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Sonication synthesis of micro-sized silver nanoparticle/oleic acid liquid marbles: a novel SERS sensing platform

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ABSTRACT

Liquid marbles are entities made of a small amount of liquid encapsulated by micro/nano scale particles. The functionality of liquid marbles depends on both the core liquid and particle coating. In this work, functional silver nanoparticle (Ag NPs)/oleic acid liquid marbles are developed using Ag NPs to encapsulate micro-sized oleic acid liquid spheres, which is achieved *via* sonication. We demonstrate that both the size of the encapsulated spheres and the order of the Ag NPs coating are a function of the sonication time. These micro-sized liquid marbles are investigated for sensing an organic thiolate as a model material. Their capacity for increasing solar light absorption and energy conversion into heat is also studied. The liquid marbles generated after sonication for 60 min show the strongest Raman peak signals which originate from the thiolate. They also demonstrate the highest solar energy absorption. We ascribe these enhancements to the increased surface area of the Ag NPs/oleic acid spheres and the optimum order of Ag NPs to produce the strongest surface enhanced Raman scattering. The liquid marbles can be used for the development of future biosensors and solar-thermal absorbers.

KEY WORDS: Liquid marble; Sonication; Oleic acid; Silver nanoparticle; Surface-enhanced Raman scattering

1. Introduction

Liquid marbles are liquid droplets encapsulated by micro- or nano-sized particles.[1, 2] The encapsulated liquid is separated from the outside media, which is either air or liquid, resulting in a non-adhesive entity. This unique structure provides the potential for liquid marbles to be used for a variety of applications such as sensing,[3, 4] liquid manipulations and microfluidics,[5, 6] and establishment of micro-reactors.[5] Magnetic particles have also been utilised in ferrofluid marbles and have been shown to deform under the application of an external magnetic force.[7, 8] Besides macroscopic liquid marbles, marbles with micro and nano-sizes have also been developed *via* breaking down bulk liquid droplets in suspensions of fine particles, typically under high sonication forces.[9] This results in complex and small-sized liquid marbles that can be used in suspension or in packed films. Depending on the choice of liquid core and coating, these liquid marbles offer a variety of functionalities. We have previously demonstrated applications of such liquid marbles, when the core is made of liquid metal, for sensing, catalysis, and plasmonics.[10-12] Micro- or nano-sized liquid marbles have also been applied in the development of cosmetics and pharmaceuticals, when suitable liquid cores and coatings are chosen.[13] Both cores and coatings can have significant effects on the functionality of these micro- and nano-sized marbles. However, the incorporation of a metallic coating on a liquid core has not been fully considered so far. Metallic coatings can be of special interest, as they can play the base for surface-enhanced Raman scattering (SERS).

SERS is a process in which Raman signals of molecules are enhanced by augmented local electromagnetic fields at nano-sized tips and boundaries of a material.[14] It is generally suggested that the excited surface plasmon resonances (SPRs), which are collective electron excitations, can significantly enhance the local electromagnetic field.[15] In particular, it is known that noble metal nanoparticle assemblies and complex structures are capable of

producing strong SPRs at visible wavelengths.[14] Relevant observations have led to considerable research on the development of silver (Ag), platinum (Pt) and gold (Au) nanostructures, consisting of nanoparticles,[16, 17] nanoshells,[18, 19] nanoplates,[20, 21] nanorods,[22, 23] and nano-sized dendrites.[24, 25]

Most recently, it has been demonstrated that a liquid-liquid interface, such as oil-water, can facilitate the accumulation of Ag, Pt and Au nanoparticles (NPs) at the interface.[22, 26-28] The established systems are capable of probing oil-soluble molecules, by taking advantage of their plasmonic properties. The idea of using such functional interfaces is attractive. However, the potential of these liquid-liquid interfaces is limited by their surface area. Enhancing the surface area of such interfaces, by micro- and nano-structuring processes, can increase the chances of interactions between the marbles and dissolved chemical species, resulting in augmented performances in applications such as catalysis,[11, 12] energy storage/generation[29, 30] and sensing.[3, 31]

Sonication is commonly used in material processing, such as breaking down aggregates and the synthesis of particle suspensions.[32, 33] It is also an effective approach to produce micro- and nano-spheres of one immiscible liquid in another.[9, 34-36] Advantageously, the size and surface morphology of these spheres can be tuned by varying factors such as sonication time, power and temperature.[11, 12]

In this work, we demonstrate the formation of a suspension of Ag NPs encapsulated oleic acid micro-sized liquid marbles in water. These liquid marbles are synthesized using sonication and their functional properties are investigated. We show that this innovative yet simple method can control the dimensions of the marbles and the compactness of the Ag coating as a function of the sonication time. Two model applications are demonstrated: one

shows the possibility of SERS enhancement for the sensing of chemical species and the other illustrates the illumination induced heating effect.

2. Experimental

2.1 Synthesis of micro-sized Ag NPs/oleic acid liquid marbles

Fig. 1 illustrates the process for producing the suspensions of oleic acid micro-sized droplets with a coating of Ag NPs. To produce the liquid marble suspensions, 1 mL of high purity oleic acid ($\geq 99\%$ Sigma-Aldrich) was added into a glass vial filled with 6 mL of DI water. 6 mg of dry Ag NPs powder (Sigma-Aldrich diameter < 70 nm) were added to the vial. The vial was kept in a sonication bath (UNISONICS AUSTRALIA, FXP10DH, 240V AC, 5 V, 50 Hz) at 25 °C for a desired time.

2.2 Preparation of thiolate suspensions

The upper layer of the suspensions shown in Fig. 1d was collected. In the investigation of sonication time effects on Raman signals for thiolate molecules, each testing sample was made by mixing 0.5 mg of sodium 1-phenyl-1H-tetrazole-5-thiolate (PPT) with 10 μ L of Ag NPs/oleic acid liquid marble suspensions. Four liquid marbles were chosen. They were prepared after sonication for 20, 40, 60 and 80 min, respectively. As a control measurement, 0.5 mg of PPT was dissolved in 10 μ L of pure oleic acid. The liquid marble suspensions and oleic acid were drop casted on glass substrates coated with Au/Ti (100nm/10nm) layers. In addition, 0.5 mg of PPT was also placed on this substrate and measured, as a benchmark. All liquid marbles and oleic acid were incubated together with PPT for 40 min prior to measurement.

In the investigation of different loadings of thiolate, each testing sample was made by mixing different amounts of PPT with 10 μ L of the Ag NPs/oleic acid liquid marble suspension after 60 min of sonication. Four different amounts of PPT were chosen, which were 0.4, 0.6, 1.2 and 2 mg. As a control measurement, 0.4 mg of PPT was placed on the glass substrate coated with the Au layer (mentioned above). The extra incubation time of all samples was also 40 min.

2.3 Characterization of light absorption

Four groups of Ag NPs/oleic acid liquid marble suspensions were prepared (20, 40, 60 and 80 min, respectively) under the same procedure shown in Fig. 1. Pure oleic acid (7 mL) was also added to a similar glass vial as a control sample. These five glass vials were placed under a simulated solar lamp (Abet Technologies LS150) and illuminated simultaneously for 30 min. The lamp was located at a distance of 10 cm from the top surface of the vials. Thermal images were taken using a FLIR ThermoVision A320 camera. The ambient temperature was 24 °C.

2.4 Other characterization

Optical images were obtained using a Nikon Eclipse Ti optical microscope. Average sizes of oleic acid spheres were evaluated using the software ImageJ. We utilized a FEI Quanta 200 Environmental scanning electron microscope and a JEOL 2100F High resolution transmission electron spectroscopy (HRTEM) for Environmental scanning electron spectroscopy (ESEM) and Transmission electron spectroscopy (TEM), respectively. The UV-visible (UV-vis) measurements were conducted using a CRAIC 20/30 microspectrophotometer with a 150 W Xenon lamp source. We used a $\times 15$ mirror lens with a numerical aperture (NA) of 0.28 and a focal distance of 35 mm. Small angle X-Ray scattering (SAXS) measurements were performed on a Bruker Microcalix instrument, using 50 W Cu

K α radiation at a wavelength of 1.54 Å. Scattered light was detected using a Pilatus 100 k detector. Scattering and transmission measurements were performed with 1 hour exposure time. The Raman spectra were obtained using a Perkin RamanStation 400F with an excitation wavelength of 785 nm. The laser has a set power of 350 mW with a working distance of 15 mm and a spot size of 100 μ m in diameter. Each sample was measured 10 times with a 5 s exposure time. For the Raman measurement, the centre of a liquid marble was chosen to obtain the maximum SERS signal.

