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Microbead-Based Colorimetric and Portable Sensors for Polyphenol Detection

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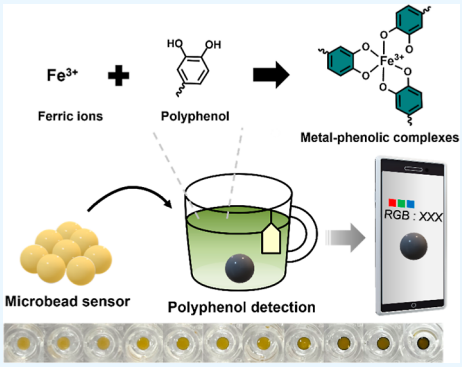
ABSTRACT: Natural polyphenols found in health supplements and drinks have antioxidant and anti-inflammatory properties. In particular, to determine the beneficial qualities of antioxidant drinks and beverages, consumers demand precise quantification of the total amount of polyphenols as on-site detection. Herein, we developed a new concept of portable beads suitable for the field detection available: colorimetric quantification of polyphenols equipped with color converting software applications in a smartphone or tablet PC. The yellowish beads contain ferric ions to react with polyphenol to produce blackish metal-phenolic complexes. It is simple to perform the detection procedure: dipping the beads in the analytical sample and out—taking a photo—converting into RGB color values and quantification of the existed polyphenol. The overall process was completed within 5 min. Compared with the Folin−Ciocalteu assay, which is a representative optical sensor kit for total phenolic content, the bead-based sensor showed a better limit of detection of 0.0415 mM for tannic acid and comparable sensing capability for a polyphenol-containing plant extract and brewed tea. The beads conserved the shape and sensitivity after months of storage or under environmental interference such as a change in the temperature.



1. INTRODUCTION

Natural polyphenols in health supplements and foods are key components with antioxidant and anti-inflammatory properties. For instance, the administration of polyphenol-rich grape seed extract tablets for 12 weeks significantly reduces oxidized low-density lipoprotein levels.[1,2] Furthermore, resveratrol containing abundant polyphenol inhibits the pro-inflammatory cytokines TNF-α and IL-6[3,4] Thus, natural polyphenols contribute antioxidant activity to blood vessels and cells, and mitigate inflammatory responses. To standardize and determine the beneficial quality of foods, the analytical quantification of polyphenols present in healthy foods is important.

There are several analytical techniques for quantifying polyphenols, including liquid chromatography (LC) spectrophotometry, electrochemical measurements, and optical detection kits.[5−7] The LC method has high sensitivity for identifying polyphenol components from plant extract samples (as low as 0.1 ng/mL),[8] although it requires large and expensive instruments and professional trainees. As an alternative analytical method, researchers developed electrochemical sensing of caffeic acid over a concentration range of 10−1000 μM[9] and fabricated portable ceria nanoparticles that show a colorimetric response to several phenolic antioxidants, with detection in the range of 20−400 μM.[10]

As simpler methods of detection and analysis, optical detection kits for phenolic compounds,[11−14] such as phenolic compound assay kits and Folin−Ciocalteu assays,[15] have been commercialized. However, these methods require several reagents and analytical tools, such as an absorption spectrophotometer. Therefore, a user-friendly and highly sensitive polyphenol detection method is necessary for the food and healthcare industries.[16−19]

Herein, we propose colorimetric bead-based sensors that are simple to detect (beads drop in and out) and available for field detection systems without heavy instruments. The colorimetric response of polyphenols is inspired in nature by colored metal-phenolic complexes when interacting with metal ions.[20,21] In marine mussels, the interactions between ferric ions (Fe^{3+}) and phenolic amino acids in mussel proteins generate brown−brown coordination complexes. Based on the formation of the colored coordinated complex, we developed a platform where Fe^{3+} was embedded inside alginate microbeads that responded to natural polyphenols as target analytes. First, we prepared microbeads using alginate-Fe^{3+} cross-linking. Using microbeads, we investigated the detection of diverse polyphenols as target analytes, from one galloyl-group-containing polyphenol (pyrogallol) to five galloyl-group-containing polyphenols

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(tannic acid; TA). We also determined the limit of detection (LOD) of TA, which was compared with the LOD of TA using a well-established polyphenol detection kit, the Folin−Ciocalteu assay. As a practical demonstration of the portable bead sensor platform, we tested the detection of polyphenols in plant extract samples (spearmint, garlic, spinach, and green tea) and an infused solution from health drink products (berry, ginger, and green tea).

2. EXPERIMENTAL DETAILS

2.1. Materials. Sodium alginate (SA), diethylene glycol, and sodium hydroxide (NaOH) were purchased from Daejung Chemicals (Gyeonggi-do, Korea). Epigallocatechin gallate (EGCG), gallic acid (GA), pyrogallol (PG), Folin−Ciocalteu reagent, thiazolyl blue tetrazolium bromide (MTT), and 2′,7′-dichlorodihydrofluorescein diacetate (DCF-DA) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Anhydrous iron(III) chloride ($FeCl_3$) and TA were obtained from Thermo Fisher Scientific (Waltham, MA, USA). 2,2′-Azinobis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS) was purchased from Tokyo Chemical Industry (Tokyo, Japan). Spearmint (*Mentha spicata* L.) samples were collected from Nepal. Garlic (*Allium sativum* L.), spinach (*Spinacia oleracea* L.), and green tea [*Camellia sinensis* (L.) Kun] samples were collected from Bangladesh. All of the samples were extracted by adding methyl alcohol and using an ultrasonic extractor. The final extract was collected by filtration and dried. Berry and ginger teas were purchased from TWININGS (London, England) and green tea was purchased from OSULLOC (Jeju, Korea).

