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ORIGINAL PAPER

Dense immobilization of gold nanoparticles onto a cotton textile for obtaining plasmonic heating

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Abstract

Cotton textiles with plasmonic functions were obtained by dense immobilization of gold nanoparticles (AuNPs) performed by reduction of tetrachoroaurate (III) ion electrostatically adsorbed on the cotton fibers. Polyethyleneimine (PEI) adsorbed on the cotton fibers supports dense adsorption of tetrachloroaurate (III) ions, and the subsequent reduction with trisodium citrate provides dense AuNPs. The resulting cotton textile immobilized with AuNPs performed heating by irradiation of continuous visible light based on a plasmonic photothermal effect.

Introduction

Local surface plasmon resonance (LSPR) occurs by coupling of incident light and collective oscillation of free electrons of metal nanostructures. The plasmonic photothermal effect brings about the wavelength-selective interaction between the metal nanostructures and the nearby substances [1, 2]. Dynamics of vapor and gas-bubble growth in water by plasmonic heating [3], control of thermoresponsible polymer [4], and nanofabrication for glass [5] have been reported as attractive interactions between metal nanoparticles and the surrounding media and substances. Recently, antiviral materials have been attracted against the backdrop of Covid-19 pandemic. Abraham et al. have been recommended use of heat to kill SARS-CoV-2 in the sterilization, for example, 20 min above 60 °C, through the review of the current existing literature including World Health Organization guidelines [6–8]. Cotton textiles have been widely used for medical and nursing clothing and bedclothes and so on in medical and care facilities. Currently, medical facilities use methods such as chemical washing and UV light irradiation to sterilize the clothes, which cause damage to the fibers. If visible light irradiation such as indoor light can be used to inactivate viruses attached to the clothes, reduction of damage of them and efficient inactivation of viruses can be achieved. In the case of dyeing cotton clothes, the general method is to immobilize anionic dyes by electrostatic adsorption after a treatment of bare cotton fibers with cationic reagents [9]. Here, we hypothesized that if we could immobilize metal nanoparticles on cotton fibers by electrostatic adsorption based on the dyeing method, the nanoparticles, which are locally heated by visible light irradiation, would be able to inactivate nearby viruses by the photothermal effect through LSPR. In this study, we fabricated cotton textiles with gold nanoparticles (AuNPs) which show plasmonic absorption in visible light region by electrostatic adsorption using polyethyleneimine (PEI) as a cationic reagent and tetrachloroauric acid as a anionic dye precursor and by chemical reduction. In addition, the surface temperature change due to visible light irradiation was measured to observe the plasmonic photothermal effect.

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Materials and methods

Sample preparation

Hydrogen tetrachloroaurate (III) tetrahydrate ($HAuCl_4 \cdot 4H_2O$) was purchased from FUJIFILM Wako Chemicals. Trisodium citrate dihydrate and

polyethyleneimine, branched (PEI, $M_n \sim 10{,}000$) are purchased from Sigma-Aldrich.

A plain-woven natural cotton textile tape (24 mm in width, without use of fluorescent bleaching agent) was cut into pieces 30 mm in length. The pieces were washed with stirring in ethanol at 40–50 °C for 30 min for removal of contamination and dried in an oven at 40 °C for 24 h. Immobilization of gold nanoparticles (AuNPs) on the cotton fibers was carried out as follows (Fig. 1). Cotton fibers have negative charge due to consisting of cellulose with carboxyl and hydroxyl groups [10]. The pre-treatment with PEI as a cationic regent was adopted for accelerating electrostatic adsorption of $AuCl_4^-$ by reference to the typical dyeing of anionic dyes on cotton [9]. The cotton textile piece was immersed into a 1.0 wt.% PEI aqueous solution in a beaker placed in a desiccator for 30 min under reduced atmosphere at room temperature. Then, it was rinsed with stirring in Milli-Q grade water twice and dried in the oven at 40 °C for 24 h under reduced atmosphere. The PEI-immobilized cotton textile piece (C-PEI) and the bare one (bare-C) were immersed into a 10 mM $HAuCl_4$ aqueous solution separately in each beaker placed in the desiccator for 30 min under reduced atmosphere at room temperature. Subsequently they were rinsed with stirring in Milli-Q grade water twice and dried in the oven at 40 °C for 24 h with a light-shielding cover under reduced atmosphere. The tetrachloroaurate-immobilized cotton textile piece (C-PEI-AuCl) was immersed into a 100 mM trisodium citrate aqueous solution in a conical flask placed in the desiccator for 30 min under reduced atmosphere at room temperature. Then, the flask was placed on the hotplate in the air, and the 100 mM trisodium citrate aqueous solution was heated to 95 °C. The temperature was kept between 95 and 100 °C for 60 min to reduction of $AuCl_4^-$ [11]. The colored textile piece was rinsed in 100 mL of Milli-Q grade water in a 200 mL beaker given a rotation of 600 rpm by a magnetic stirrer twice for 10 min for removal of substances which were not immobilized. The rinsing condition was determined such that the release of gold nanoparticles into the water used for rinsing could not be confirmed by visible-NIR spectroscopy. The resulting sample was dried in the oven at 40 °C for 24 h under reduced atmosphere (C-PEI-Au). An AuNP-immobilized cotton textile piece without immobilization of PEI (C-Au) was also prepared following adsorption of tetrachloroaurate on the bare one (C-AuCl) as a control sample.