3. Results and discussion

The optical images of the suspensions of micro-sized Ag NPs/oleic acid liquid marbles are shown in Fig. 2a. It is observed that after sonication for 60 min, the original oleic acid droplet is broken down into micro-sized spheres which are coated with Ag NPs. Fig. 2b shows the magnified image. It is seen that the Ag NPs form a relatively uniform coating on the surface of the oleic acid spherical droplets. The nearly transparent area on some of the spheres could be due to a less dense coating of nanoparticles. Fig. 2c shows the TEM image of only Ag NPs. It can be seen that the dimensions of Ag NPs are less than 30 nm. Fig. 2d shows the selected area electron diffraction (SAED) pattern of Ag NPs. This pattern corresponds to the (1 1 1), (2 0 0) and (2 2 0) planes of Ag.[37]

To characterize the size distribution of liquid marbles, we compared the optical images of the Ag NPs/oleic acid liquid spheres synthesized after four different sonication times (Fig. 3). The average diameters of the liquid marbles were obtained using the software ImageJ. In Fig. 3a, the average diameter of the spheres is \sim 175 μ m. As discussed previously, the transparent areas on the surface of some of the spheres is due to a less dense coating of Ag NPs. Increasing the sonication time results in a decrease in the diameter of the spheres, which can be observed in in Fig.s 3b and c. In addition, the coating of Ag NPs tends to be more uniform

after longer sonication times. In Fig. 3d, the average diameter of the oleic acid spheres is $\sim 110 \mu\text{m}$, after a sonication time of 80 min. The average diameters are included in Fig. 3e. It is seen that the average diameters of the spheres decrease almost linearly as the sonication time increases.

Fig. 4a compares the absorption spectra of Ag NPs/oleic acid liquid marbles synthesized after 20 and 80 min of sonication. The absorption spectrum of Ag NPs powder is also presented as a reference. There is a broad peak at $\sim 500 \text{ nm}$ in the spectrum of the reference Ag NPs, which is generally associated with SPR and indicates some aggregation of the Ag NPs.[38] The spectrum of the liquid marbles after 20 min of sonication also has an absorption peak at nearly the same wavelength. However, it was found to be significantly tapered. It seems that at this sonication time the coating is not thick enough to produce a strong signal. Interestingly, the absorption peak for the liquid marbles obtained after 80 min of sonication is located at a much lower wavelength of $\sim 400 \text{ nm}$. This blue shift could be associated with more order for the agglomeration of Ag NPs on the surface oleic acid droplets due to the longer sonication time.[38, 39]

SAXS measurements were carried out to investigate the order of the Ag NPs coating distribution on the oleic acid spheres. The results are shown in Fig. 4b. It can be seen that the bandwidth of the lowest peak reduces by increasing the sonication time up to 60 min. This is associated with the higher order of the Ag NPs on the sphere. The silver nanoparticles in oleic acid appear to be clustering in some complex manner which cannot be simply modelled. The nanoparticles on the surface of oleic acid spheres show similar behaviour, suggesting that the nanoparticles are clustering. The sonication reduces the clustering, which increases the Ag NP orders and coat the droplets. The fact that the sample generated after 80 min of sonication show a less ordered behaviour suggests that this process is optimized at 60 min.

To further investigate the effect of sonication time on surface signals, we obtained and assessed the SERS spectra of PTT on the Ag NPs/oleic acid liquid marbles. The liquid marbles were obtained after 20, 40, 60 and 80 min of sonication. It has been reported that flat hydrophobic substrates are advantageous in concentrating target chemicals to enhance the SERS signal.[40] It should be noted here that PPT was mixed with Ag NPs/oleic acid liquid marbles through the same procedure for all samples to ensure consistency. It was found that the samples remained a stable suspension for at least an hour on the surface of the substrate. As a result, a relatively uniform distribution of PPT on the surface of liquid marbles was always accessible for measurements. All results were obtained under same condition for consistency. The SERS results are shown in Fig. 5a. The Raman peak shifts associated with PTT are marked with stars. The peaks at 414 and 700 cm^{-1} are ascribed to C-C torsion and C-C bending, respectively.[41] The peaks located at 1004, 1501 and 1599 cm^{-1} are related to vibrational modes of the phenyl ring.[41] N-N and N-C stretching coordinates contribute to the peak at 1094 cm^{-1} . [41]

As the peak at 1004 cm^{-1} is the strongest, its intensity is used as an indicator of the signal enhancing ability of the liquid marbles after four different sonication times. The comparison is shown in Fig. 5b. It can be seen that 0.5 mg of PTT on Ag NPs/oleic acid liquid marbles generates a much stronger Raman signal in comparison with the same amount of PTT on Au substrates. Among the four studied groups of liquid marbles, the PPT on the liquid marbles achieved after 20 min of sonication showed the weakest SERS response. The peak intensity showed a slight increase when the sonication time was increased to 40 min. By further increasing the sonication time to 60 and 80 min much stronger SERS responses were obtained, which are almost 10 times greater than those for PTT on the Au substrate. There was no noticeable difference in the responses for liquid marbles generated after sonication for 60 and 80 min.

As shown in Fig. 3, longer sonication times resulted in smaller average diameters of the liquid marbles. The decrease in the liquid marble sizes increases the size of oil-water interface, which allows more Ag NPs to be accessible. As a result, stronger SERS responses can be generated from liquid marbles after sonication for 60 and 80 min. As it has been reported that the enhancement depends on the degree of aggregation of NPs on the surface,⁷ it is likely that longer sonication times result in a more homogenous distribution of Ag NPs, with a more ordered structure (according to the SAXS patterns) that enhance the local electromagnetic field at hot spots and increases the overall SERS signal intensity.

Different loadings of PTT were then incorporated with Ag NPs/oleic acid liquid marbles after 60 min of sonication (the optimum time according to the previous experiments). The results are shown in Fig.s 6a and b. The control data is also provided. In Fig. 6b, the 0.4 mg of PTT on liquid marbles demonstrates a more intense Raman response, which is nearly 10 times greater than the control experiment. This is consistent with the measurement shown in Fig. 5. When increasing the amount of PTT from 0.4 to 2 mg, the peak intensity showed a near linear increase. It is believed that the binding between PPT and liquid marbles is via the formation of covalent bonds. Therefore, longer incubation time results in a higher concentration of PPT bonded to the surface of the Ag NPs. A similar near linear increase in SERS signal intensity was observed from the results of Raman measurements conducted after various incubation durations. The outcomes are shown in Fig. S1. The results were not normalized via the method reported by Gervinskis because the Raman measurements were conducted using a laser with a set power level.[42] However, all samples were measured 4 times and the average was taken to assure consistent and reliable measurements.