2.2. Preparation of Microbeads and Characterization. SA was completely dissolved in deionized (DI) water at room temperature (24 ± 2 °C) under magnetic stirring (C-MAG HS 7, IKA, Staufen, Germany). The solution was injected into an aqueous $FeCl_3$ solution using a syringe (18G needle, Korea Vaccine, Seoul, Korea) with a syringe pump (injection speed: 44.15 mL/h) (KDS-100CE, KD Scientific, Holliston, MA, USA) and stirred for 30 min. The beads were then rinsed three times with DI water. The beads were prepared with component combinations of SA (0.5−2.0 wt %) and $FeCl_3$ (0.05−0.5 wt %). The components of prepared microbeads were characterized by an FT-IR spectrometer (Nicolet iS20, Thermo Scientific, Waltham, MA, USA) and microplate reader (iD5MultiMode Microplate Reader, Molecular Devices, San Jose, CA, USA).

We determined the reproducibility of bead fabrication by measuring the sphericity factor (SF), which was a dimensionless indicator of shape (see eq 1)[22]

$$SF = \frac{d_{max} - d_{per}}{d_{max} + d_{per}} \quad (1)$$

where d_{max} is the maximum diameter passing through the bead centroid (mm) and d_{per} is the diameter perpendicular to d_{max} passing through the bead centroid (mm). A bead is considered spherical if its SF is below 0.05, whereas a bead with an elongated shape has its SF approaching unity 1.

2.3. Detection Test of Polyphenol Using Microbeads. To examine the colorimetric transition of the beads for polyphenol, each prepared bead was dipped in 1.5 mM PG aqueous solution (100 μL) in a Falcon 96-well plate (Falcon, New York, USA). The shapes and colors of the beads were captured using a smartphone (iPhone 13, Apple, Cupertino, CA, USA) based on the detection time (immersion time of the beads in the analyte samples).

To explore the selectivity of the bead sensor for polyphenol, the beads prepared with SA (2 wt %) and $FeCl_3$ (0.5, 0.4, 0.3, and 0.2 wt %) were dipped in TA, EGCG, GA, and PG (0.5 mM in DI water). To quantify the amount of polyphenol from the extract samples (spearmint, garlic, spinach, and green tea), the sample solution (20, 6.7, 4.0, 2.9, and 2.2 mg/mL) was prepared by diluting the extract with DMSO (20 μL) and corresponding to DI water (80, 280, 480, 680, and 880 μL). To detect and quantify infused samples, berry, ginger, and green tea were brewed in 150 mL of 70 °C water for 1−3 min.

To determine the sensitivity of the bead sensor, SA/$FeCl_3$ (2/0.5 wt %) beads were tested in various concentrations of TA (0.005−0.5 mM) and then images were captured over detection time. The colorimetric signal intensity at each TA concentration was converted into RGB (%) using ImageJ (Java, Maryland, USA) (eq 2).

$$\text{RGB (\%)} = \frac{\text{RGB}_i - \text{RGB}_f}{\text{RGB}_i} \times 100\ (\%) \quad (2)$$

where RGB_i is the initial RGB value of the microbeads before detection and RGB_f is the final value of the microbeads after detection.

We determined LOD and LOQ which were calculated as follows (see eqs 3 and 4)

$$\text{LOD} = \text{standard error (SE)} \times \sqrt{N} \times 3.3 \div \text{slope} \quad (3)$$

$$\text{LOQ} = \text{standard error (SE)} \times \sqrt{N} \times 10 \div \text{slope} \quad (4)$$

where N is the number of data, slope is the value of linear fitting, and standard error is a standard deviation of the regression line calculated using OriginPro 8 software (Northampton, MA, USA).

2.4. Total Phenolic Measurement Using Folin−Ciocalteu Assay. The Folin−Ciocalteu reagent was used to determine the total phenolic content.[23] In a concise summary, 50 μL of the extract was mixed with an equal amount of the Folin−Ciocalteu reagent. The mixture was left at room temperature for 5 min, after which 200 μL of a 7.5% sodium carbonate solution and 500 μL of DI water were added. After 2 h of incubation, the absorbance was measured at 725 nm. GA was used as a standard for the calibration curve.

2.5. Total Flavonoid Measurement. A colorimetric assay was performed to determine the total flavonoid content.[24] The sample (100 μL) was mixed with 1000 μL of 90% diethylene glycol and 100 μL of NaOH solution. After mixing, the solution was allowed to stand for 1 h at 37 °C. After incubation, the absorbance was measured at 420 nm. Naringin was used as the standard for the calibration curve.

2.6. Free Radical Scavenging Activity Using ABTS Assay. Measurements were conducted as described by Re et al.[25] with some modifications. Stock solutions of 7 mM ABTS (10 mL) and 2.45 mM potassium persulfate (5 mL) were prepared. The working solution was prepared by mixing the two stock solutions (2:1) and incubating them in the dark for 12 h at room temperature. The solution was diluted with DI water to obtain an absorbance of 0.7 ± 0.01 at 734 nm. Plant extract samples (10 μL) were reacted with 990 μL of the ABTS working solution in the dark at 37 °C. After incubation for 6 min, the absorbance of the mixture was measured at 734 nm.

