying, CMHG did not affect the touch control experience of the screen (an interesting movie was provided in the ESI Movie S1†).

As schematic illustration in Fig. 1, CMHG was composed of PVA, HA and polymer-functionalized cubic Cu_2O NPs (Fig. 1a). The PVA served as cross-link agent in the three-dimensional network.[24–26] HA was a natural moisturizing factor, which modulated the time of drying.[27,28] And, as the core material, polymer-functionalized cubic Cu_2O NPs provided dual harmful blue light attenuation and antimicrobial functions (Fig. 1b). The image of HG film and similar sized CMHG film were provided in ESI Fig. S2a and b† respectively. The relative SEM observation indicated some cubic sized Cu_2O NPs were dispersed in the film (Fig. S2c and d†). Since Cu_2O NPs wrapped in HG was not clear to be observed, the insert image in Fig. S2d† offered a view of naked Cu_2O NPs. The average diameter of these uniform cubic Cu_2O NPs was around 500 nm. Apart from Energy Dispersive Spectrometer (EDS) characterization (Fig. S2e and

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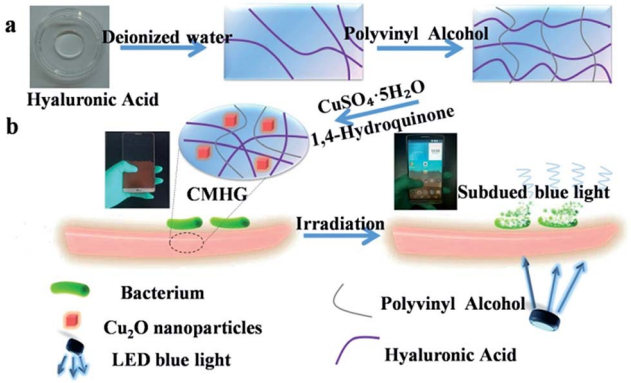

Fig. 1 The preparation of CMHG film (a) to sterilize the surface of screen under blue light irradiation (b).

f†), XRD (X-ray diffraction) was also used in this study. Fig. S2g† reported a series of XRD patterns for HG and polymer-functionalized cubic Cu_2O NPs in two different concentrations (12.5 mg ml^{-1}, 25 mg ml^{-1}), respectively. The diffraction peaks of the CMHG film samples agreed well with the cubic Cu_2O (JCPDS card no. 34-1354). The mechanical property of this CMHG was also evaluated (ESI Fig. S3†).

To test the antibacterial property of HG film and CMHG film, *Escherichia coli* (Gram-negative) and *Staphylococcus aureus* (Gram-positive) were chosen as the model bacteria and evaluated by Spread Plate Method.[29,30] For *E. coli* (Fig. 2a), the HG film owned a good bacteriostatic rate, reached to 91.15%. When under the irradiation of blue light, the bacteriostatic rate had no apparent different. As a comparison, the CMHG film expressed a better bacteriostatic rates (92.88%). More importantly, once blue light was used to "activate" CMHG film, bacteriostatic rate

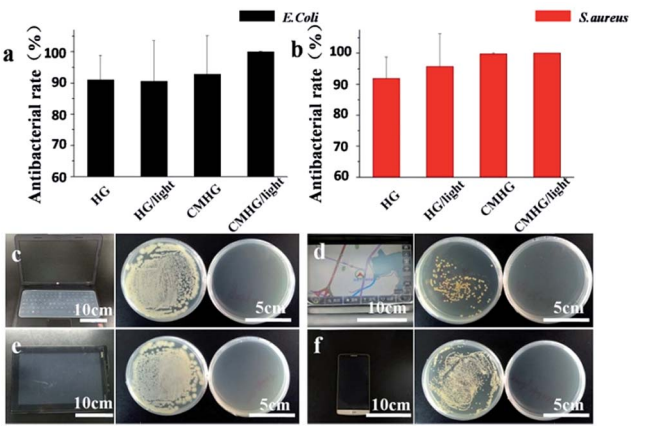

Fig. 2 The antibacterial experiments of HG film and CMHG film for *Escherichia coli* (a) and *Staphylococcus aureus* (b) with or without blue light irradiation. Four touch screen were chosen, and antibacterial experiments of the screens were carried show that which sterilize by CMHG under irradiation of blue light; antibacterial experiments of different CMHG coated screens under blue light irradiation (left plates: control groups; right plates: experiment groups), including computer (c), automobile navigation (d), tablet computer (e) and mobile phone (f).

reached to 100% ($n = 3$) (ESI Fig. S4†). For *S. aureus* (Fig. 2b), bacteriostatic rate of CMHG film could reach 99.75%. Under blue light, the antibacterial rate also improved to 100%. In totally, CMHG film cooperated with blue light irradiation had the best antibacterial ability. An unexpected discovery was that, pure HG film also showed certain antibacterial effects. We concluded that HG film induced an anaerobic condition which could suppress the growth of *Escherichia coli* and *Staphylococcus aureus*. Moreover, the subsequent tearing of HG film also provided a strong physical cleaning of the bacteria.