It is known that the intense absorption of SPR can be utilized for the absorption of solar energy and the conversion of energy to heat. The Ag NPs/oleic acid liquid marbles were evaluated under high intensity illumination of simulated solar light to investigate the light

harvesting properties of the liquid marbles obtained after different sonication times. Thermal images were taken of four different liquid marbles under the same illumination conditions. The exposure time was 30 min. The results are shown in Fig. 7. Pure oleic acid was also included as a control sample. It is observed that the final temperature of oleic acid is the lowest, reaching 32.9 °C. Among the four groups of liquid marbles, the one after 60 min of sonication demonstrated the highest temperature increase, reaching 35.1 °C. Temperatures of liquid marbles after 40 and 80 min of sonication reached very similar temperatures (34.6 and 34.5 °C, respectively), lower than the 60 min sample. The liquid marbles after 20 min of sonication had the lowest temperature rise. The Ag NPs/oleic acid liquid marbles showed the highest solar energy absorption efficiency when sonication time is 60 min. This can be ascribed to the higher order of the Ag NPs (according to the SAXS measurements) that is obtained after this sonication time. As the samples have the same concentration of oleic acid and Ag NPs, the temperature rise is most likely to be due to the localized heating effect of the plasmon resonances of the more ordered Ag NPs, which is induced by the light radiation.[43] The composition of the four groups of Ag NPs/oleic acid liquid marbles are quite similar. Therefore we make the assumption that their hue, opaqueness and colour are also very similar. As such, it is reasonable to assume the same thermal emissivity values for those four samples. The results therefore suggest that the sonication time varies the order of the Ag NPs coating, and that the different ordering of the NPs leads to different energy absorption properties.

4. Conclusion

In summary, we developed functional Ag NPs/oleic acid liquid marbles using sonication. The micro-sized oleic acid spheres are encapsulated by Ag NPs. We demonstrated that the size of marbles and the order of Ag NPs were functions of the sonication time. The size of liquid marbles showed a near linear decrease from ~175 to ~110 μm when the sonication time was increased from 20 to 80 min. The SAXS measurements showed that the highest

order for the Ag NPs was gained after 60 min of sonication time. At this sonication time the Ag NPs/oleic acid liquid marbles also had high surface to volume ratio, which led to its enhanced properties. We demonstrated that the Ag NPs/oleic acid liquid marbles could be utilized as an effective SERS platform for thiolate sensing, with the strongest signals obtained for a sonication time of 60 min. In addition, we also demonstrated that the Ag NPs/oleic acid liquid marbles are capable of absorbing solar energy, which we ascribed to the SPR generated by Ag NPs. After 30 min illumination, the liquid marbles prepared after 60 min of sonication had experienced the highest temperature increase of ~ 11 °C.

Altogether, our demonstrations showed two important effects of the sonication process: (1) the developed functional Ag NPs/oleic acid liquid marbles had an enhanced surface area for interactions with chemical components and light absorption and (2) the Ag NPs on the surface of the spheres were more ordered than the original powder in a suspension, which resulted in augmented LSPR. We believe that our Ag NPs/oleic acid liquid marbles have great potential in forming future sensing and optical devices, and should be further investigated in order to discover their multi-faceted properties.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at

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Fig. 1. Schematic illustrating the synthesis of Ag NPs/oleic acid liquid marbles. (a) Adding oleic acid into a glass vial filled with DI water, (b) adding Ag NPs into the vial, (c)

positioning the glass vial in a sonication bath for a desired time, and (d) obtaining the micro-sized Ag NPs/oleic acid liquid marble suspension.

Fig. 2. Optical image of (a) micro-sized Ag NPs/oleic acid liquid marbles after 60 min sonication, and (b) magnified image. (c) TEM image and (d) TEM diffraction pattern of Ag NPs.

Fig. 3. Optical images of Ag NPs/oleic acid liquid marbles after sonication for (a) 20, (b) 40, (c) 60, and (d) 80 min. Scale bar = 200 μm . (e) The plot of average diameters of oleic acid spheres coated with Ag NPs at four different sonication times.

Fig. 4. (a) UV–vis absorption spectra of micro-sized Ag NPs/oleic acid liquid marbles after different sonication times, and Ag NPs powder. (b) SAXS spectra of Ag NPs/oleic acid liquid marbles after four different sonication times. Inset shows the magnified region of interest.

Fig. 5. (a) Raman spectra of 0.5 mg PTT on Ag NPs/oleic acid liquid marbles after 20, 40, 60 and 80 min of sonication. The Raman spectra of 0.5 mg of PTT on Au substrate and in oleic acid are presented as control measurements. The Raman spectrum of Ag NPs/oleic acid liquid marbles after 60 min of sonication is also measured. The spectra were shifted vertically for clarity. (b) Raman peaks (1004 cm^{-1}) intensity of 0.5 mg of PTT on liquid marbles after four different sonication times, and on gold substrate.

Fig. 6. (a) Raman spectra of different loadings of PTT on Ag NPs/oleic acid liquid marbles after at 60 min of sonication. The spectra were shifted vertically for clarity. (b) Raman peaks (1004 cm^{-1}) intensity of different loadings of PTT on liquid marbles after 60 min of sonication. Raman peak (1004 cm^{-1}) intensity of 0.4 mg of PTT on Au substrate is also presented, shown as a yellow dashed line.

Fig. 7. Thermal images of Ag NPs/oleic acid liquid marbles after four different sonication times and pure oleic acid under illumination for 30 min. Room temperature is $24\text{ }^{\circ}\text{C}$.

Supplementary information

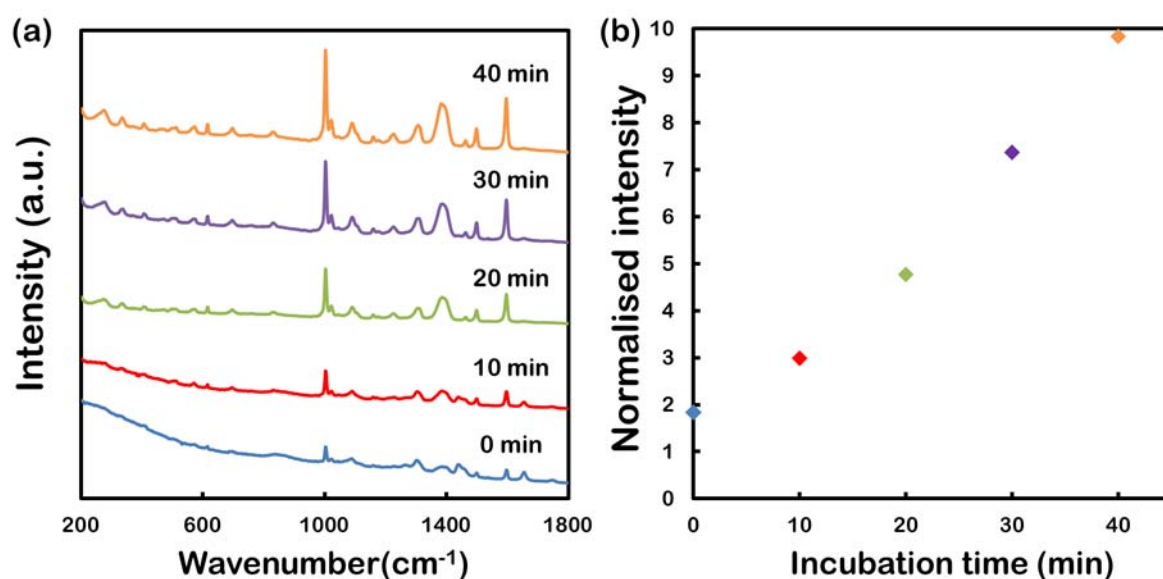


Fig. S1. (a) Raman spectra of 0.5 mg PTT on Ag NPs/oleic acid liquid marbles after 60 min of sonication. The incubation time is then varied. (b) Raman peak (1004 cm⁻¹) intensity of 0.5 mg of PTT on liquid marbles with various incubation durations on a gold substrate.

Fig. S1. shows the Raman spectra with respect to various incubation times. The amounts of PPT and Ag NPs/oleic acid liquid marbles were kept constant for consistency. The peak intensity also showed a near linear increase when the incubation time was increased.