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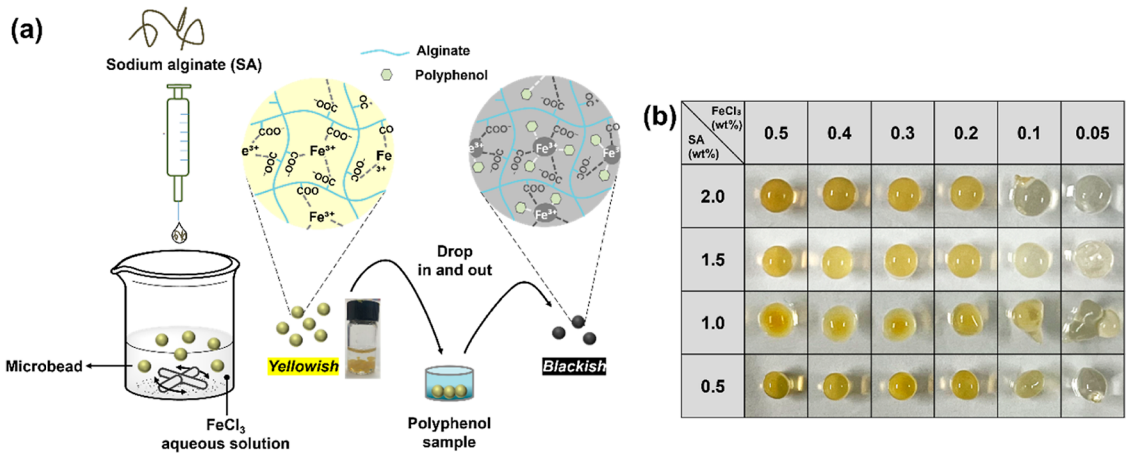

Figure 1. (a) Schematic illustration of the microbead preparation and detection tests for polyphenol. The microbeads exhibited a colorimetric transition from yellowish to blackish by dipping into liquid samples containing polyphenols. (b) Photograph of microbeads prepared by various concentrations of SA and $FeCl_3$ aqueous solutions.

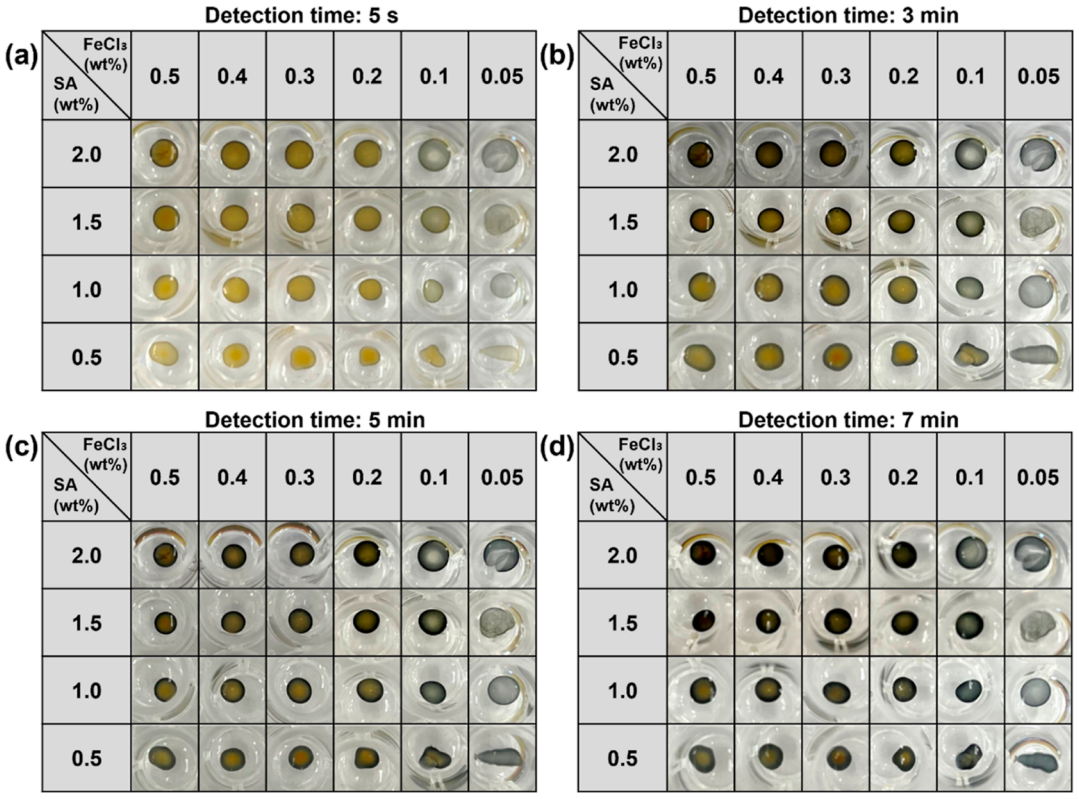

Figure 2. Photograph of colored microbeads when dipped into 1.5 mM pyrogallol solution according to detection time [(a) 5 s, (b) 3 min, (c) 5, and (d) 7 min].

The radical scavenging activity was calculated as follows (see eq 5)

$$\text{ABTS radical scavengina activity (\%)} = \frac{A_B - A_A}{A_B} \times 100 \quad (5)$$

where A_B is the absorbance of ABTS radicals in DI water and A_A is the absorbance of ABTS radicals mixed with the antioxidants after incubation.

FSC_{50} was defined as the concentration required for 50% free radical scavenging activity.

