

Novel measurement method of determining PS nanoplastic concentration via AuNPs aggregation with NaCl

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(Received 18 January 2022 • Revised 12 April 2022 • Accepted 24 April 2022)

Abstract—Microplastics, or nanoplastics fragmented to sizes in the nanoscale, can easily penetrate living organisms as well as human organs, increasing the risk of toxicity. However, it is challenging to obtain the size of nanoplastics using thermal analysis methods such as pyrolysis gas chromatography/mass spectrometry or thermal desorption-gas chromatography/mass spectrometry, which are used to analyze nanoplastics. In this study, the coupling effect due to the aggregation of gold nanoparticles (AuNPs) was used to measure the concentration of polystyrene nanoplastics (PSNPs). Experiments were conducted to measure the concentration of PSNPs using an ultraviolet-visible spectrophotometer using the phenomenon that the color of the colloid changes when AuNPs are aggregated. The differences in absorbance before and after aggregation after the addition of NaCl were measured. As a result of the experiment, when 20 mM NaCl was added to the solution in which AuNPs and PSNPs were dispersed, the difference in absorbance before and after aggregation and the concentration of PSNPs exhibited high linearity. In addition, 350 and 880 nm-sized PSNPs could be distinguished from each other because of their different linearities. The concentration of PSNPs was measured easily and conveniently without requiring a skilled operator, expensive analytical equipment; additionally, the process was not time or labor intensive, and it was shown that particle size can be measured by distinguishing particles of different sizes.

Keywords: Nanoplastics, Microplastics, Polystyrene, Aggregation

INTRODUCTION

Microplastics and nanoplastics are miniscule fragments of plastics that are abundant in the environment, including seawater, freshwater, sediments, soils, ambient air, drinking water, food, living organisms, and humans [1-3]. Currently, they are also classified as nanoplastics with sizes less than 1 μm , microplastics with sizes between 1 μm and 1 mm, and macroplastics with sizes larger than 1 cm [4-7]. The amount of microplastics increases as the size of microplastics decreases owing to fragmentation via breaking down or decomposition [8,9].

The polymers detected worldwide in the increasing order of the detected amounts can be arranged as polyethylene > polypropylene > polystyrene (PS) > polyvinyl chloride > polyethylene terephthalate. The most abundant microplastics present in Korean beaches is expanded polystyrene (EPS), accounting for ~95% of microplastics with sizes ranging from 1-5 mm [10,11]. Because EPS is lighter than other plastics, it is readily moved by the wind and is broken down by various factors, such as waves, wind, and sunlight, to create a plethora of nano-sized PS particles [8,9]. Meanwhile, the total production of plastics has been significantly accelerated owing to the coronavirus disease (COVID-19). Based on the data obtained from 2008 to 2019, it was only projected to reach 600 million tons in 2040, but it is estimated that 698 million tons were used in 2020

alone owing to COVID-19 [12,13].

Microplastics can be introduced to the environment via monomers, chemical by-products, and additives such as antioxidants, light stabilizers, plasticizers, flame retardants, and pigments added during manufacturing; these microplastics can also serve as carriers of contaminants [14]. Among the absorbed particles on aquatic organisms, those smaller than 150 μm can cross the gastrointestinal epithelium of the mammalian body and cause systemic exposure; the organs are more permeable to smaller sizes, and particles smaller than 2.5 μm can even penetrate into cells [15]. Therefore, in general, the smaller the particle size, the more hazardous it is.

Although a method for measuring the size and concentrations microplastics has not yet been standardized, it is generally performed in the order of sampling, pre-separation, separation, and analysis. The step before analysis, separation, is the process of removing substances, such as organic matter, that interfere with the analysis, and dividing substances presumed to be microplastics by their sizes. As an analysis method, microplastics are generally estimated and quantified by the naked eye and an optical microscope, and the quantified microplastics are qualitatively analyzed using spectroscopic techniques such as Fourier-transform infrared spectroscopy (FTIR) and Raman spectroscopy [16]. For micro-FTIR coupled with an optical microscope, the minimum particle size must be greater than approximately 10 μm . Moreover, because micro-Raman spectroscopy has a superior spatial resolution than micro-FTIR, it can be used to analyze smaller particles with sizes as low as 1 μm [16]. However, the analysis of microplastics using spectroscopic techniques is labor intensive and time consuming. Unlike non-destructive anal-

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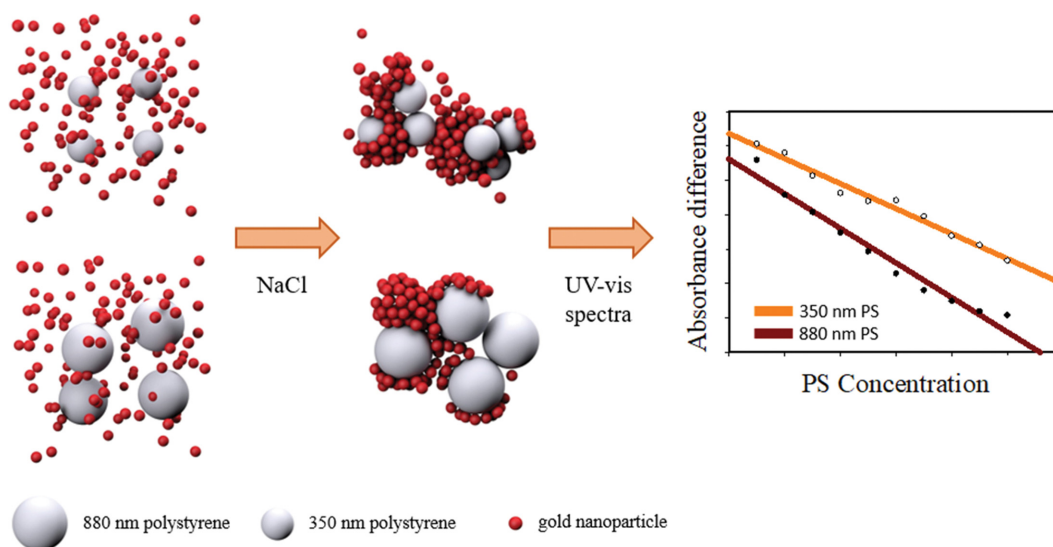