The screens of four different electronic products were then selected for further practical applications, including notebook computer (Fig. 2c), automobile navigation (Fig. 2d), tablet computer (Fig. 2e) and mobile phone (Fig. 2f). Through colony counting method, the left plate represented the original bacterial number on each screen surface. The right plate exhibited the bacterial number after sterilized by CMHG, which was activated by the emitting of blue light from the screen itself. After 1 hour usage, the obtained results showed that CMHG film had a remarkable antibacterial ability for all the tested light emitting screens.

The capability of CMHG film on blue light attenuation was subsequently investigated. For the convenience of calculation, blue light wavelength was defined ranging from 400 nm to 500 nm and visible light wavelength was defined ranging from 400 nm to 700 nm. Through the UV-Vis spectrometer, pure HG film absorbed about 10% in full spectrum of visible light, with no apparent difference between 400 nm and 700 nm wavelength (Fig. 3a), and the inset of Fig. 3a also reported this phenomenon. In the case of CMHG film, the strong absorption of blue

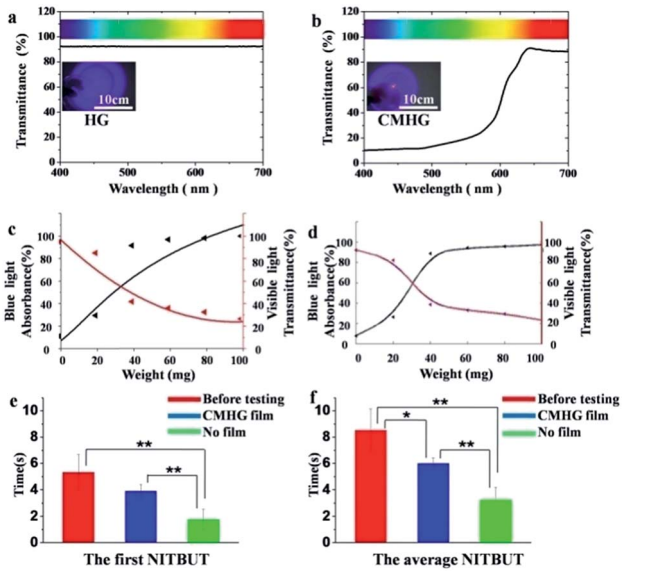

Fig. 3 The transmittance of blue light for HG film (a) and CMHG film (b). The inset of color tape represents a complete visible wavelengths. CMHG film with various concentrations of polymer-functionalized cubic Cu_2O NPs (0 mg, 20 mg, 40 mg, 60 mg, 80 mg, 100 mg in 2 ml HG); the black point was fitted by S-curve equation and the red point was fitted by quadration equation (c) and Savitzky–Golay was used for smooth curve (d). First NITBUT (e). Average NITBUT (f) ($n = 3$, $^*p < 0.05$; $^{**}p < 0.01$).

light was appeared in 400–500 nm wavelength (Fig. 3b) and the inset of Fig. 3b also approved they had significant color shift between inside and outside of circle. Therefore, CMHG film had a strong absorbing of blue light, filtered around 90% of the blue light irradiation.

With the increasing of polymer-functionalized cubic Cu_2O NPs, the blue light absorbance would be enhanced, but the visible light transmittance would be decreased also. In order to understand polymer-functionalized cubic Cu_2O NPs based relationship between blue light absorbance and visible light transmittance, we had tested six kinds of CMHG, photos of CMHG film with different concentration of polymer-functionalized cubic Cu_2O NPs (0 mg, 20 mg, 40 mg, 60 mg, 80 mg, 100 mg in 2 ml HG) (ESI Fig. S5†) the obtained the average results were summarized in ESI Table S1.† Next the average value of blue light absorbance and visible light transmittance were plotted in the graph to get twelve points, so two series of fitting curves (eqn (1) and (2)) were generated. Then, the black point was fitted by S-curve equation and the red point was fitted by quadration equation (Fig. 3c), details was shown in ESI Table S2.†