2.7. In Vitro Tests. Normal human dermal fibroblast (NHDF) cells (ATCC, Manassas, VA, USA) were cultured in a minimum essential medium (MEM; Welgene, Gyeongsan, Korea) supplemented with 10% fetal bovine serum, 100 IU/mL penicillin, and 100 μg/mL streptomycin at 37 °C in a humidified atmosphere containing 5% CO_2. Cell viabilities of NHDF cells were measured using an MTT assay. For the MTT assay, NHDF were seeded in a 24-well plate at a density of 5×10^4 cells per well and incubated for 24 h. When the density of the cells reached 70%, cells were incubated with a plant extract for 24 h. To assess the protective effects of the extract, cells were exposed to 150 μM of H_2O_2. After 4 h of

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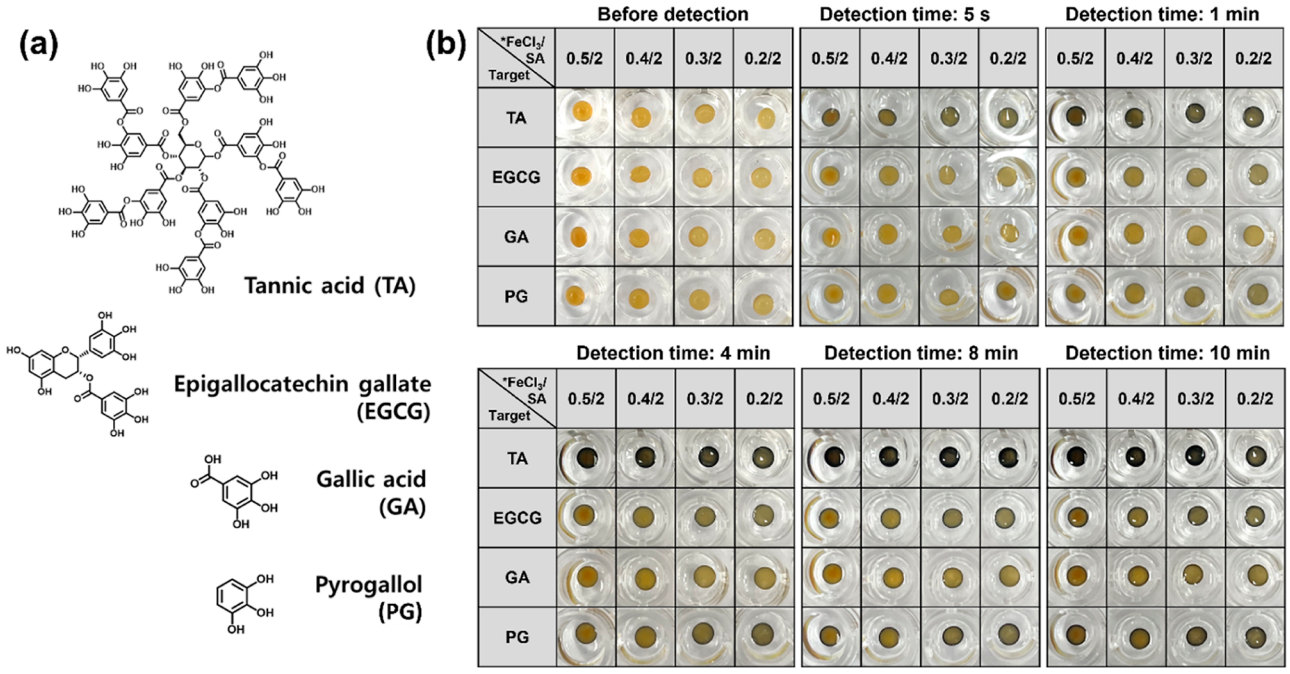

Figure 3. (a) Chemical structures of four polyphenols (tannic acid, EGCG, GA, and pyrogallol). (b) Detection tests using the microbeads for 0.5 mM polyphenols at different detection times (5, 1, 4, 8, and 10 min). *$FeCl_3$/SA: experimental concentration of $FeCl_3$ (wt %)/SA (wt %) used for microbead preparation.

incubation, the medium was replaced with 1 mL of MTT solution (0.5 mg/mL) and incubated for 2 h at 37 °C. The optical density was measured at 570 nm.

2.8. DCF-DA Assay. Reactive oxygen species (ROS) were measured using DCF-DA assays. NHDF cells were cultured in MEM with a plant extract for 24 h, as described above. A total of 150 μM H_2O_2 was added for 4 h, and cells were exposed to 10 μM DCF-DA solution for 15 min at 37 °C. The cells were washed with phosphate-buffered saline. The fluorescence was measured using an EVOS M5000 microscope (Thermo Fisher Scientific, Sunnyvale, CA, USA).