Fig. 1. Schematic diagram showing the method of measuring the concentration or size of PSNP from the ratio of the difference in absorbance before and after aggregation.

yses such as FTIR and Raman spectroscopy, destructive analyses such as thermal desorption-gas chromatography/mass spectrometry (TDS-GC/MS) and pyrolysis gas chromatography/mass spectrometry (py-GC/MS) are advantageous thermoanalytical methods for the analysis of nanoplastics. However, owing to the limit of detection, it is challenging to analyze the samples without sample pre-concentration, and the size information of the particles is lost [17].

Based on the above discussion, in this study, an experiment was performed to analyze the concentration of the nanoplastics sized 1 μm or less in a simple and convenient manner. We attempted to obtain the concentration of nanoplastics from the changes in color or absorbance to enable the measurement without requiring skilled labor or techniques. Among nanoplastics, PS nanoparticles of different sizes were used to test whether information regarding the size and concentration could be measured. To analyze the nanoplastics that are fragment to smaller particles in the environment, rather than directly measuring the plastic particles, we attempted to use the characteristics of a kind of interaction with them. Fig. 1 shows how to obtain the size and concentration of PSNPs from the absorbance after adding NaCl to the AuNPs mixed solution in which PSNPs of 350 nm and 880 nm in size are dispersed, respectively.

Gold nanoparticles (AuNPs) of 20 nm size exhibit a red color because of the localized surface plasmon resonance (LSPR) effect, in which free electrons in the conduction band oscillate collectively when a light of a specific wavelength is irradiated [18]. When the distance between two AuNPs is sufficiently small so that the plasmon field overlaps, the LSPR band red-shifts toward the red wavelength and turns either purple or blue depending on the distances between the particles [19-21]. The gold colloid prepared by the Frens method is electrostatically stabilized because it is coated by a negatively charged citrate [22]. However, this electrostatic repulsion disappears when salt is added, and the charge of the particles is neutralized, consequently leading to aggregation [23]. At the same time, the plasmon peak at a wavelength of ca. 520 nm red-shifts, and the color changes to either purple or blue. Various colorimet-

ric sensors for detecting various targets, such as metal ions, proteins, and biological small molecules, based on the color change due to the aggregation of colloidal gold have been studied [24,25]. However, as studies on the detection of polymer nanoparticles have not been conducted yet, we conducted an experiment to detect polystyrene nanoplastics (PSNPs) using the aggregation of AuNPs that were not functionally modified.

EXPERIMENTAL

1. Materials and Reagents

The following reagents were prepared for the aggregation experiments using a mixture of AuNPs and PSNPs. Sodium chloride (NaCl, 99%) and sodium citrate tribasic dehydrate (TSC, $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$, 99%) were purchased from Duksan Pure Chemical (Korea). Two sizes of carboxylate-modified PSNPs, 880 nm (10 wt%) and 350 nm (2.5 wt%), were purchased from Sigma-Aldrich and Alfa Aesar, respectively. Auric acid (HAuCl_4 , 99%) was purchased from Kojima. All chemicals were used as received without further treatment. To increase the dispersibility of nanoplastics in the liquid phase, PSNPs treated with a carboxyl group having hydrophilicity were selected instead of adding a surfactant.

2. Preparation for Absorbance Measurement after Aggregation

To measure the change in absorbance spectra after aggregation by adding NaCl to the mixed solution of AuNPs and PSNPs, the following preparations were performed. AuNPs with a size of 20 nm were prepared using the following procedure. First, 6 mL of 25 mM HAuCl_4 was added to 200 mL of boiling deionized water (DW). Then, 6 mL of 73.4 g/L TSC was added and cooled at room temperature while stirring. The prepared AuNPs were refrigerated at 4 $^\circ\text{C}$ and used within two weeks. AuNPs were concentrated in a centrifuge (11,000 rpm, 10 min, repeated twice) and then stored in a refrigerator. NaCl aqueous solution was prepared at concentrations of 100 mM and 1 M, and then diluted according to the experimental condition. Further, the purchased 10 and 2.5 wt% of 880

and 350 nm-sized PSNPs, respectively, were diluted with DW. The aggregation experiment of 1 mg/L PSNPs was performed as follows. After 2.8 mL of DW was added to 2.1 mL of 236 mg/L AuNPs, the solution was vortexed for 30 s. Then, 0.1 mL of 0.01 wt% of 350 nm or 880 nm-sized PSNPs was added and vortexed for 30 s. Then, 5 mL of 0.1 M NaCl was added, and the absorbance was measured after 3 min. In this manner, the aggregation experiments were performed ten times each, with up to 10 mg/L PSNPs.