What's more, Savitzky–Golay was also used for calculated for smooth curve, by using MATLAB (Fig. 3d). Collectively, blue light absorbance was rising with the adding of polymer-functionalized cubic Cu_2O NPs. On the contrary, visible light transmittance was decreasing with the adding of Cu_2O NPs. Based on the results from the algorithms, CMHG could reach a good balance between blue light absorption and visible light transmitting, when the content of polymer-functionalized cubic Cu_2O NPs was ranging from 20 mg to 40 mg.

$$f(x) = \exp\left(5.241 - \frac{3.241}{x}\right) \quad (1)$$

$$f(x) = 3.205x^2 - 36.958x + 130.471 \quad (2)$$

Some interesting practical applications of CMHG on fashion electronics were also tested in this study. It has been demonstrated that retinal pigment was sensitive to blue light and caused some eye disease.[31] Xerophthalmia was a common eye disease in clinic. It is proper way to evaluated the degree of xerophthalmia by testing the first NITBUT (noninvasive tear break-up time) and the average NITBUT.[32] So xerophthalmia patients watched CMHG coated VR (virtual reality) film for 3 h movie. Regular VR film without CMHG modification was used as a control.

An obvious decreasing on NITBUT was discovered after watching movies for 3 hours without CMHG ($p < 0.01$), which meant a 3 h-watching can cause a significant damage to eyes. After coated with CMHG, this damage could be minimized effectively ($p > 0.05$). The subsequent NITBUT results further demonstrated that CMHG could protect eyes from blue light irradiation (Fig. 3f). According to the features of CMHG, it offered a convenient manner to protect vision and sterilize the surface of various formed electronics.

To evaluate toxicity of CMHG, two methods were adopted seperately. HG, CMHG (15.0 mg ml^{-1}), Cu_2O NPs (15.0 mg ml^{-1}), ZnO NPs (15.0 mg ml^{-1}) and CMHG NPs (7.5 mg ml^{-1}), four kinds of materials had been used in the cytotoxicity experiment (Fig. 4a). HG showed a lowest cytotoxicity and Cu_2O NPs could damage almost cells in a certain concentration. Once Cu_2O NPs was coated with HG, there were nearly a half cells surviving.

For further research, CMHG (15.0 mg ml^{-1}) was also evaluated by using a mouse skin model. In this study, the mouse back skin was shaved and then washed by PBS buffer before the experiments. One group of mouse was only treated with PBS buffer, which served as the blank control (Fig. 4b). Then HG and CMHG were applied onto the skins of the other two groups separately. After a 3 day treatment, mouse skin treated with CMHG maintained its normal structure without any indications of toxicity such as erythema or edema (Fig. 4e–g).

Following the skin morphology examination, some skin biopsy were collected at the end of the treatment and further investigated by hematoxylin and eosin (H&E).[33] The HG and CMHG treated skin maintained an undisturbed structure with a clear layer of healthy epidermal cells on top of the dermis layer, which was identical to the PBS treated skin sample (Fig. 4h–j). The absence of any skin reaction and toxicity within a 3 day treatment suggested that topically applying CMHG was safe to the skin. However, long-term toxicity test is still recommended, before CMHG based products becomes available to the general public.

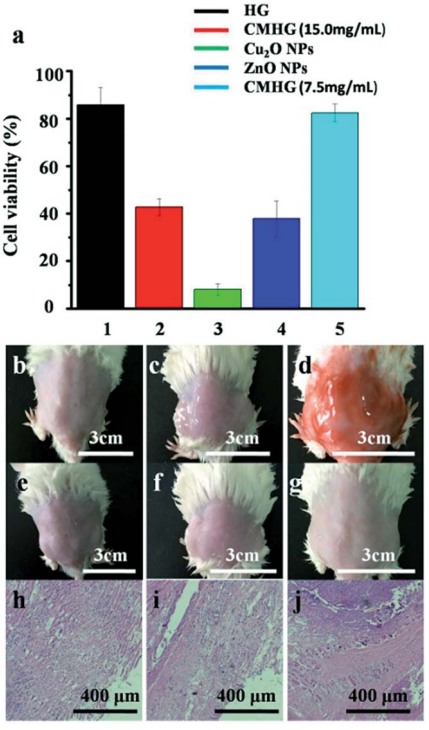

Fig. 4 Cytotoxicity test for HG, CMHG (15.0 mg ml^{-1}), ZnO NPs (15.0 mg ml^{-1}) and CMHG (7.5 mg ml^{-1}) on 293T cells (a). The shaved of mouse skin treated with PBS buffer (b), HG (c), CMHG (d). After a 3 days treatment, appearance on mouse skin (e–g), and H&E stained imaging of the skin sections (h–j).