3. RESULTS AND DISCUSSION

We developed colorimetric bead-based sensors capable of detecting free natural amino acids via loading ninhydrin onto alginate beads.[26] Ninhydrin reacts with the amino groups of free amino acids to form Ruhemann's purple chromophore. Sensor beads are portable and easy to use and can detect free natural amino acids with sufficient sensitivity. Herein, we extend a portable bead-based sensor platform to detect polyphenols by adding Fe^{3+} to alginate beads. This is because Fe^{3+} forms coordinate bonds with polyphenols, producing brownish or blackish coordinated complexes.[27]

Figure 1a shows a schematic diagram of the microbead preparation and polyphenol detection procedure by simply dropping the beads into the analyte solution. Anionic alginate can form ionic cross-links with trivalent cationic Fe^{3+} ions to form microbeads. The syringe injection method for bead preparation enabled the mass production of more than 200 beads within 5 min. The colorimetric change from yellowish to blackish was anticipated because the ionically cross-linked Fe^{3+} of the beads would competitively react with polyphenol, which could then be replaced when polyphenol was incubated with the beads. Polyphenol $-Fe^{3+}$ has a binding constant of 1.1×10^9, whereas alginate $-Fe^{3+}$ has a binding constant of 3.0×10^5, indicating a greater binding affinity between polyphenol and Fe^{3+}.[28,29]

We explored beads preparation by the component combination of alginate (0.5−2 wt %) and $FeCl_3$ (0.05−0.5 wt %), mainly formulating a size of 3.0 ± 0.1 mm in diameter (Figure 1b). At low concentrations (0.05 and 0.1 wt %) of $FeCl_3$, the beads were not stably formed (nonspherical and nonuniform architectures with fragile bead shells) owing to the weak ionic interactions between alginate and Fe^{3+}. The beads were stably formed at the component combination of alginate (0.5−2 wt %) and $FeCl_3$ (0.2−0.5 wt %).

To determine the appropriate component (SA or $FeCl_3$) concentrations for polyphenol detection, the beads were tested by using a PG aqueous solution as the polyphenol analyte according to the detection time (Figure 2). The color of the beads changed from yellowish to blackish within 5 s of dipping. Fe^{3+} has a high redox potential and is easily reduced to ferrous iron (Fe^{2+}), changing to a dark black or green color in the presence of polyphenols.[30,31] Overall, the beads became darker and blackish as the detection time increased. The difference in color between the detection times of 3 and 5 min was indistinguishable from that with the naked eye. After 7 min of detection, the black color was saturated.

A black region was observed in the shell of the beads; interestingly, polyphenol did not penetrate the inner space of the beads (Figure S1). Thus, the penetration of polyphenol and the competitive reaction between alginate and polyphenol for Fe^{3+} mainly occurred in the shells of the beads. We traced the FT-IR spectra of microbeads before and after polyphenol detection (Figure S2). Before polyphenol detection, the bead showed a new band at 1732 cm^{-1} associated with the ionic interaction among the carboxylate groups of alginates with Fe^{3+}.[32] After polyphenol detection, the Fe−O band of the phenol-ferric ion complex appears at 600 cm^{-1}.[33] Based on these results, we propose that the Fe^{3+} in the beads newly form

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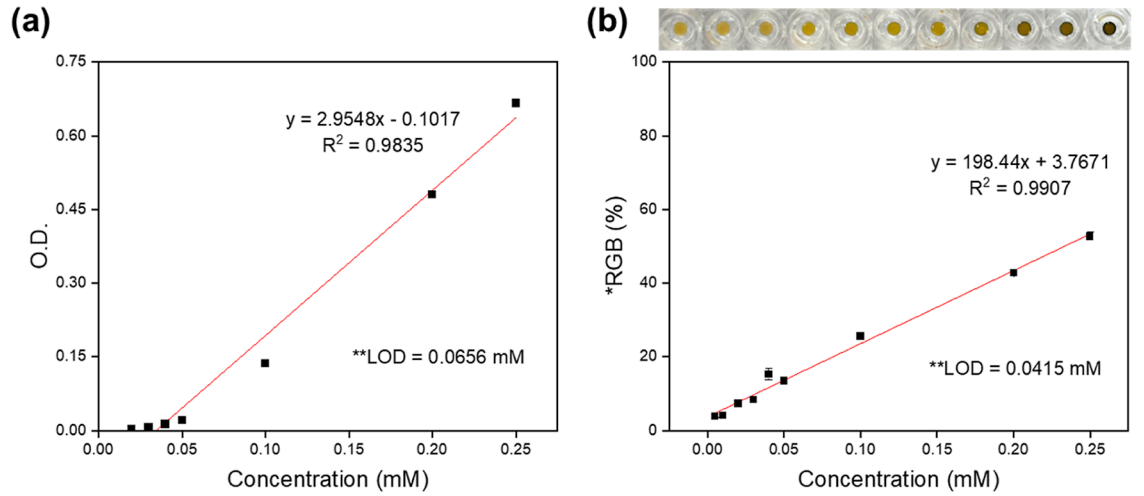

Figure 4. Comparison of detection tests for TA solutions between Folin−Ciocalteu assays and the microbead-based colorimetric sensor. (a) Optical density (OD) at 725 nm for TA detection measured using Folin−Ciocalteu assays. (b) RGB values of colored microbeads for TA solutions. Inset: photograph of colored microbeads according to TA concentrations. * RGB (%) $= \frac{RGB_i - RGB_f}{RGB_i} \times 100(\%)$; *i*: initial RGB value before microbead incubation, *f*: final RGB value after microbead incubation, and ** LOD: limit of detection.

Fe^{3+}-polyphenol complexes as the polyphenol sensing mechanism.

To investigate the origin of the color change, an aqueous solution of TA, a representative polyphenol, and Fe^{3+} were mixed. They exhibited absorption at 500−700 nm (Figure S3a), which was based on ligand−metal charge transfer (typically observed between 600 and 700 nm).[34] The degree of blackish color change increased with increasing TA concentration owing to the formation of more Fe^{3+}-polyphenol complexes (Figure S3b).