3. Characterization

The morphologies of the AuNPs and PSNPs were analyzed using transmission electron microscopy (TEM, JEM-2010, Jeol). The ultra-violet-visible (UV-vis) spectra were obtained using a spectrophotometer (UV-1800, Shimadzu). The concentration of AuNPs was analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 2000DV, PerkinElmer). The hydrodynamic diameter (HDD) of the AuNPs and PSNPs was analyzed by DLS spectroscopy (ELS-Z, PHOTAL, Otsuka Electronics).

RESULTS AND DISCUSSION

The absorbance spectra and photo images of as-made AuNPs at concentrations of 47, 94, 188, 282, 376, and 470 mg/L are shown in inset pictures of Fig. S1(a). AuNPs have a light red color at 47 mg/L, and as increasing of AuNPs concentration, the color changed to be dark red, which is a typical color of gold nanoparticles with a size of 20 nm [20]. When the concentration of AuNPs is higher than 282 mg/L, noise in UV-vis absorbance spectra is observed at wavelengths below 600 nm. Because the maximum absorbance intensity is significantly high, the concentration of AuNPs was mainly performed at concentrations of 200 mg/L or lower for aggregation between AuNPs and PSNPs. Fig. S1(b) shows the absorbance linearity of AuNPs at various wavelength of 560, 580, 600, 620, 640, and 660 nm with respect to the concentration. Except for the 560 nm wavelength where noise appears, the concentration and absorbance of AuNPs at each wavelength showed good linearity.

To observe the color change due to aggregation between AuNPs and PSNPs, the effect of ions in the medium should be evaluated. The ionic strength of the AuNPs and PSNPs solution was measured to determine the concentration of NaCl for clearly aggregated point of AuNP and PSNP. To measure the ionic strength of the AuNPs, the NaCl concentration was increased from 0 to 50 mM at intervals of 5 mM, and HDD change of the AuNPs was measured with DLS (Fig. S2(a)). As shown in the graph, the ionic strength for AuNPs is obtained as 12.3 mM of NaCl. When the NaCl concentration increases to a value higher than this concentration, the size of the AuNP aggregates increases rapidly. When a salt such as NaCl is added to AuNPs, the zeta potential of AuNPs is decreased from -35 mV to -19 mV, and thus the stability of the particles is reduced, followed by readily aggregation between AuNPs. On the other hand, hydrophilic PSNPs modified with carboxyl groups were expected to have high ionic strength due to excellent particle stability. The ionic strength of PSNPs with a size of 350 nm is 750 mM, as shown in Fig. S2(b). This indicates that the PSNPs do not aggregate at NaCl concentration for AuNPs aggregation point (12.3 mM). In addition, PSNPs are highly dispersed in aqueous phase and do not easily aggregate, suggesting that they can act as a long-

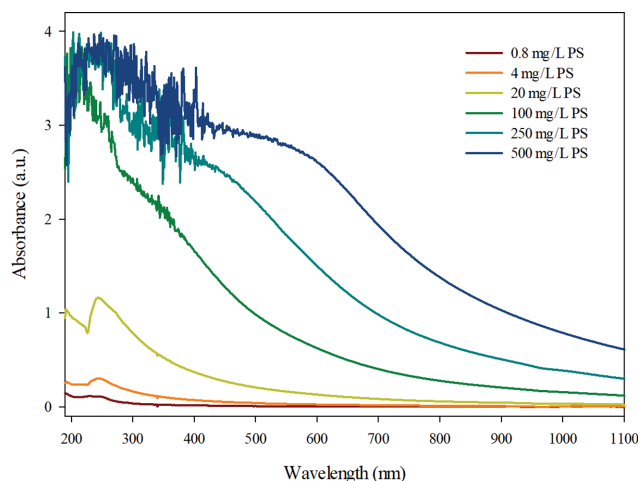


Fig. 2. Absorbance spectra of different concentrations of PSNPs.

term exposure source in the water phase.

Fig. 2 shows the absorbance spectra of 8-500 mg/L of 350 nm-sized PSNPs. The absorbance peak is located in the wavelength range of 230-245 nm. However, at a concentration of 100 mg/L or higher, the noise is sufficiently high to measure. Therefore, it is not easy to find the linearity between absorbance and concentration of PSNPs in the solution. Namely, because it is challenging to measure the absorbance of high-concentration PSNPs, the aggregation experiments were performed using low-concentration PSNPs.

In the aggregation test, regardless of the addition of small amount of PSNPs (0.8 μ g/L) to the colloidal gold solution of the same concentration, the absorbance spectra do not change (Fig. 3(a)). This indicates that no change in absorbance is observed because it is a simple mixing of a trace amount of PSNP in the AuNP solution. However, when aggregation occurs by addition of NaCl to AuNPs solution, the presence or absence of PSNPs affects the absorbance spectra. The difference is discernible in the wavelength region longer than approximately 600 nm, and not in the vicinity of the plasmon resonance peak at 550 nm. As shown in Fig. 3(b), when 30 mM NaCl is added in the solutions of AuNPs and PSNPs, followed by stirred for 3 min, absorbance spectra in the range of 600 to 1,200 nm are significantly changed, compared to that observed in Fig. 3(a) before aggregation. Namely, depending on the presence or absence of PSNPs, the aggregation properties of AuNPs by the addition of NaCl were different. When AuNPs aggregate, it can be considered that absorbance change is observed because the morphology of the aggregation changes under the influence of the surrounding PSNPs. According to previous studies, the aggregation of AuNPs tends to cause or inhibit aggregation, further depending on the presence or absence of the target material. This causes color and absorbance changes due to aggregation [16]. This feature provides a clue that aggregation of AuNPs around PSNPs may enable one to analyze the concentration of PSNPs in the solutions.