Measurements

Diffuse reflection spectra were measured by integrating sphere method with a SHIMADZU SolidSpec-3700DUV spectrophotometer. The reference spectrum was measured using a standard barium sulfonate plate. Surface photothermal measurement of the cotton textile samples immobilized with gold nanostructures was performed with irradiation of an ASAHI SPECTRA MAX-303 xenon lamp (300 W)

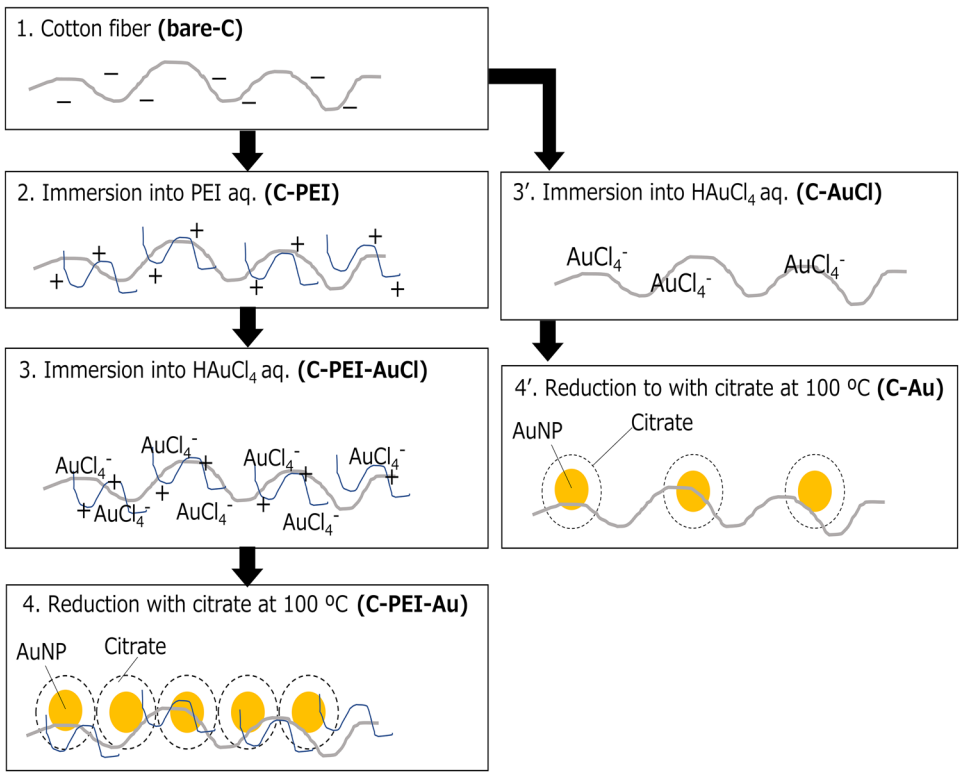

Fig. 1 Schematic procedure of immobilization of AuNPs onto cotton fibers. The sample names are shown with bold characters

