

A New Approach to Obtain Correct and Simplified Equation Applied to Inner Space Assessment for Capsule-like Superstructures

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Polypyrrole-Gold (PPy/Au) segment nanowires are prepared using anodized aluminum oxide (AAO) templates and assembled into a curved superstructure. Since the shape of the obtained superstructures can be designed to be capsule-like with inner space for containing materials, and their openings and closures can be controlled with external stimuli, these structures can be useful for a large variety of applications. Inner space of capsule-like superstructures is an important factor for their applications, and the volume of the inner space can be assessed using the generalized equation suggested by J. K. Lim (*Bull. Korean Chem. Soc.* 33, 2699 (2012)). In this paper, we introduce a new approach to obtain correct and simplified equation without redundant assumption which was used to induce the previous equations, and recalculate the volume of the inner space in the capsule-like superstructure using a new equation.

Key Words : Segment nanowires, Microencapsulation, Actuation, Assembled structures

Introduction

Polypyrrole-Gold (PPy/Au) segment nanowires are prepared within the pores of anodized aluminum oxide (AAO) templates and assembled owing to capillary and van der Waals forces following which AAO templates are placed in aqueous sodium hydroxide solution and the water is evaporated (Scheme 1(a), 1(b), 1(c)). The obtained superstructures are rolled up to form a curved superstructure with further evaporation of the water from the matrix of PPy segment that makes the diameter of the PPy segment smaller than that of the Au segment (Scheme 1d).^{1,2} Traditional photolithographic technique allows curved superstructures to be complete capsule-like superstructures with inner space available for containing materials.^{2,3} Recently, it has been reported that opening and closure of curved superstructure can be controlled by external stimuli, such as humidity, temperature, and light.⁴ This actuation can be explained by the change of PPy segment volume, which is increased (or decreased) by absorbing (or desorbing) the water vapor that makes the curved superstructure expand (or shrink), accordingly (Scheme 1(d), 1(e)). Remotely-controlled capsule-like superstructures can be used for a large variety of applications (e.g. microcapsules, microreactors, and delivery systems).

The radius of the inner space in the capsule-like superstructure can be assessed using simple equation suggested in the previous paper (Eq. 1).⁴

$$R = \frac{d_{Au}}{\alpha} - l_{PPy}, \alpha = 2 \tan^{-1}(\Delta d / 2l_{PPy}) \quad (1)$$

According to the equation, the radius of the inner space (R) is determined by the length of PPy (l_{PPy}), the diameter of Au (d_{Au}), the diameter of PPy (d_{PPy}), and the diameter difference between Au and PPy segments ($\Delta d = d_{Au} - d_{PPy}$). This equation yields good results under assumption that the

length of the PPy segment is comparable or much longer than that of the Au segment. In recent paper, the equation was modified, and generalized for all lengths of the PPy segment (Eq. 2).⁵

$$R = \frac{d_{PPy} + \Delta d \cos(\alpha/2)}{\alpha} - l_{PPy}, \alpha = 2 \tan^{-1}(\Delta d / 2l_{PPy}) \quad (2)$$

In both equations (1 and 2), however, the radius of the inner space is induced from the circumference of hypothetical circle (dotted circle in Fig. 1(a)). In this paper, we discard this redundant assumption, and introduce a new equation for better assessing the volume of the inner space.

Derivation of New Equation

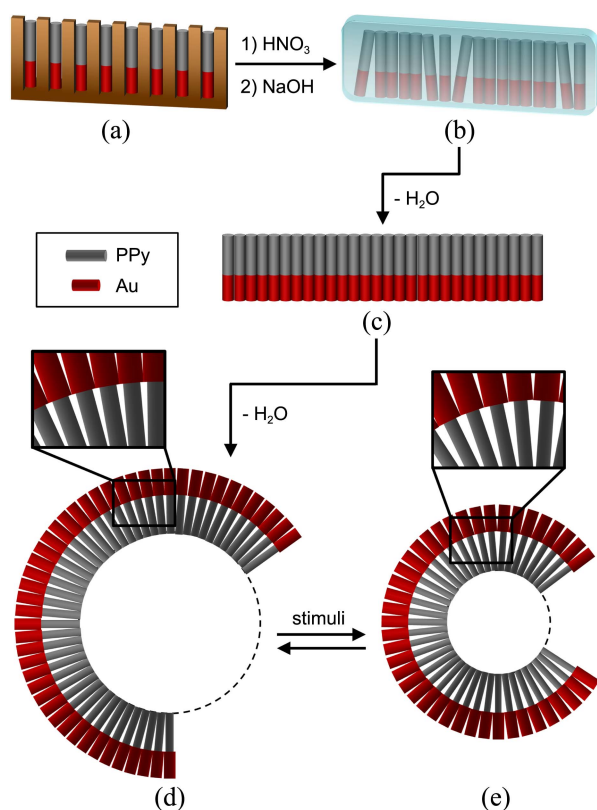
Let the radius of the inner space in the capsule-like superstructure as R (Fig. 1(a)). Angle α ($\angle AOC$ Fig. 1(b)) is the included angle between the two adjacent wires. AC (Fig. 1(b), (c)) is the segment connecting the centers of the ends of the two adjacent PPy (Fig. 1(c)). The angle $\angle AOD$ is the same as $\angle BAD$ (Fig. 1(c)) and amounts to $\alpha/2$, because $\triangle OAB$ equals to $\triangle ABD$. The length of AD , defined as y , is calculated either from $\triangle OAD$ or from $\triangle ABD$ (Eq. 3).