To determine the absorbance change of the AuNPs solution with and without PSNPs after aggregation, the difference in absorbance for ca. 200 mg/L AuNP with PSNPs was measured as shown in Fig. S3. The concentration of PSNPs was changed from 3.2×10^{-3} to 200 mg/L, and the absorbance of various wavelength in UV-vis

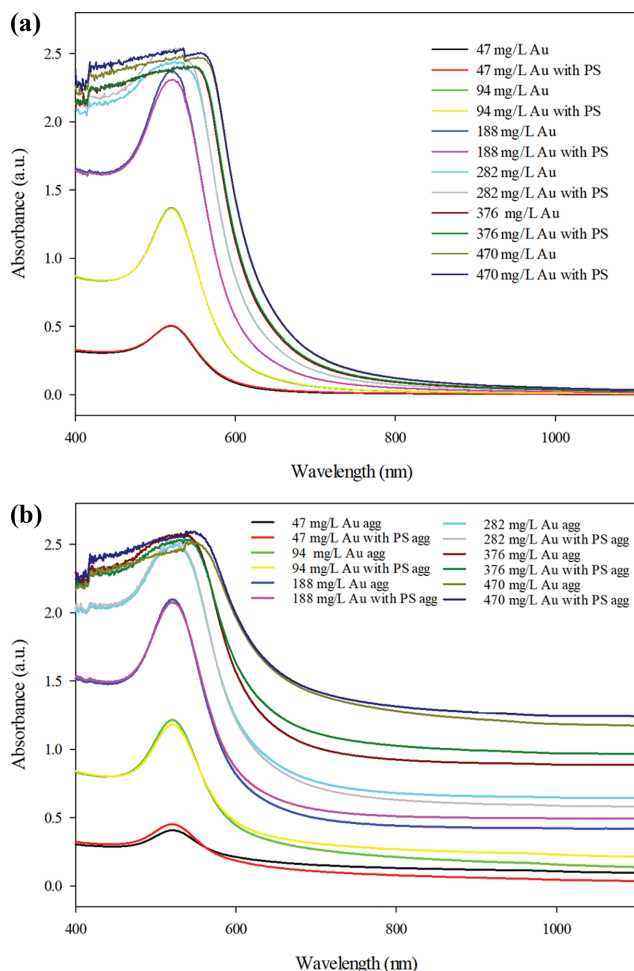


Fig. 3. Absorbance spectra (a) before and (b) after adding 30 mM NaCl to a mixed solution of $0.8 \mu\text{g/L}$ of 350 nm-PSNPs and AuNPs with a concentration of 47–470 mg/L.

spectra in Fig. 3(b) after aggregation was measured at each concentration. At high concentrations of 0.32 mg/L or higher, the absorbance tended to increase with the concentration of PSNPs, but at a concentration lower than 0.32 mg/L, rather than decreasing, the absorbance increased. Namely, there was no linearity in the variation of absorbance with PSNP concentration in the corresponding range for each wavelength at 10 nm intervals from 600 nm to 700 nm wavelength.

To find the appropriate aggregation point between AuNPs and PSNPs with NaCl addition, an additional aggregation test was performed with different concentrations of AuNPs and NaCl. When 50 mM NaCl was added to 400 mg/L AuNPs for aggregation, all of them aggregated rapidly, except for PSNPs with a high concentration of 0.035 mg/L, and most of them formed a precipitate and settled down at the bottom in vial. It seems that excessive aggregation occurred by adding 50 mM NaCl to AuNPs with an ionic strength of 12.3 mM. While the low-concentration of PSNPs with AuNPs and NaCl addition readily formed a precipitate due to the aggregation between each AuNPs; the high-concentration of PSNPs with AuNPs and NaCl addition did not form a precipitate. This seems to be because when there is a high concentration of PSNPs,

all sodium or chloride ions in aqueous solution do not contribute to weakening the surface charge of AuNPs, but also are hindered to form aggregation between each AuNPs or AuNPs-PSNPs by the carboxyl groups on the surface of PSNPs. While the surface charge of 350 nm- and 880 nm-PSNPs for high concentration without addition of NaCl was -21.8 and -25.3 mV, respectively, that after addition of NaCl was slightly changed as -18.4 and -14.3 mV, respectively. Therefore, the test condition of 400 mg/L AuNPs with 50 mM NaCl was not suitable to find the linearity for the concentration of PSNPs.

Fig. S4(a) shows the absorbance change after the aggregation experiment under the conditions of 300 mg/L AuNPs and 50 mM NaCl. It can be seen that excessive aggregation occurred and the characteristic peak of AuNPs at a wavelength of 520 nm disappeared. As similar to Fig. 3, aggregation negligibly occurred at a high concentration (0.089 mg/L) of PSNPs, but rapid aggregation occurred at concentrations lower than 0.089 mg/L, and the color of the solution changed to a darker color. The absorbance intensity with concentration of PSNPs did not find the linearity in the full range of wavelength. Fig. S4(b) shows the aggregated HDD according to the concentration of PSNPs. At 0.089 mg/L of PSNPs, where aggregation negligibly occurs, two peaks of 23.7 (AuNPs) and 353 nm (PSNPs) are measured, indicating that the AuNPs and PSNPs used in the experiment are dispersed in a non-aggregated state. That is, while a small amount of PSNPs is added to a colloidal gold solution and aggregated with NaCl, similar aggregation occurs at relatively high concentration of PSNPs.