Conclusions

Along with the development of high-tech and the arrival of the electronic age, various light emitting touch screens had been intensively used in our daily life. In this study, we developed a CMHG for the current touch screen age. That contains Cu_2O NPs for topical antibacterium and eye-protection. By which means, harmful blue light irradiation could be absorbed and transformed to the photocatalysed power source to sterilize the surface of screen. Comparing with the pure Cu_2O NPs, the living time and safety of Cu_2O was further improved in the form of CMHG. Taken together, CMHG provides a simple and high efficient hybrid formulation for eye-protection and topical sterilization. However, some copper(II) penetrated from CMHG may threaten our health. The ongoing research interests will focus on the systematical optimization of CMHG, including a series of long-term toxicology tests.

Experimental section

Ethical statement

15 Kunming mice (18–22 g) were purchased from Animal Center of Nanchang University (Nanchang, China). The animals were maintained in a room temperature (20–22 °C) and 40–50% humidity. Mice were provided with water and a 12 h light/dark cycle. All animal procedures were performed according to protocols approved by the Institutional Animal Care and Use Committee at Institute of Translational Medicine, Nanchang University (no. 2016NC-020-02) and animal handling followed the dictates of the National Animal Welfare Law of China. All the procedures performed involving human participants were in accordance with the ethical standards of the Affiliated Eye Hospital of Nanchang University. The research has been approved by the Bioethics Committee of Translational Medicine of Nanchang University (permission no. YK/92/2016). Informed consent was obtained from all the participants before the study began. No personal patient data were analysed or included in this work.

Synthesis of CMHG

To synthesize the Cu_2O NPs, 5.000 g $CuSO_4 \cdot 5H_2O$ and 2.923 g EDTA were dissolved in 30 ml deionized water and stirred for 30 min at 55 °C. Then, the solution was reduced by 250 ml NaOH solution (0.6 M) and 5.0 g 1,4-hydroquinone (1,4-$C_6H_4(OH)_2$), stirring occasionally until the solution fell to room temperature. Following the reaction, the solution was repeatedly washed with deionized water and anhydrous alcohol to remove impurities and then centrifuged at 10 000 rpm for 8 min. Finally, the precipitates were obtained and dried in vacuum oven under 50 °C. The cubic Cu_2O nanoparticles with a mean diameter of 500 nm.

A given weight (2.0 g) of PVA was dissolved in a amount of distilled water (4 ml). Then the solution was heated to 90 °C regulated with an oil bath. The solution was added to 6 ml HA (10%) one time to crosslink HA. Subsequently, Cu_2O NPs were functionalized with the crosslinked blend by using the crosslinked blend to embed Cu_2O NPs (30.0 mg ml^{-1}). The polymer was selected to modify Cu_2O NPs in order to enable the electrostatic interaction of Cu_2O NPs with the slightly negatively charged (zeta potential, ζ: −7.9 mV). The solution was purified by precipitating into pured water and centrifuged at 6000 rpm for 30 min, the supernatant was removed and washed by pured water three times to remove the excess polymer.

Characterization of CMHG

The crystalline phases of the samples were characterized by the X-ray diffractometer (XD-3, Beijing) with Cu Kα radiation; the morphologies of the as-prepared Cu_2O NPs were investigated by field-emission scanning electron microscopy (JSM-6701F, Japan); CMHG film was tested by UV-Vis spectrometer (UV-2550, Shimadzu).

Preparation for HG film and CMHG film

HG film were prepared using heat-drying process. Briefly, 2.0 g PVA was diluted by 8 ml deionized water at room temperature and stirred for 6 h. Then 2 ml HG was added into completely. Finally, HG film were obtained by vacuum drying under 60 °C. A certain amount of polymer-functionalized cubic Cu_2O NPs was added into HG. After being stirred for 30 min, CMHG film was obtained by vacuum drying under 60 °C.

Conflicts of interest

The authors declare no competing financial interest.

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Notes and references

1 C. P. Gerba, A. L. Wuollet, P. Raisanen and G. U. Lopez, *Am. J. Infect. Control*, 2016, **44**, 358–360.
2 Y. S. Kim, Light emitting device and system providing white light with various color temperatures, *US Pat.*, 8297783, 2012.