80 min
34.6 °C

60 min
35.1 °C

20 min
33.8 °C

SP03

SP04

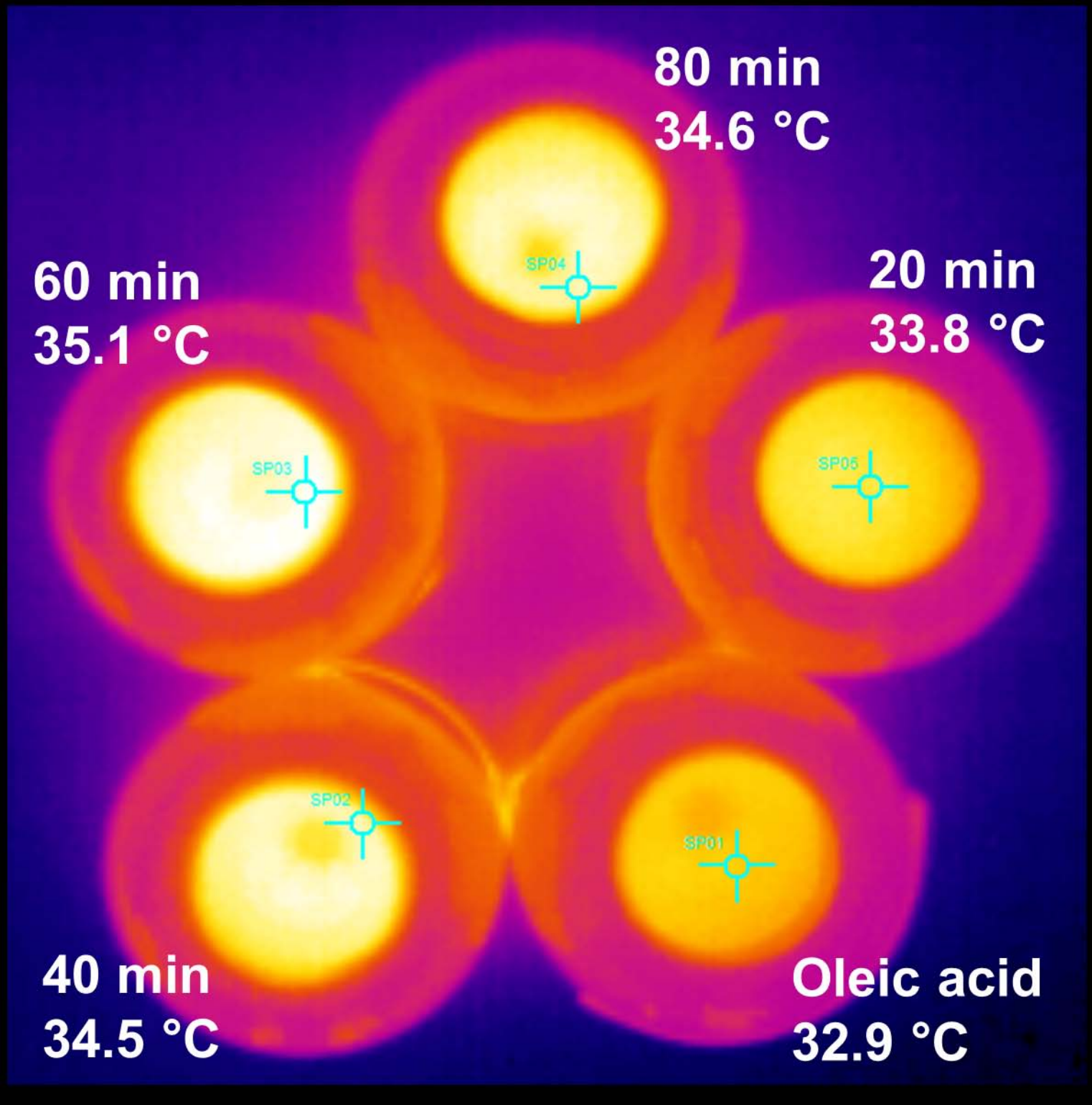
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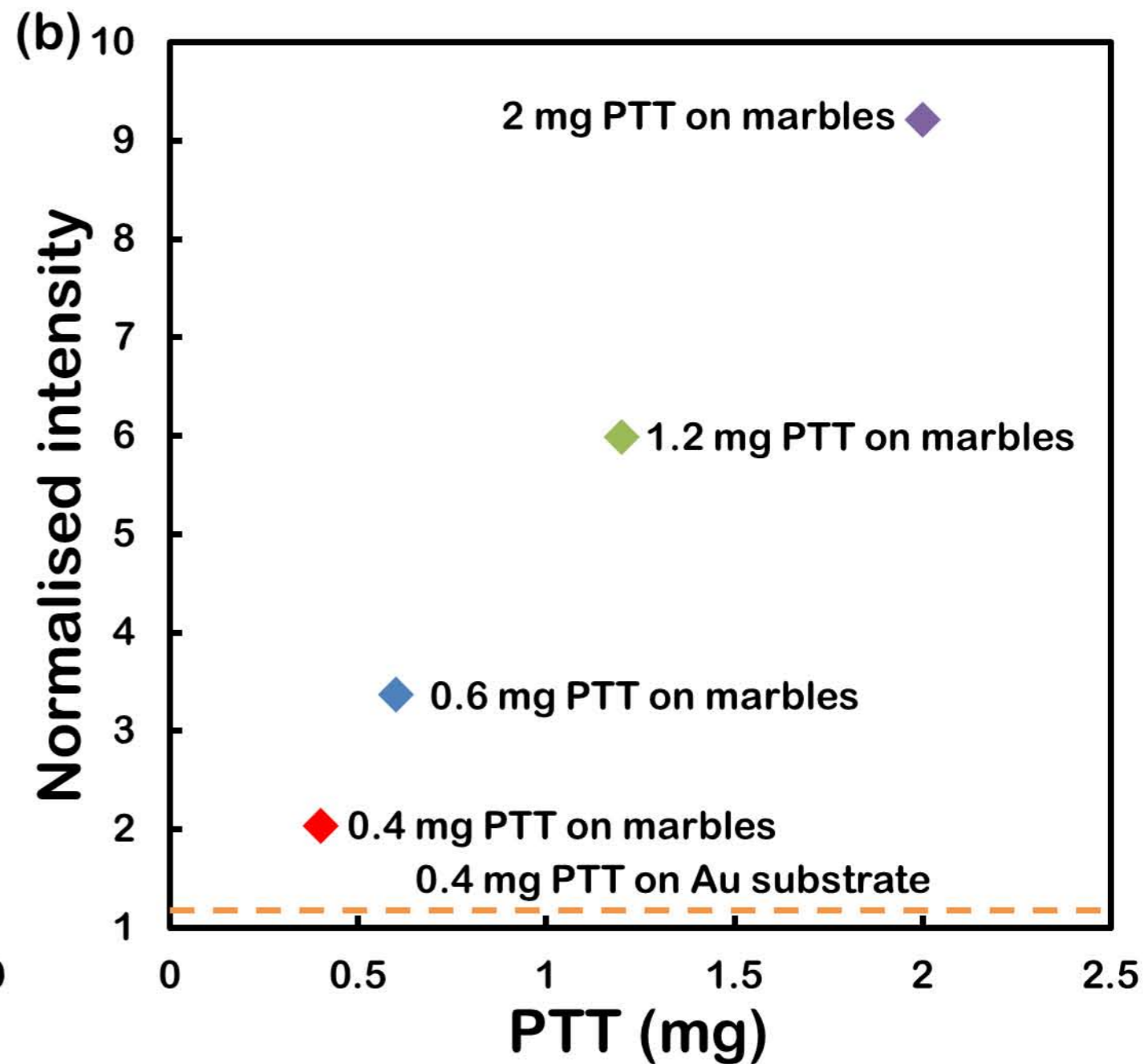
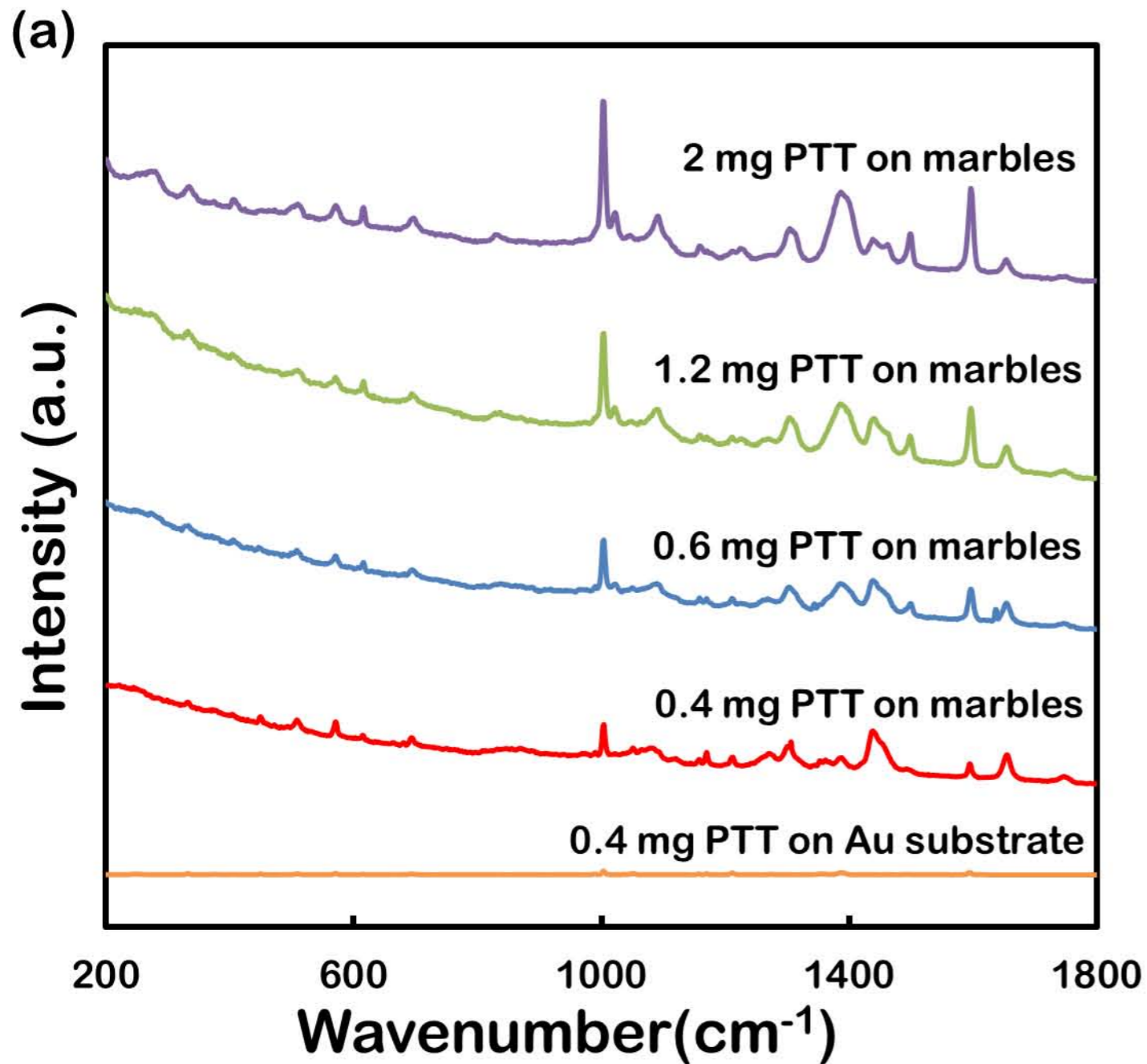