As additional test to find the linearity of the PSNPs concentration under the conditions of 300 mg/L AuNPs and 50 mM NaCl, the ratio of the absorbance values at wavelengths of 630 and 520 nm was determined. This method was previously used to determine the linearity, using the ratio of the absorbance value at a wavelength of 520 nm, which is a typical plasmon peak of AuNPs, and that at a wavelength of 630 nm, where the intensity changes owing to aggregation [26]. However, no linearity was observed even if the absorbance ratio value of 0.089 mg/L PSNPs, in which aggregation hardly occurred, is excluded. Because it is necessary to measure the absorbance when AuNPs or PSNPs are mixed together, rather than without mixing, aggregation experiments and absorbance analysis have been conducted under various concentration conditions. As shown in Fig. 3(b), the difference in absorbance before and after aggregation is significant, so the difference in absorbance is also measured in the following aggregation experiment.

Finally, to conduct an aggregation test under less excessive conditions than the previous test that caused excessive aggregation using 50 mM NaCl, an aggregation test was performed with 20 mM NaCl and 100 mg/L AuNPs. Fig. 4 shows the absorbance spectra after adding 1–10 mg/L of 350 nm-sized PSNPs and 880 nm-sized PSNPs to 100 mg/L AuNPs and aggregating them with 20 mM NaCl. For comparison, the characteristic peak at 520 nm in absorbance spectrum of 50 mg/L AuNPs was maintained. As the concentration of PSNPs increases, the absorbance at wavelengths in the range of 500–700 nm increases. For 880 nm-sized PSNPs, the absorbance constantly increases as the concentration increases. Because of the slow aggregation at low NaCl concentrations, most of the aggregation observed is reversible, as shown in Fig. 5. The

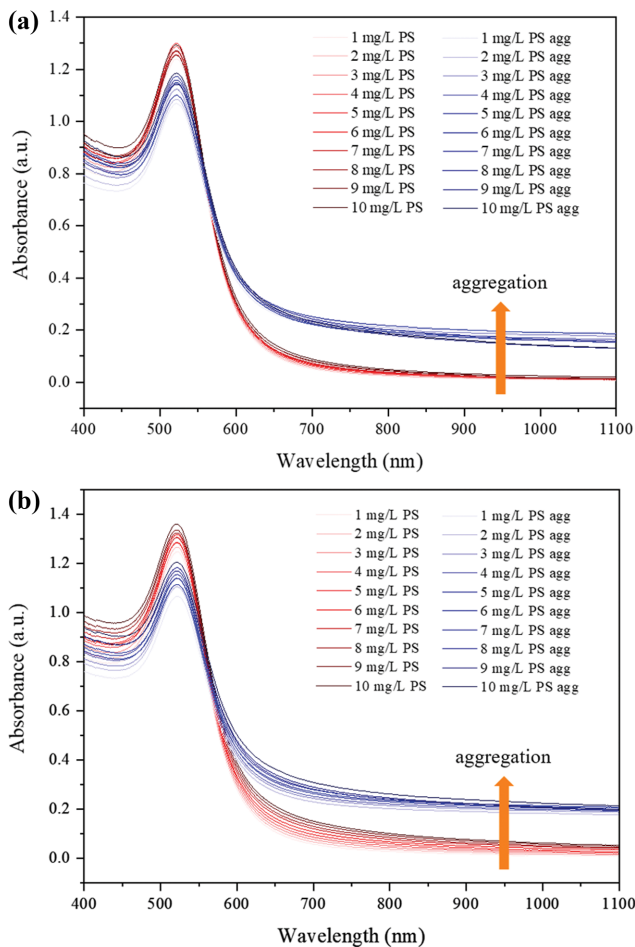


Fig. 4. Absorbance spectra after adding 1-10 mg/L of (a) 350 nm-sized PSNPs and (b) 880 nm-sized PSNPs to 100 mg/L AuNPs and aggregation with 20 mM NaCl.

weak aggregation of AuNPs increases the linearity of the change in absorbance with the increase in the concentration of PSNPs and, thus, it is easier to calculate the concentration of PSNPs from the change in absorbance.

As shown in Fig. 4, after aggregation of both the 350 and 880-nm-sized PSNPs, the plasmon peak intensity at 520 nm decreases and the absorbance increases at wavelengths longer than 600 nm. That is, after aggregation, the ratio of the absorbance at 520 and 650 nm decreases than that before aggregation. For example, as shown in Fig. 6(a), A_{520}/A_{650} of the 350 nm-sized PSNPs before aggregation is 12.1, but after aggregation it decreases to 4.1, and the difference between the two status is 8. The difference in the absorbance ratio before and after aggregation is shown with respect to the concentration of PSNPs in Fig. 6. The diamond solid line shows a linear decrease as the concentration of PSNPs increases in the given PSNP concentration range of 1-10 mg/L. Fig. 7 shows the regression of the absorbance ratio before and after aggregation with respect to the concentration of PSNPs. The coefficient of determination was calculated as 0.97 for 880 nm PSNPs and 0.98 for 350 nm PSNPs.