$$y = R \cdot \sin\left(\frac{\alpha}{2}\right) = \frac{d_{PPy}}{2} \cdot \cos\left(\frac{\alpha}{2}\right) \quad (3)$$

Eq. (3) can be converted using a tangent function, and $\tan(\alpha/2)$ can be replaced with Δd , the difference of diameters between the PPy and the Au segment and l_{PPy} (Eq. 4).⁴

$$\tan\left(\frac{\alpha}{2}\right) = \frac{\Delta d}{2l_{PPy}} \quad (4)$$

Finally, the radius of the inner space, R is represented with only variables, d_{PPy} , l_{PPy} and Δd (Eq. 5).



Scheme 1. Schematic picture representing the procedure for forming the curved superstructures through the guidance of anodized aluminum oxide templates, (a, b, c, and d), and their opening and closure by external stimuli (d and e).

$$R = \frac{d_{PPy} \cdot l_{PPy}}{\Delta d} \quad (5)$$

Results and Discussion

The radius of the inner space in capsule-like superstructure R is a function of Δd which is variable value from 20 to 60 nm.¹⁻⁴ This range depends on environmental conditions, such as temperature, humidity, and light intensity. R is calculated at different length of the PPy segment (l_{PPy}) using Eqs. (1), (2), or (5), under the assumption that Δd falls in the above range, and then plotted against to l_{PPy} (Fig. 2(a), 2(b)). When Δd equals 20 nm, R calculated with Eq. (2) (dotted line in Fig. 2(a)) is almost the same as calculated with Eq. (1) (dashed line in Fig. 2(a)). At all length of the PPy segment, however, Eq. (5) shows better results (solid line in Fig. 2(a)) which is slightly less than that calculated from Eq. (1) and (2). On the other hand, when Δd becomes 60 nm, R calculated with Eq. (2) (dotted line in Fig. 2(b)) is slightly different, while R calculated with Eq. (5) (solid line in Fig. 2(b)) is significantly different from that calculated with Eq. (1) (dashed line in Fig. 2(b)), as the length of PPy segment decreases.

This difference can be clearly seen in Figure 2(c) where the difference of radii from different equations is plotted against l_{PPy} . In Figure 2(c), filled and blank marks show the

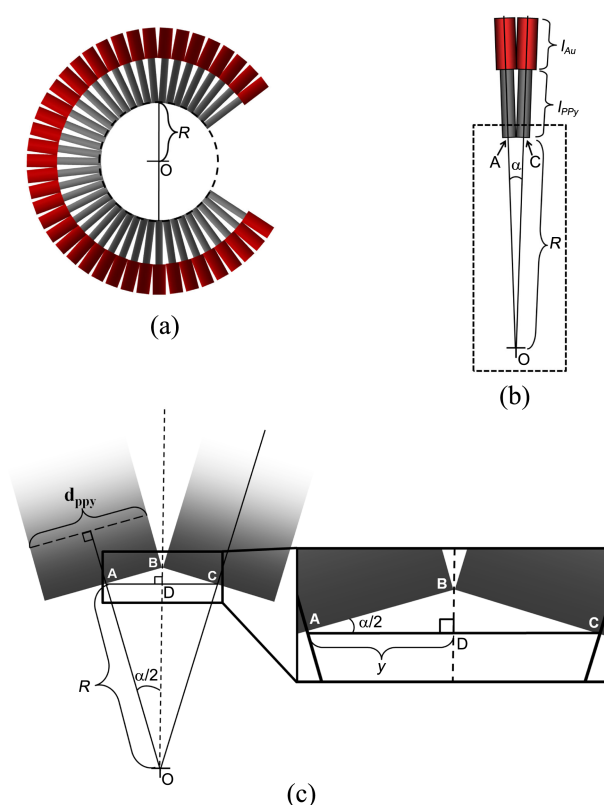


Figure 1. Schematic picture of the curved superstructure, (a), and its magnified image, (b). Dashed area of (b) is highlighted in (c).