through bandpass filters allowing to pass the lights of 400, 450, 500, 550, 600, 650, and 700 nm ± 5 nm in air at room temperature. The light emitted from the quartz fiber with 200 µm of the core diameter and the irradiation area on the surface of samples was ca. 10 mm of the diameter. The radiative temperature was measured by an Optris PI 640 thermo-camera with 640 × 480 pixels of optical resolution. The flame rate was 32 Hz, and the temperature resolution was 0.075 °C. X-ray diffraction (XRD) patterns were obtained with a RIGAKU SmartLab X-ray diffractometer. Scanning electron microscopic (SEM) images were collected with a JEOL field emission scanning electron microscope. X-ray photoelectron spectra (XPS) were measured with an ALVAC-PHI 5000 VersaProbe spectrometer using monochromatic Al Kα radiation (1486.6 eV, 100 V). Extinction spectrum with a peak at 550 nm and photon absorption cross-sectional area (C_{abs}) of AuNP were calculated according to Mie theory using MiePlot ver. 4.6.20.

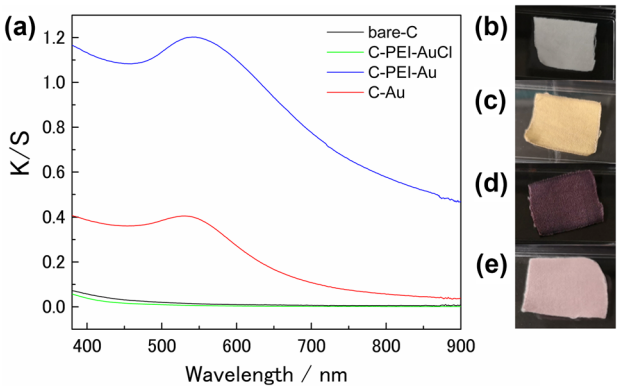

Fig. 2 Kubelka–Munk-transformed visible-NIR diffuse reflectance spectra of cotton textile samples (**a**), bare-C (black), C-PEI-AuCl (green), C-PEI-Au (blue), and C-Au (red) and the photos of bare-C (**b**), C-PEI-AuCl (**c**), C-PEI-Au (**d**), and C-Au (**e**)

Results and discussion

Immobilization of AuNPs on the cotton fibers

Dyeing of textiles has been often evaluated using the color strength (K/S) values [12]. Here, diffuse reflection spectra of the cotton textile samples were transformed into *K/S* spectra obeying the Kubelka–Munk equation,

$$K/S = \frac{(1-R)^2}{2R}$$

where R is reflectance, as shown in Fig. 2a. The spectrum of bare-C has no peaks and colors, which corresponds to the photo image (Fig. 2b). The spectrum of C-PEI-Au has a broad peak between 450 and 900 nm with the center at 550 nm due to LSPR of the immobilized AuNPs, while the spectrum of C-Au has smaller and narrower peak at the same central wavelength. The colors of C-PEI-Au and C-Au are deep violet (Fig. 2d) and pale pink (Fig. 2e), respectively, which are consistent with the K/S spectra. These results suggest that adsorption of PEI on the bare cotton fiber contributes to denser immobilization of AuNPs. The broader peak is attributed to proximate immobilization of multiple AuNPs. C-PEI-AuCl is pale yellow (Fig. 2c), and it has no peaks in the K/S spectra between 380 and 900 nm.

SEM images of *bare-C* and *C-PEI-Au* are shown in Fig. 3a and b. AuNPs with the size of 60–70 nm are observed on the cotton fiber. According to calculation based on Mie theory, when the diameter of isolated AuNPs is 150 nm and the surrounding medium is air, the peak wavelength of the extinction spectrum is estimated to be 550 nm. The difference between the size used in the calculation and the observed one in the SEM image (Fig. 3a) is presumably due to electromagnetic interactions between multi-nanoparticles [13] caused by aggregation of the nanoparticles and the presence of the cotton fibers as the substrate [14, 15].