This indicates that the concentration of PSNPs can be calculated from the difference in the absorbance ratio before and after aggregation. It is not easy to find the appropriate concentration of NaCl and AuNPs to form aggregation slowly between each AuNPs around PSNPs. Therefore, as described before, various testing conditions were conducted as trial-and-error method. To the best of our knowledge, this is the first attempt to measure the concentration of nano-scale microplastics using the change in absorbance. In addition to classical analysis methods, such as FTIR, Raman scattering, and GC/MS, new analysis methods, such as isotopes and fluorescence staining, can be used to directly analyze microplastics. However, the analysis method used in this study can be differentiated by analyzing the concentration of microplastics indirectly from the aggrega-

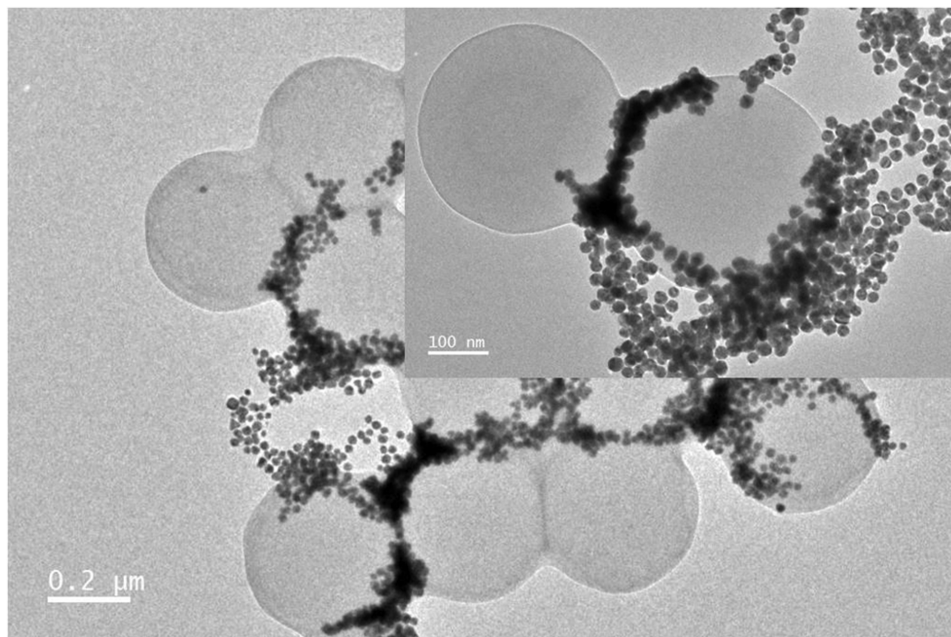


Fig. 5. TEM image in which 350 nm-PSNPs and 20 nm AuNPs were reversibly aggregated at 47 mM NaCl. Inset: TEM image, scale bar: 100 nm.

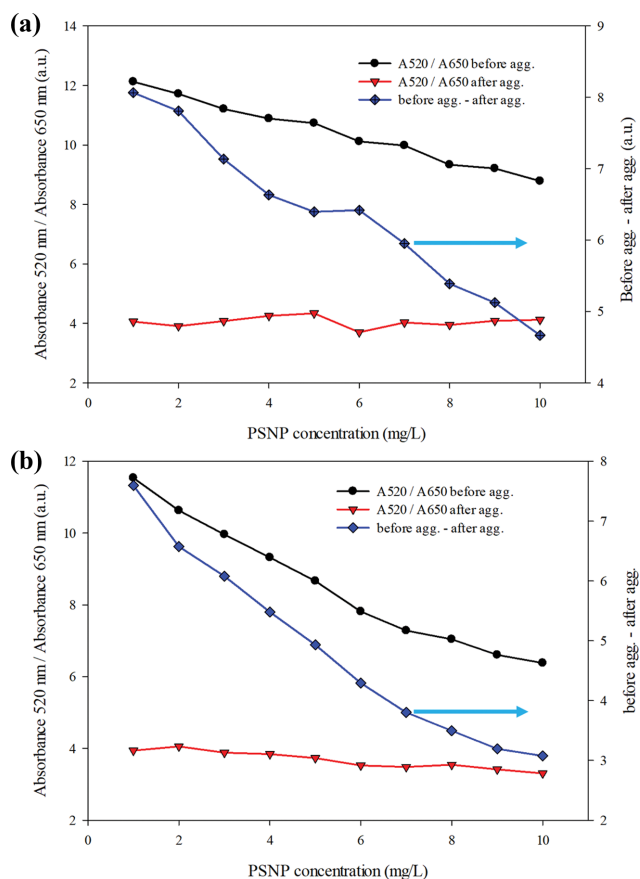


Fig. 6. The difference in absorbance before and after aggregation in the range of 1-10 mg/L concentration of (a) 350 nm-sized PSNPs and (b) 880 nm-sized PSNPs.