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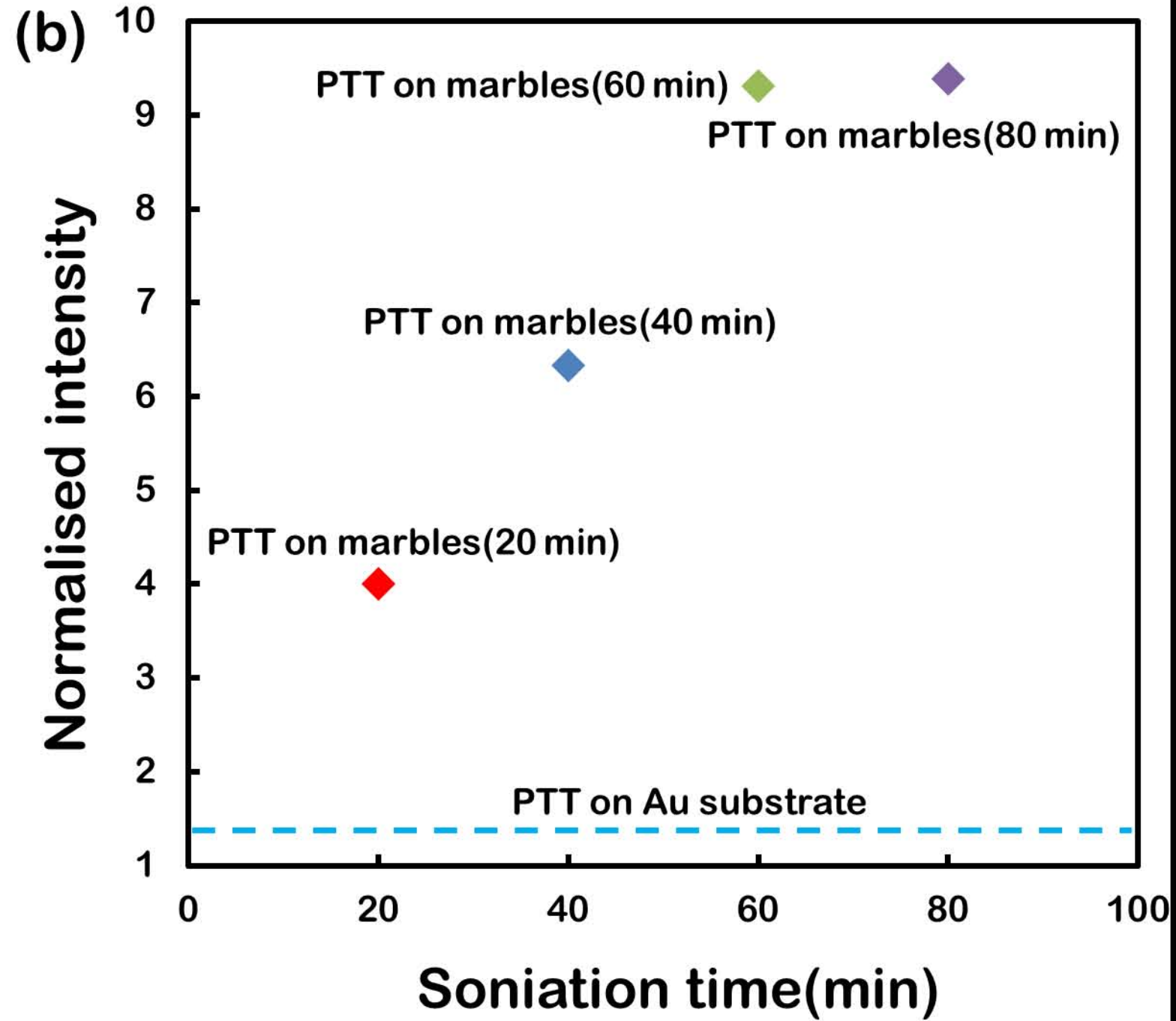
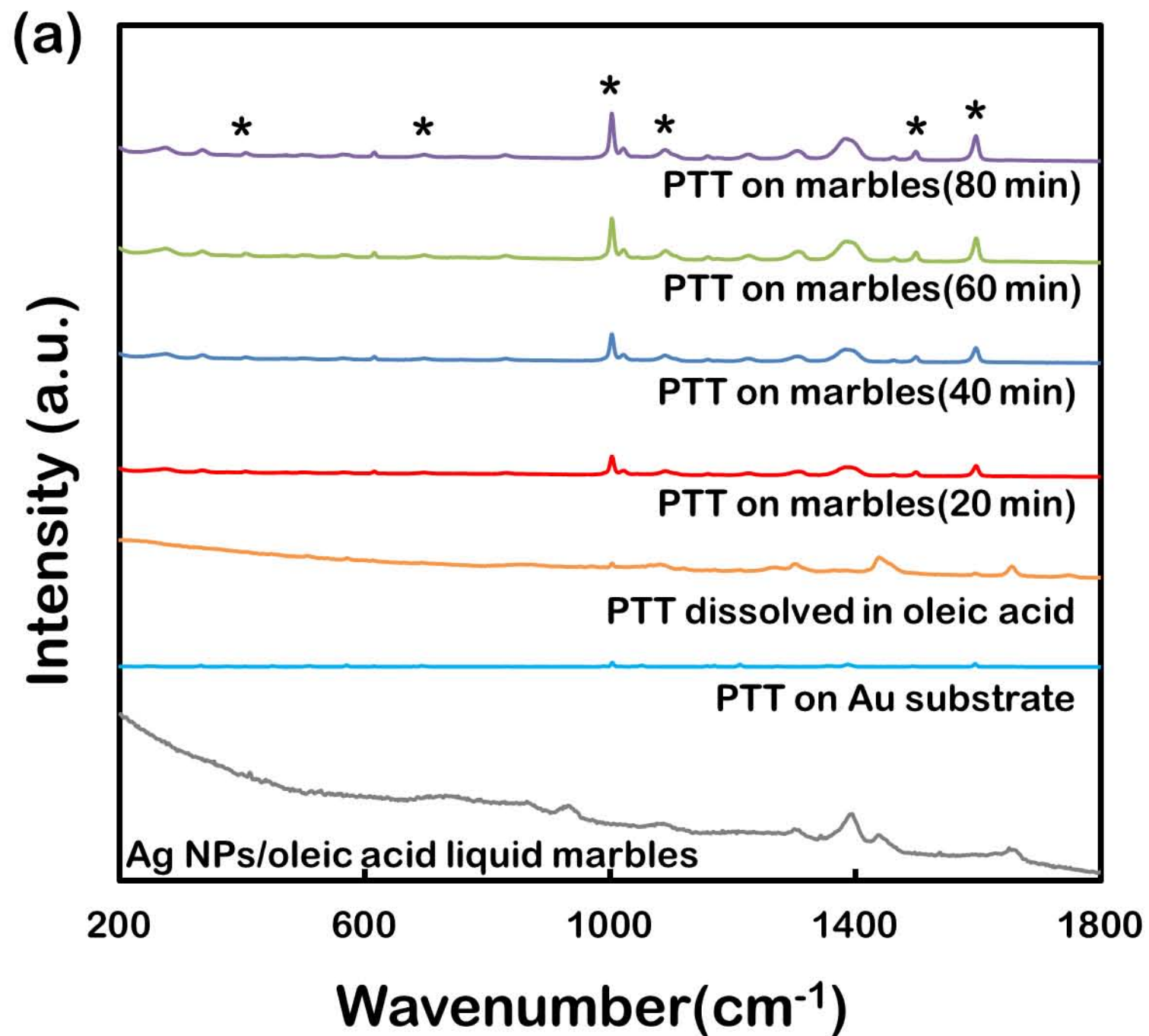
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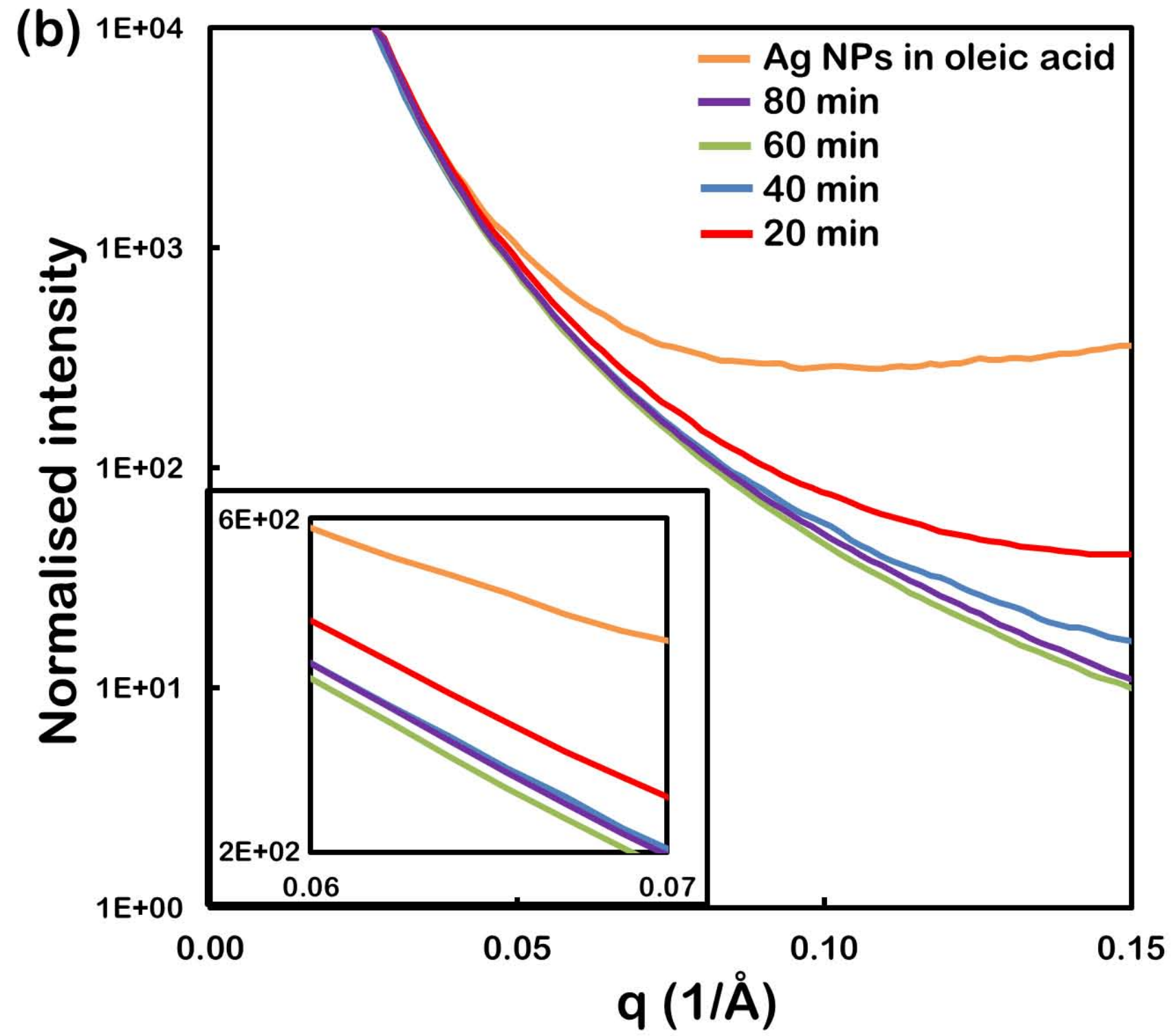
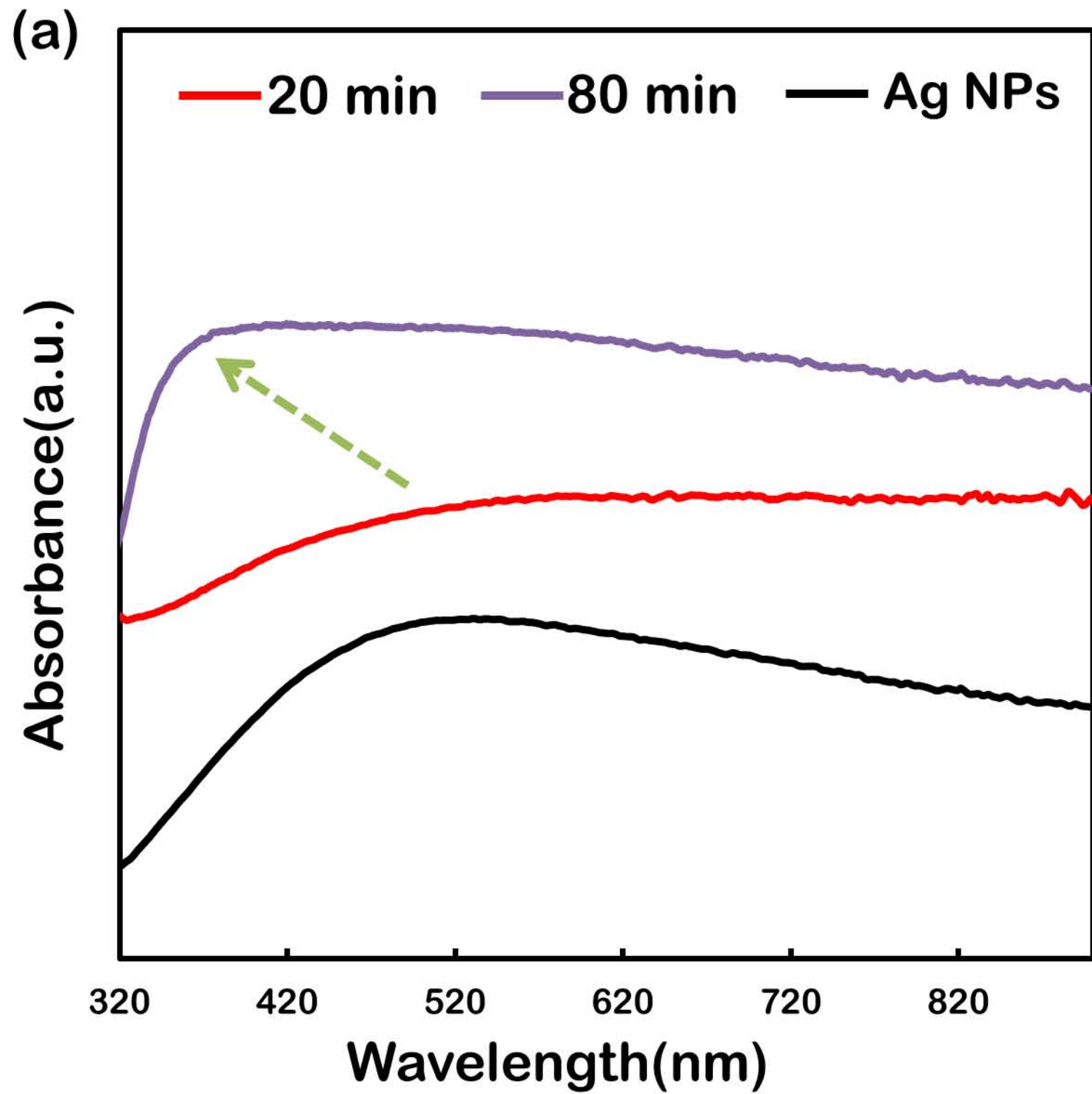
40 min
34.5 °C