Based on the degree of the colorimetric transition and stability of formulated beads, we narrowed down the condition of $FeCl_3$ (0.5−0.2 wt %) and SA (2 wt %) of bead preparation for further studies. The selectivity of the bead sensor for polyphenols was explored using four aqueous solutions of polyphenols (500 μM) with different numbers of galloyl groups (TA: five groups; EGCG: two groups; and GA and PG: one group) (Figure 3). The 0.5/2 ($FeCl_3$/SA) beads showed the fastest and most discernible color change. This is attributed to the fact that many Fe^{3+} ions in the beads can react with the galloyl groups, producing a greater number of Fe^{3+}-phenolic coordinate complexes. Among the polyphenols, a color change in the beads was noticeable for TA, which had the highest number of galloyl groups. The order of degree in the colorimetric transition was TA > EGCG > PG $\gtrsim$ GA. The numbers of coordination bonds of PG and GA for Fe^{3+} were similar; however, the number of bonds of TA for Fe^{3+} was much higher. The phenolic hydroxyl (−OH) activity of polyphenols can be significantly enhanced by increasing the number of hydroxyl groups.[35] The number of hydroxyl groups in a polyphenol determines its coordination bonds with metal ions and its colorimetric transitions.

The bead sensor prepared with 2 wt % alginate and 0.5 wt % $FeCl_3$ gradually increased the intensity of the color change to blackish upon detection from 5 s to 20 min (Figure S4). In particular, at 2 min of detection, the color change had the greatest linear dependency on the analyte TA concentration (R^2 = 0.9907). Therefore, an incubation time of 2 min was selected for further experiments.

As a common method to quantify phenolic content in unknown samples, total phenolic content activity was measured using the Folin−Ciocalteu assay. The Folin−Ciocalteu reagent was used to oxidize the phenolic compounds, producing a blue-colored reduced Folin−Ciocalteu reagent (absorption measured at 760 nm).[36,37] Figure 4 shows the standard curves for the Folin−Ciocalteu assay and bead sensors according to the TA concentration. The LOD (or LOQ) values of TA using the Folin−Ciocalteu assay and the bead sensor were 0.0656 mM (0.2 mM) and 0.0415 mM (0.13 mM), respectively. The bead sensor showed a lower LOD and LOQ than the Folin−Ciocalteu assay, indicating that the bead sensor could achieve higher sensitivity for the TA analyte.

We further investigated the anti-interferent performance of the bead sensor. We first checked the ability of selectivity to distinguish between polyphenols and nonpolyphenolic compounds, even when they possess a similar chemical structure. Although EGCG (polyphenol) and flavones (nonpolyphenol) share structural similarities, the microbeads do not show colorimetric response for flavones (Figure S5). Even when purple delphinidin (a type of anthocyanin) is mixed with EGCG, the beads showed a sensory signal mainly from EGCG detection. This selectivity is attributed to a strong interaction between the ferric ion of the microbeads and the hydroxyl groups present in polyphenols.

As a demonstration of practical on-site sensors without a personal computer system, we could use smartphone applications, e.g., "RGB color detector", for converting to the RGB value (Figure S6). In field testing the quality of antioxidant drinks and beverage, e.g., tea, determining the total amount of polyphenol is important, rather than detecting each polyphenol. Tea, vegetables, and fruits contain a wide range of polyphenols.[38,39] Green tea and spearmint extracts contain 273 and 110 mg/g of total polyphenol,[40,41] respectively. Spinach has a brown color with a relatively low content (1.8−4.9 mg/g) of polyphenols.[42] Accordingly, a standard quantification method is required for a wide range of phenolic contents in practical samples. To apply the bead sensor to plant extract samples, the beads were dipped in

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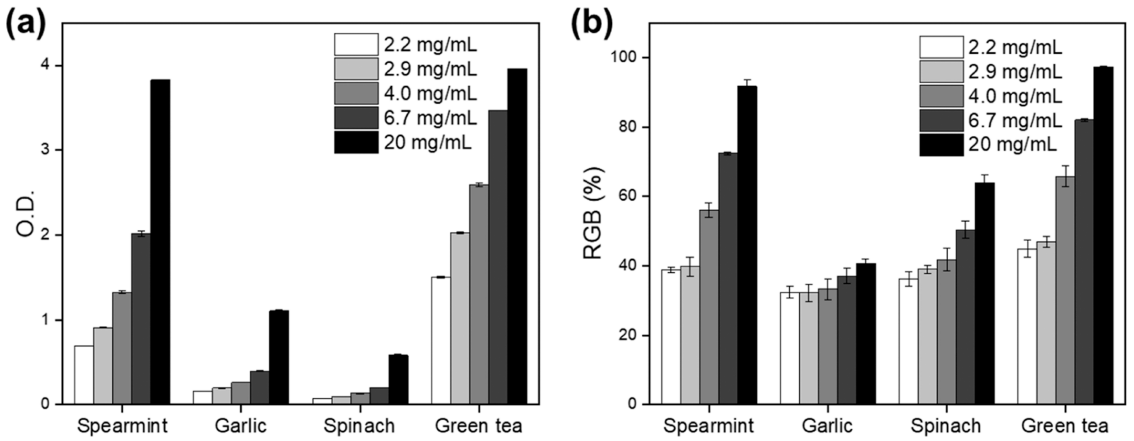

Figure 5. Comparison of detection tests for plant extract (spearmint, garlic, spinach, and green tea) solutions between Folin−Ciocalteu assays and the microbead-based colorimetric sensor. (a) OD at 725 nm for the plant extract detection measured using Folin−Ciocalteu assays. (b) RGB values of colored microbeads for each extract.

extract solutions of spearmint, garlic, spinach, and green tea (Figures 5 and S7). Similar to the results of the Folin−Ciocalteu assay, the color change and RGB intensity of the tested beads increased depending on the concentration of the extract samples (2.2−20 mg/mL). The most discernible color change was detected in green tea extract (RGB of 96.63% at 20 mg/mL) and spearmint (RGB of 94.91% at 20 mg/mL), which contain the most abundant polyphenols among the tested samples. Notably, the bead sensor detected polyphenols in the extract without further purification steps, even though the extract itself had a unique color and a variety of ingredients.