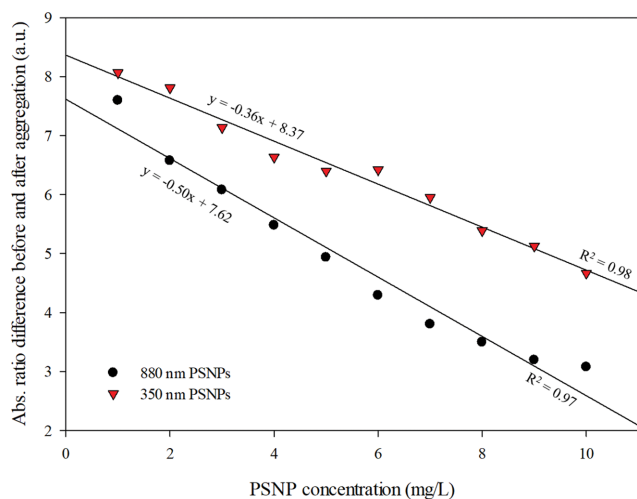


Fig. 7. Graph showing the difference in absorbance ratio before and after aggregation of PSNPs of 350 and 880 nm-sized PSNPs and the concentration of PSNPs by regression.

gation of AuNPs. Furthermore, because 350 and 880 nm-sized PSNPs show different regression lines, there is a possibility that information about the size can be approximated by this method, unlike by thermal analysis such as py-GC/MS, in which the infor-

mation on the size of nanoparticles is lost. Because the existing analysis method is limited to investigating the size information by directly measuring nanoscale microplastics, the application of this novel analysis method provides an alternative for size measurements.

CONCLUSIONS

The currently used microplastic analysis method in the nanoscale is limited, and information on the size cannot be investigated by thermal analysis. To measure the concentration of nanoscale sub-micron sized plastics, 350 and 880 nm-sized PS nanoparticles were dispersed in a colloidal gold solution and agglomerated with NaCl. After dispersing 1-10 mg/L of PSNPs in 100 mg/L AuNPs, they were aggregated by adding 20 mM NaCl. As a result of measuring the absorbance after and before aggregation, the plasmon peak intensity at a wavelength of 520 nm after aggregation decreased and the absorbance at wavelengths longer than 600 nm increased. It showed a linear relationship with the concentration of PSNPs based on the difference in absorbance ratio (A_{520}/A_{650}). In the aggregation experiment on 350 and 880 nm-sized PSNPs, each regression line was different. Thus, the concentration and size of PSNPs could be measured from the difference in absorbance before and after aggregation after the addition of NaCl. To the best of our knowledge, this is the first attempt to measure the concentration of nanoscale microplastics using the difference in absorbance. This proposed methodology has still many limitations to apply for other plastics, various size, and media type. Moreover, detection of nanoplastics in the environment is extremely difficult due to their low concentration relative to other substances of interest. Only a few papers have been published so far addressing the quantification of nanoplastics in real environmental samples [27]. Therefore, a sampling method study suitable for nanoplastics should be preceded, like continuous flow centrifugation, which is currently being studied [28]. Nevertheless, we hope that this suggestion will give rise to a new measurement method that can be used to measure various sizes and types of microplastics in the future.

ACKNOWLEDGEMENTS

This work was supported by Korea Environment Industry & Technology Institute (KEITI) through Measurement and Risk assessment Program for Management of Microplastics Project, funded by Korea Ministry of Environment (MOE) (2022003120002).

SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at <http://www.springer.com/chemistry/journal/11814>.

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Supporting Information

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(Received 18 January 2022 • Revised 12 April 2022 • Accepted 24 April 2022)

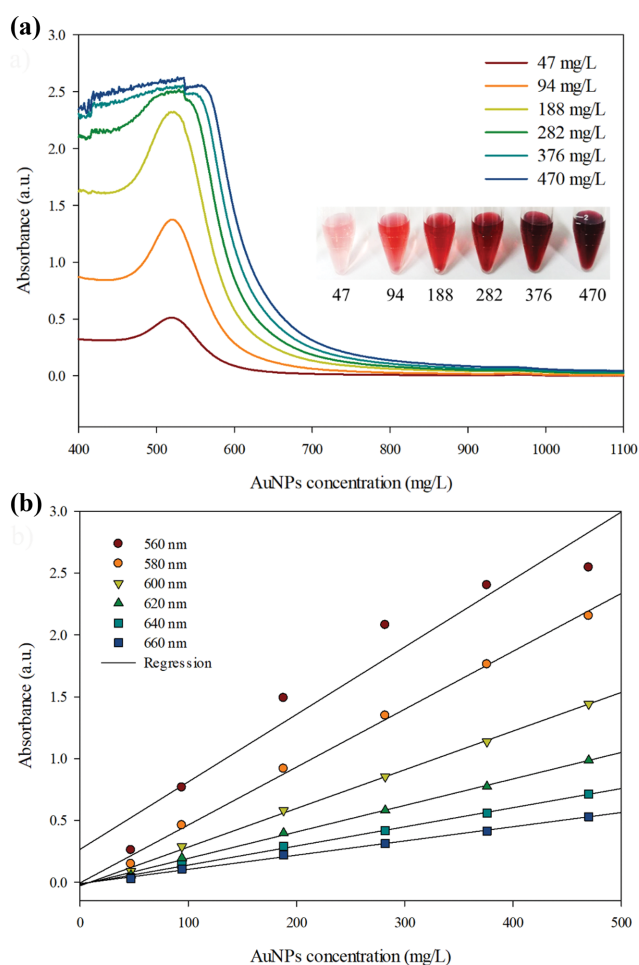


Fig. S1. (a) Absorbance spectra of AuNPs of 47-470 mg/L concentration. Inset shows photographs of gold colloid. (b) Absorbance intensity variation with various AuNP concentrations in the wavelength range of 560-660 nm.