difference of radii when Δd equals 20 or 60 nm, respectively. In the case of small Δd ($\Delta d = 20$ nm), the difference of radii (filled diamonds, or squares in Fig. 2(c)) gradually increases. On the other hand, when Δd is 60 nm, difference of radii calculated with Eqs. (1), (2), and (5) shows distinctly increased behavior, as l_{PPy} becomes below 1000 nm (empty diamonds, or squares in Fig. 2(c)).

Since capsule-like superstructures have inner space where materials can be contained and released outside in a controllable manner, capsule-like superstructures examined in this report can be used in a number of novel microencapsulation applications. The important requirement to this end is the available volume of the inner space. The available volume can be calculated from the radius of the inner space using Eqs. (1), (2) or (5) when Δd is 20 or 60 nm (Fig. 3 or 4). Since the radius of inner space is increased with l_{PPy} as shown in Figure 2(a), (b), the volume of inner space is also increased with l_{PPy} (Fig. 3(a), and 4(a)). In Figure 2(a), (b), the rate of change for radius is nearly independent on l_{PPy} , but the rate of change for volume is completely depending on l_{PPy} in Figure 3(a), and 4(a). In addition, the rate of change for volume varies with the used equations (Fig. 3(b), (c), and 4(b), (c)). As the length of PPy is increased, the difference of volume is also increased. The difference of volume (the distances between lines in Fig. 3(b) and 4(b)) in the middle length of PPy is smaller than that in long PPy (the distances between lines in Fig. 3(c) and 4(c)). This trend means that the rate of change for the volume is dependent on