XRD pattern of *C-PEI-Au* (Fig. 3c) shows some characteristic peaks for cellulose at $2\theta = 14.6°$, 16.4°, and 22.8° [16] and for Au (111) at 38.2° [17]. It suggests that reduction of tetrachloroaurate on the fiber using trisodium citrate brings about formation of Au (111) nanocrystalline. The peaks originated from cellulose have no change before and after the immobilization process. During the process, the cotton sample has been exposed in the strongly basic PEI aqueous solution at room temperature and the strongly acidic $HAuCl_4$ aqueous solution. In addition, reduction of tetrachloroaurate on the fiber has been carried out at 100 °C. The XRD pattern for cellulose indicates that the process over a wide range of pH and at the high temperature does not affect the crystal structures. The presence of chemical species at each step of the immobilization process (Fig. 1) were confirmed by XPS measurement of the sample surfaces (Fig. 3d). The atomic ratios of N/C were estimated to be 0.028 for bare-C and 0.045 for C-PEI. The increase in the N/C after treatment with PEI is attributed to adsorption of PEI as a cationic reagent on the bare cotton fiber. The atomic ratios of Au/N were estimated to be 0.032 for C-AuCl and 1.511 for C-PEI-AuCl. It suggests that more $AuCl_4^-$ is electrostatically adsorbed on the PEI containing cationic amines. The spectra for C-Au and C-PEI-Au have no peak of Cl2p due to removal of Cl species by reduction of $AuCl_4^-$. The atomic ratios of Au/N were estimated to be 1.064 for C-PEI-Au and 0.208 for C-Au, showing contribution of PEI to denser immobilization of AuNPs as compared with C-Au.

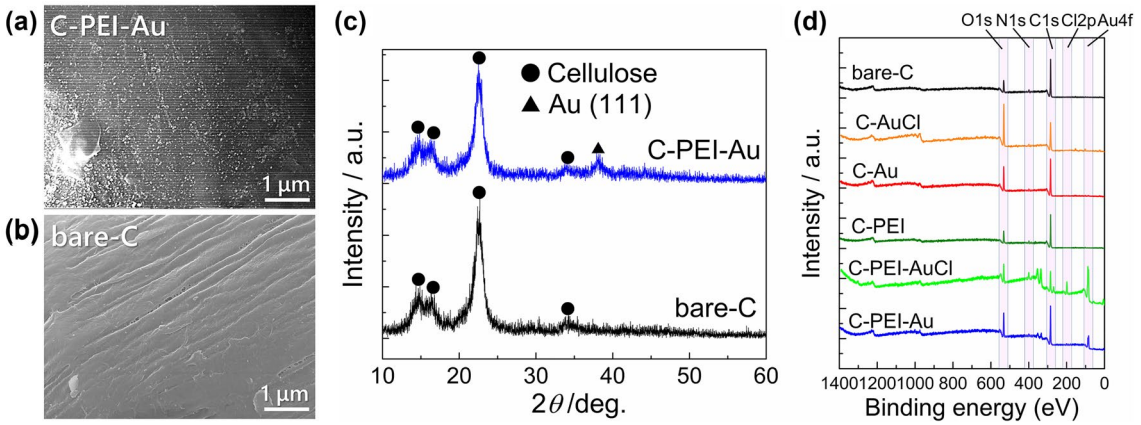

Fig. 3 SEM images of C-PEI-Au (**a**), bare-C (**b**), XRD patterns of C-PEI-Au and bare-C (**c**), and X-ray photoelectron survey spectra of the surfaces at each step in the immobilization process (**d**)