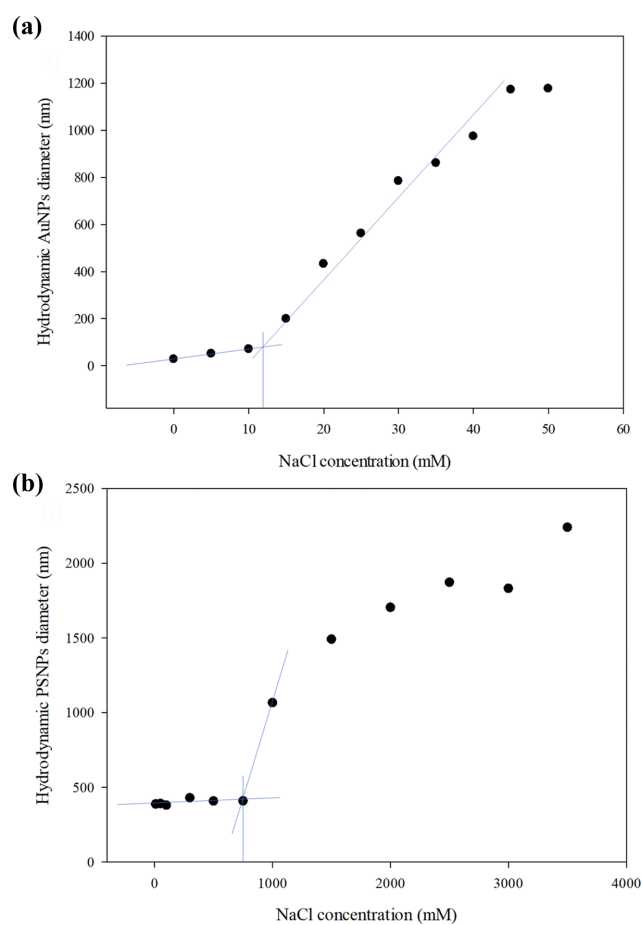


Fig. S2. The change in HDD of (a) AuNPs and (b) PSNPs with different NaCl concentrations.

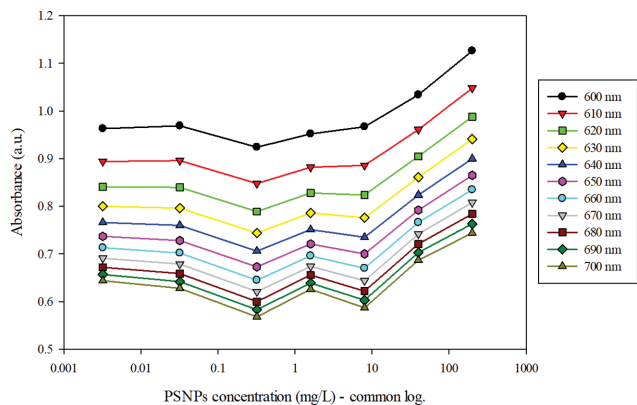


Fig. S3. Absorbance graphs of various wavelength in UV-vis spectra in Fig. 2(b), after various concentrations of PSNPs were added to ca. 200 mg/L AuNPs and then agglomerated with 30 mM NaCl for 3 min.

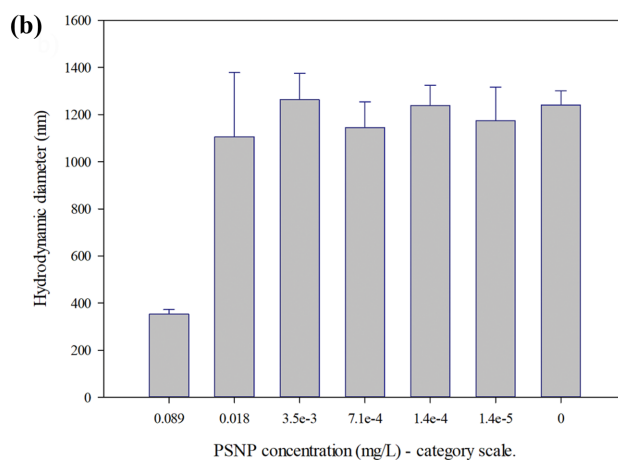
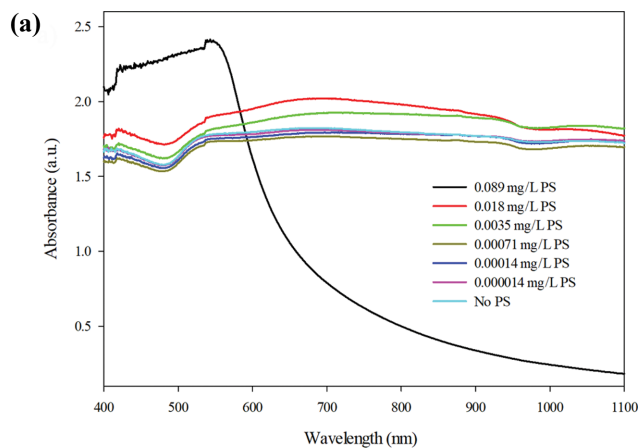


Fig. S4. (a) Absorbance spectra at different PSNP concentrations in 300 mg/L AuNPs, 50 mM NaCl. (b) HDD of aggregates at different PSNP concentrations after aggregation.