To investigate the extent of the health benefits of the plant extract samples, the antioxidant activity and potential protective effects of extracts containing polyphenols were assessed using in vitro assays. Similar to the color change reaction of beads in Figure 5b, the contents of flavonoid as a natural phenolic compound were high in extracts of spearmint (1213.4 ± 96.8 μg/mL at 20 mg/mL) and green tea (1835.7 ± 91.5 μg/mL at 20 mg/mL) (Figure 6).

To quantify the antioxidant activity, the radical scavenging activity of the extract was measured by using the ABTS (Figure 7) and DCF-DA (Figure 8) assays. Similar to the trend in color change of the bead sensor, green tea and spearmint had the highest antioxidant activity (FSC_{50} value: 14.94 μg/mL for green tea and 61.99 μg/mL for spearmint), and garlic and spinach had the lower antioxidant activity (FSC_{50} value: 497.33 μg/mL for garlic and 1268.5 μg/mL for spinach). In the DCF-DA assays, green tea and spearmint exhibited the highest antioxidant effects after H_2O_2-induced intracellular ROS production in NHDF cells. As confirmed by the color change of the bead sensor (Figure 5b), green tea and spearmint extracts containing high levels of polyphenols showed a strong protective effect against H_2O_2-induced cell death as determined using MTT assays (Figure 9). These two extracts had significantly high cell viability (100.0 ± 9.6 and 83.8 ± 9.4%) compared to that of the only H_2O_2-treated group (64.8 ± 9.8%). Therefore, the results and tendency of the antioxidant and protective abilities of the extract sample were consistent with the tendency of the polyphenol content detected via the bead sensor.

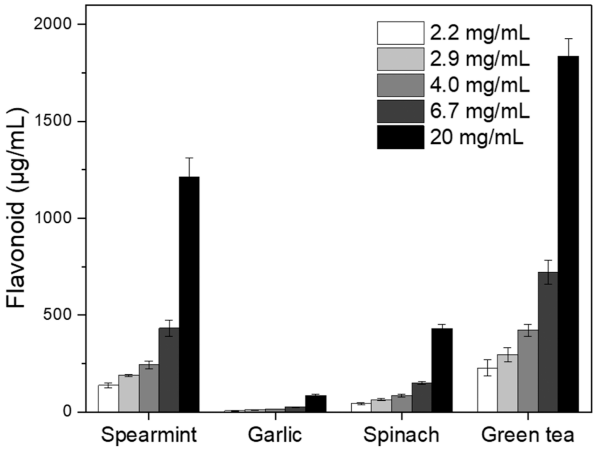

Figure 6. Total flavonoid content of plant extracts.

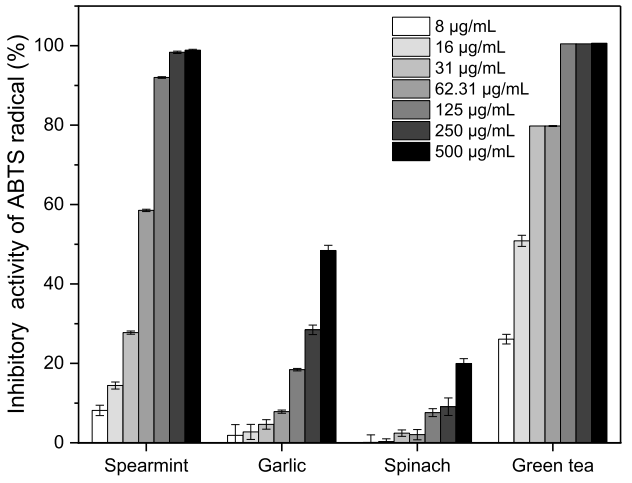

Figure 7. Antioxidant activity of plant extracts as measured with ABTS assays.

To demonstrate the bead sensor for practical health drinks, the beads were dipped into brewing samples of berry tea, ginger tea, and green tea. The tea types were selected based on their protective effects against oxidative stress. Similar to the results in the Folin−Ciocalteu assays (Figure 10a), the color change of the bead sensor was dependent on the time of tea brewing and the amount of polyphenols contained, resulting in the following order: green tea > berry tea > ginger tea (Figure 10b). Green tea contains many types of polyphenols, such as

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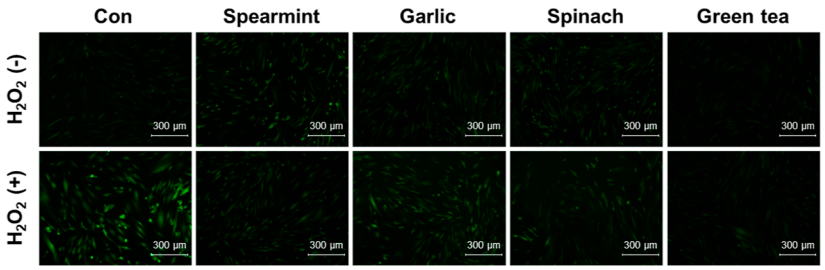

Figure 8. Intracellular ROS of plant extracts, as measured with DCF-DA assays.