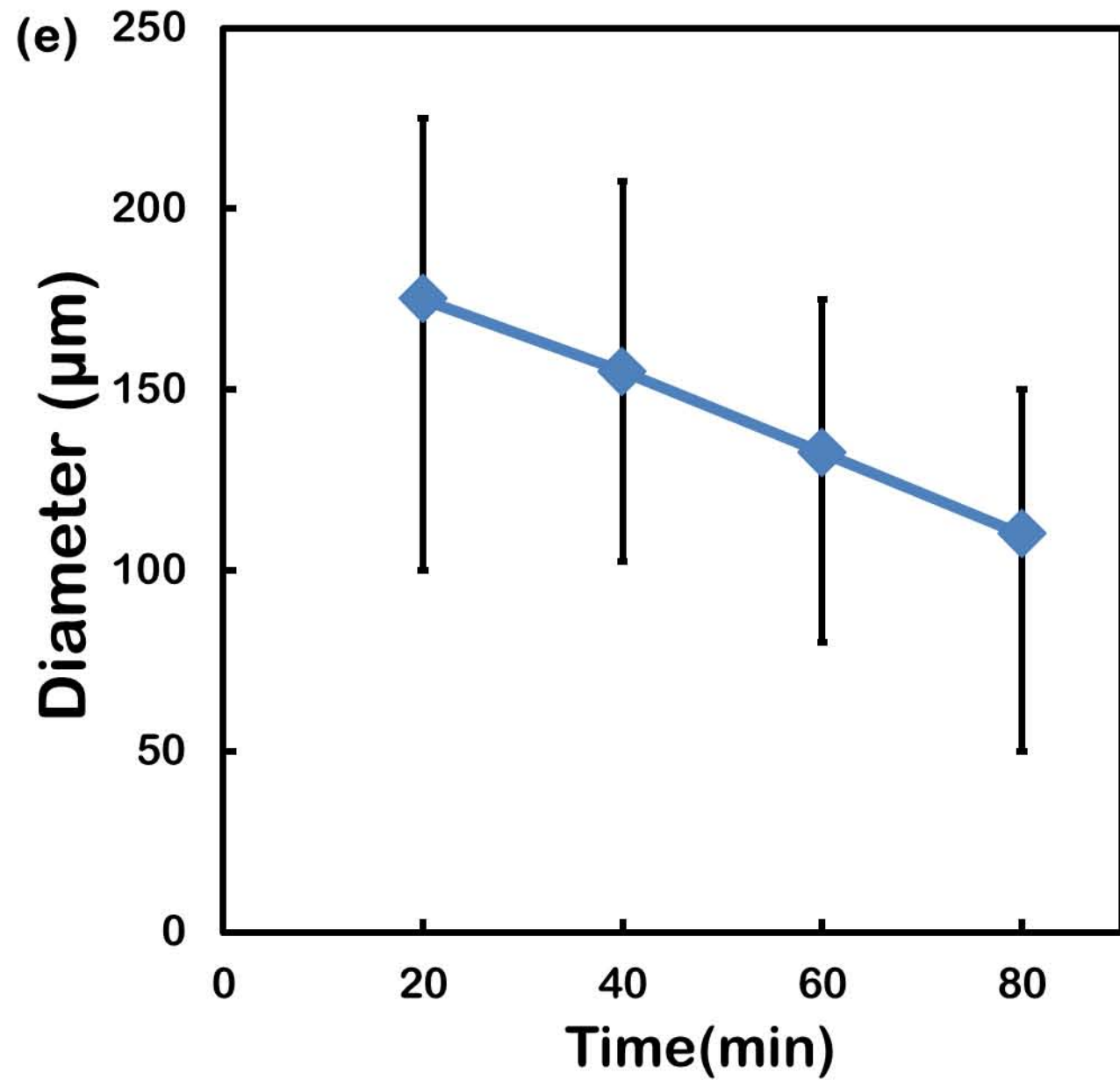
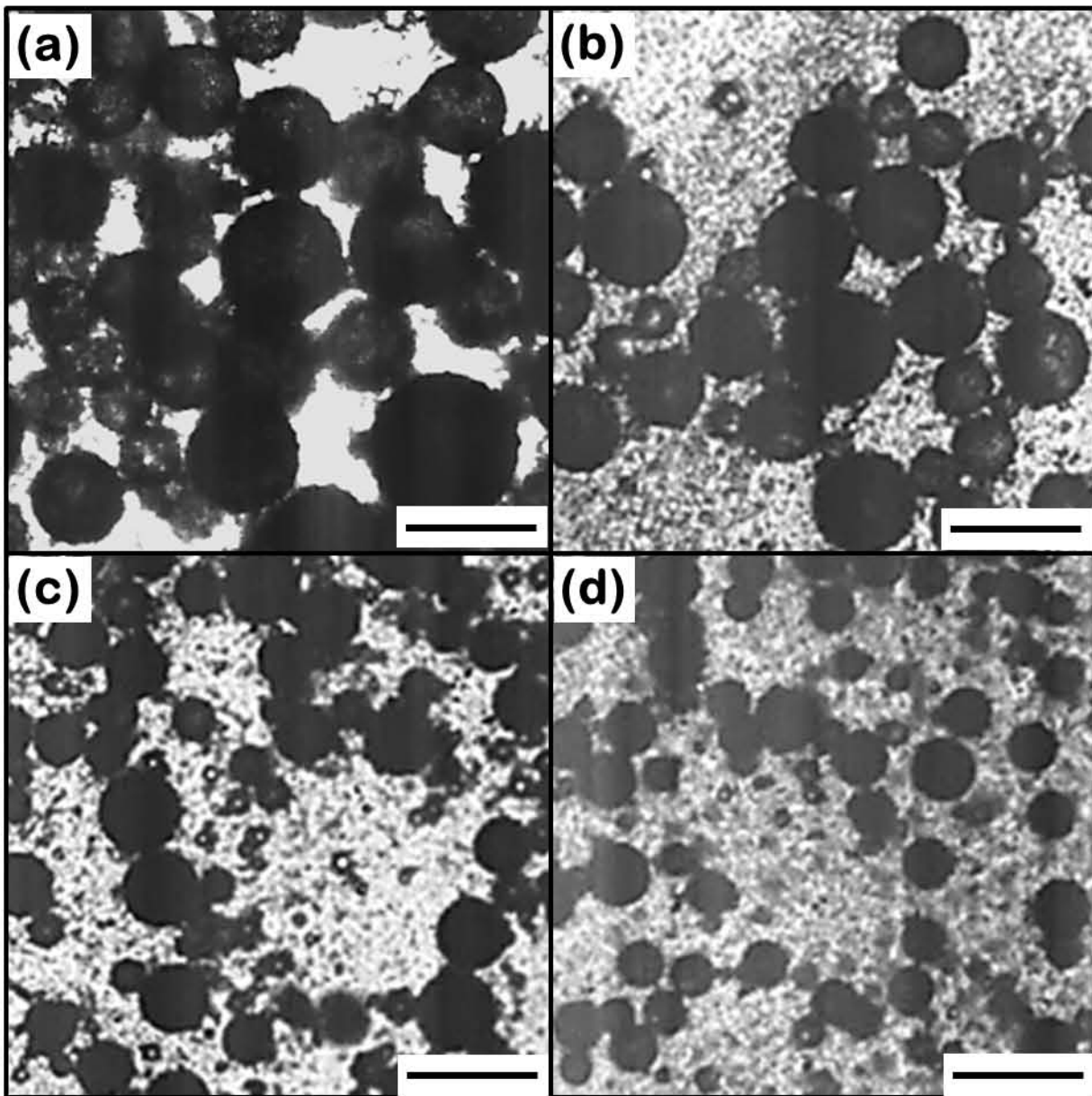
Oleic acid
32.9 °C