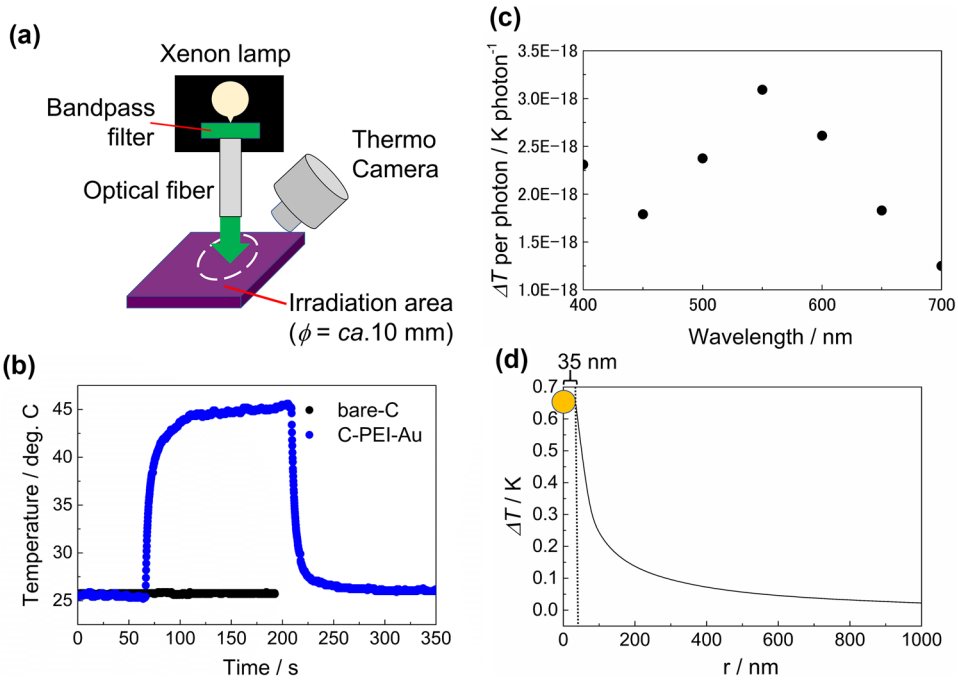

Fig. 4 Schematic of photothermal measurement set-up (**a**) and time course of temperature change by irradiation of light at 550 nm with 43 mW to bare-C and C-PEI-Au (**b**), dependence of temperature increase (ΔT) per one photon upon irradiation wavelength for C-PEI-Au (**c**), and calculated temperature distribution from the surface of AuNP to outside (**d**)

Observation of the plasmonic photothermal effect

Change in radiative surface temperature of C-PEI-Au was observed with a thermo-camera by irradiation of visible light at 550 nm with 43 mW, as shown in Fig. 4a and b. The temperature rose dramatically from 25 to 45 °C immediately after irradiation and became almost constant within 100 s. On the other hand, no change in the temperature was observed on bare-C by irradiation. In order to evaluate photothermal conversion, temperature increase (ΔT) per one photon at each irradiation wavelength in visible light between 400 and 700 nm was calculated through measurement of change in the radiative surface temperature for C-PEI-Au. The ΔT for 100 s of irradiation was divided by the number of giving photons and it was plotted against each wavelength as shown in Fig. 4c. The dependence of ΔT per one photon upon irradiation wavelength reflects the K/S spectrum of C-PEI-Au (Fig. 2a). The maximal ΔT per one photon was obtained by irradiation at 550 nm where the strongest plasmonic absorption occurs.

On the other hand, the practically obtained ΔT is much larger than the calculated one in the case of single AuNPs. Distribution of temperature outside a single AuNP with *a*

of the radius as a heat source is expressed according to the following equation [18, 19],

$$\Delta T(r) = \frac{C_{abs} I}{4\pi kr} (r \geq a)$$

where C_{abs}, I, k, and r are photon absorption cross-sectional area of the AuNP, incident light intensity, heat conductivity of the surrounding media, and distance from the center of the AuNP, respectively. When the parameters of our practical condition were substituted in the above equation, the maximal ΔT ($r = 35$ nm as the radius of AuNP) at the surface of AuNP was roughly estimated to be 0.65 K as shown in Fig. 4d. The parameters of $C_{abs} \backsim 5 \times 10^{-15}$ [m^2] which was estimated under a condition of Au sphere with 70 nm of the diameter surrounded by ambient pressure air, and $k \backsim 0.026$ for air [Wm^{-1} K^{-1}] were employed. Practical phenomena of temperature increase in this study would result from enhancement of the electric field and heating intensity under the existence of multiple and dense AuNPs [18].

Conclusion

Dense immobilization of AuNPs has been achieved onto the cotton fibers through the treatment with PEI as an accelerator for electrostatic adsorption of tetrachloroauric ions as gold seeds, and reduction with sodium citrate on the fibers. The AuNP-immobilized cotton textile shows plasmonic absorption at around 550 nm and the dense immobilization gave deep violet due to LSPR. Surface radiative temperature of the AuNP-immobilized cotton textile is increased by continuous visible light irradiation. Photothermal conversion is most effective when the wavelength is at 550 nm, corresponding to the peak due to LSPR. Dense immobilization of AuNPs would enhance the electric field and heat intensity. As the next step, we will investigate effects of plasmonic heating on virus particles attached to the AuNP-immobilized cotton textile.

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Declarations

Conflict of interest Authors declare that this study was conducted without any commercial or financial relationships that could be construed as a potential conflict of interest.

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