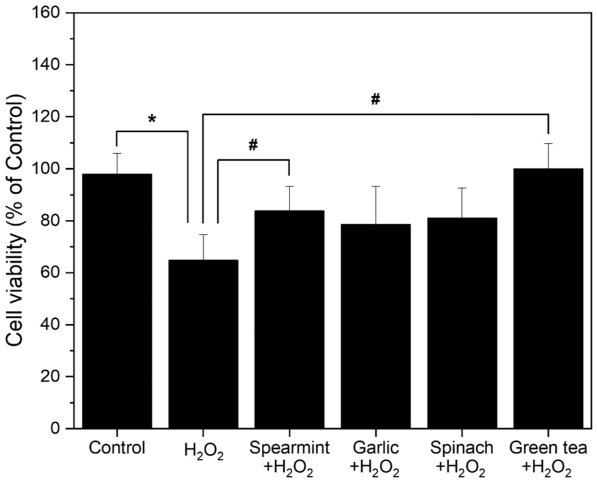

Figure 9. Cell viability tests of plant extracts against H_2O_2 treatment on NHDF cells as measured with MTT assays. *$P < 0.05$ indicates significant differences with the control (nontreated) group; #$P < 0.05$ indicates significant differences with only the H_2O_2-treated group.

EGCG and TA, and berry tea contains anthocyanins, which are phenolic flavonoids. The trend of the bead-based sensory signals was consistent with the results of the Folin−Ciocalteu assays. The microbeads are stored in deionized water at 4 °C to minimize oxidation and maintain the shape. The beads conserved shape and color up to 1.5 M NaCl salt and 40 °C (Figure S8). Notably, bead sensors were not affected by the color of the tea and extract solutions, and therefore, they are very useful for practical, portable, and simple polyphenol detection to apply in field detection and monitoring.

4. CONCLUSIONS

Without requiring chemical reagents and heavy analytical instruments, we developed a portable bead-based colorimetric sensor for polyphenol detection. The beads showed colorimetric response by dipping in and out and being converted into RGB color values. The color converting analysis enabled quantification of the total amount of existing polyphenol, and field testing is available. In particular, consumers could check the quality of antioxidant drinks and beverage even with the naked eye on-site.

Compared with the Folin−Ciocalteu assay as a representative optical sensor kit for polyphenol, the bead-based sensor showed a simpler detection procedure and comparable detection of limit in the polyphenol-containing plant extract and brewed tea. The beads maintained their shape and sensitivity after months of storage or under potential interference such as changes in the temperature.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.4c04523.

Additional experimental details, characterization of materials, calibration graphs of colored microbeads, and photographs of detection tests (PDF)

Polyphenol detection (MP4)

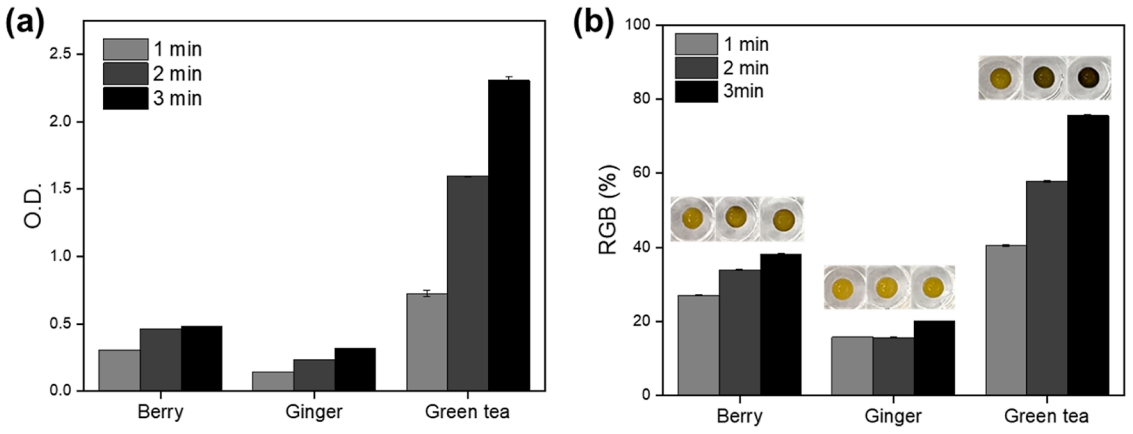

Figure 10. Comparison of detection tests for tea infusion (berry tea, ginger tea, and green tea) between Folin−Ciocalteu assays and the microbead-based colorimetric sensor. (a) OD at 725 nm of the tea infusion detection measured with Folin−Ciocalteu assays. (b) RGB values of colored microbeads for the tea infusion.

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‡‡S.J. and S.Y.K. contributed equally to this work. S.J. and S.Y.K. performed the experiments, analyzed the data, and wrote the manuscript; H.M., E.-K.L., and S.-M.A. assisted in data interpretation and manuscript preparation; H.L., K.K.S., and M.S.U. provided plant extracts and technical expertise; Y.K. and P.-I.Y. assisted in the study design and data interpretation; and B.-S.A. and S.S. supervised the overall research project and revised the manuscript. All authors have read and agreed to the published version of the manuscript.

Notes

The authors declare no competing financial interest.

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