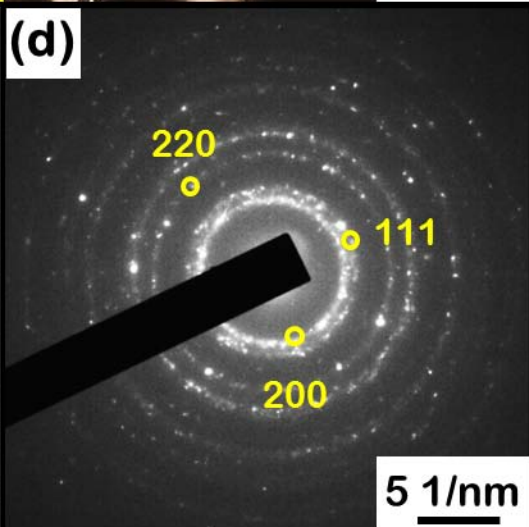
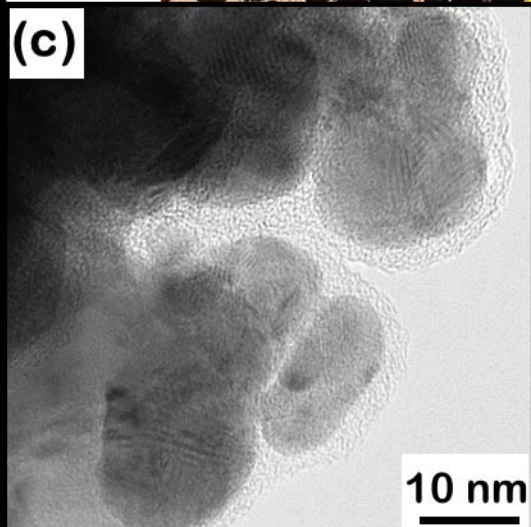
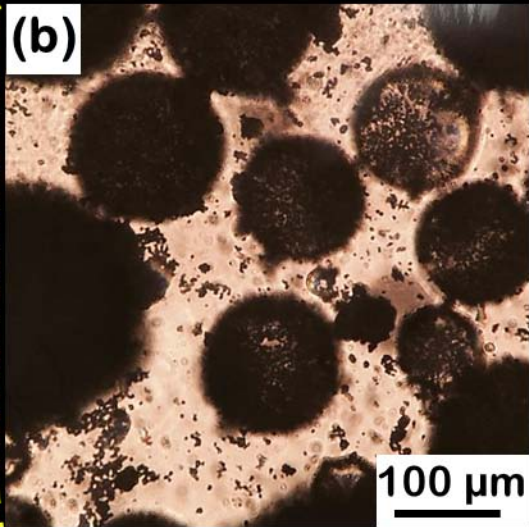
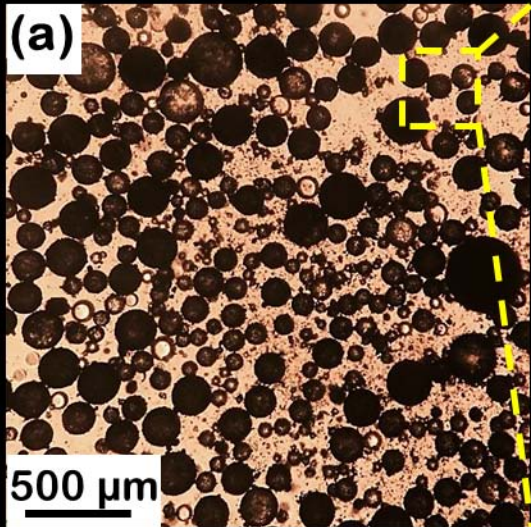