3 Y. J. Zhang, S. Li, R. Y. Gan, T. Zhou, D. P. Xu and H. B. Li, *Int. J. Mol. Sci.*, 2015, **16**, 7493–7519.
4 H. Wu, M. Claus, H. Z. Wang, H. Niels and Z. J. Song, *Int. J. Oral Sci.*, 2015, **7**, 1.
5 l. F. C. De, F. Reffuveille, L. Fernández and R. E. Hancock, *Curr. Opin. Microbiol.*, 2013, **16**, 580–589.
6 D. Bléger and S. Hecht, *Angew. Chem., Int. Ed.*, 2015, **54**, 11338–11349.
7 H. P. Iseli, N. Körber, A. Karl, C. Koch, C. Schuldt, A. Penk, Q. Liu, D. Huster, J. Käs and A. Reichenbach, *Exp. Eye Res.*, 2015, **139**, 37–47.
8 R. Zhou, D. Li, B. Qu, X. Sun, B. Zhang and X. C. Zeng, *ACS Appl. Mater. Interfaces*, 2017, **8**, 27403–27410.
9 J. Krutmann, A. Bouloc, G. Sore, B. A. Bernard and T. Passeron, *J. Dermatol. Sci.*, 2016, **85**, 152–161.
10 M. Pang, J. Hu and H. C. Zeng, *J. Am. Chem. Soc.*, 2010, **132**, 10771–10785.
11 B. G. Kumar, B. Srinivas, M. D. Prasad and K. Muralidharan, *J. Nanopart. Res.*, 2015, **17**, 1–11.
12 N. Chaubey, A. Sahoo, A. Chattopadhyay and S. Ghosh, *Biomater. Sci.*, 2014, **2**, 1080–1089.
13 S. Chernousova and M. Epple, *Angew. Chem., Int. Ed.*, 2013, **52**, 1636–1653.
14 Z. Xiu, Q. Zhang, H. L. Puppala, V. L. Colvin and P. J. J. Alvarez, *Nano Lett.*, 2012, **12**, 4271–4275.
15 H. Pang, F. Gao and Q. Lu, *Chem. Commun.*, 2009, **9**, 1076–1078.
16 X. Wang, D. Liu, J. Li, J. Zhen and H. Zhang, *NPG Asia Mater.*, 2015, **7**, 7–19.
17 G. Ren, D. Hu, E. W. C. Cheng, M. A. Vargas-Reus, P. Reip and R. P. Allaker, *Int. J. Antimicrob. Agents*, 2009, **33**, 587–590.
18 J. Chen, Z. Guo, H. B. Wang, M. Gong, X. K. Kong, P. Xia and Q. W. Chen, *Biomaterials*, 2013, **34**, 571–581.
19 Z. Zheng, B. Huang, Z. Wang, M. Guo, X. Qin, X. Zhang, P. Wang and Y. Dai, *J. Phys. Chem. C*, 2009, **113**, 462–470.
20 B. L. Ouay and F. Stellacci, *Nano Today*, 2015, **10**, 339–354.
21 C. Ramesh, M. Hariprasad and V. Ragunathan, *Curr. Nanosci.*, 2011, **7**, 770–775.
22 Y. H. Tsai, K. Chanda, Y. T. Chu, C. Y. Chiu and M. H. Huang, *Nanoscale*, 2014, **6**, 8704.
23 M. D. Susman, Y. Feldman, A. Vaskevich and I. Rubinstein, *ACS Nano*, 2014, **8**, 162–174.
24 J. H. Kim, B. R. Min, K. B. Lee, J. Won and Y. S. Kang, *Chem. Commun.*, 2002, **22**, 2732–2733.
25 J. Tang, L. Bao, X. Li, L. Chen and F. F. Hong, *J. Mater. Chem. B*, 2015, **3**, 8537–8547.
26 C. Boyer, M. R. Whittaker, V. Bulmus, J. Liu and T. P. Davis, *NPG Asia Mater.*, 2010, **2**, 23–30.
27 H. S. Jung, W. H. Kong, D. K. Sung, M. Y. Lee, S. E. Beack, d. H. Keum, K. S. Kim, S. H. Yun and S. K. Hahn, *ACS Nano*, 2014, **8**, 260–268.
28 J. C. Angello and S. D. Hauschka, *Dev. Biol.*, 2016, **73**, 322–337.
29 O. Karabay, E. Koçoglu and M. Tahtaci, *J. Infect. Dev. Countries*, 2007, **1**, 72–73.
30 L. A. Savas and M. Hancer, *Appl. Clay Sci.*, 2015, **108**, 40–44.
31 S. E. Yanni, J. Wang, C. S. Cheng, K. I. Locke, Y. Wen, D. G. Birch and E. E. Birch, *Am. J. Ophthalmol.*, 2013, **155**, 354.
32 J. Wang, J. R. Palakuru and J. V. Aquavella, *Am. J. Ophthalmol.*, 2008, **145**, 795.
33 W. Gao, V. Drew, J. Li, J. Zhu, Q. Zhang, V. Fu, J. Li, T. Soracha, D. Lu and L. Zhang, *ACS Nano*, 2014, **8**, 2900–2907.