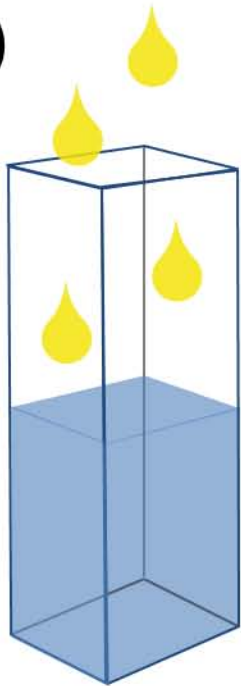




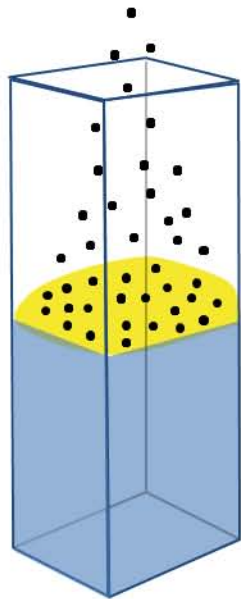




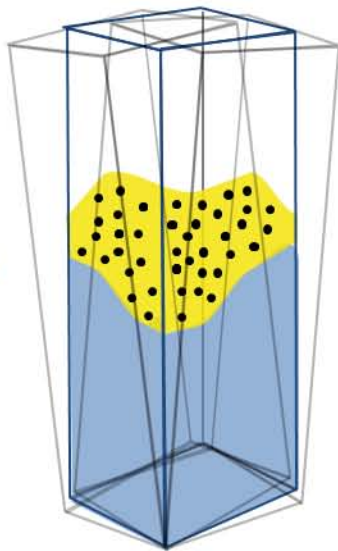
(a)



(b)



(c)



(d)