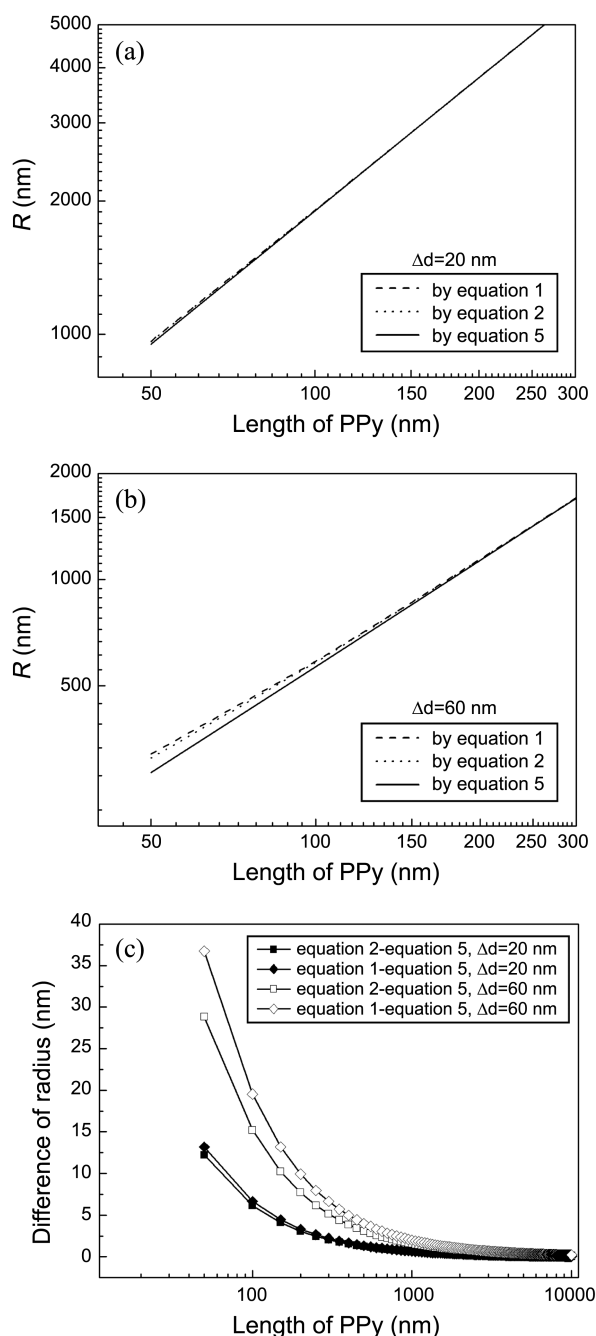


Figure 2. The radius of inner space, R was calculated using Eqs. (1), (2), or (5), and plotted against the length of polypyrrole segment, l_{PPy} , when the difference of diameter between gold and polypyrrole segment, Δd is 20 nm, (a), and 60 nm, (b). As l_{PPy} is decreased, R is also decreased in both (a) and (b), but the difference of radius (R from Eq. (1) - R from equation 2 or 5) in (b) is larger than that in (a), and which is clearly seen in (c). As increasing of l_{PPy} , the difference of radius of inner space is increased.

not only the length of PPy but also used equations.

There are big differences between radius and volume. In Figure 2(c), the difference of radius calculated using three equations is increased as the length of PPy segment is decreased, however, the volume of the inner space show completely different results in Figure 5, where the difference

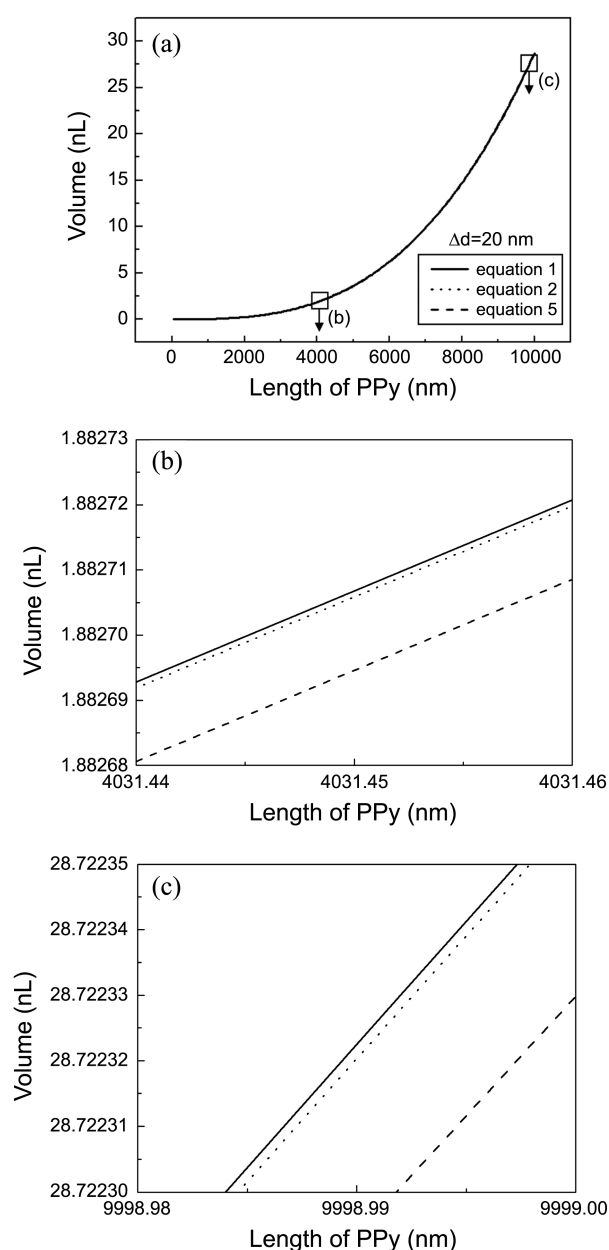


Figure 3. The volume of inner space calculated using Eqs. (1), (2), or (5) in small Δd ($\Delta d = 20$ nm) is increased, as the length of PPy is increased, (a). The difference of volume is also increased with increasing of the length of PPy, which is clearly seen in (b), and (c). The difference of volume at long PPy (distance between lines in (c)) is larger than that at short PPy (distance between lines in (b)).

of volume increases with l_{PPy} . This trend is shown not only at small Δd (filled marks) but also at large Δd (blank marks) in Figure 5. In addition, while the difference of volume is rapidly increased at small Δd more than that at large Δd in Figure 5, the difference of radius is rapidly changed at large Δd more than that at small Δd in Figure 2(c). This discrepancy between radius and volume apparently seems to be opposite, but we should consider that the volume is proportional to the 3rd power of the radius ($V \propto r^3$). In addition, we plotted not the radius (r) or volume (V) itself but the

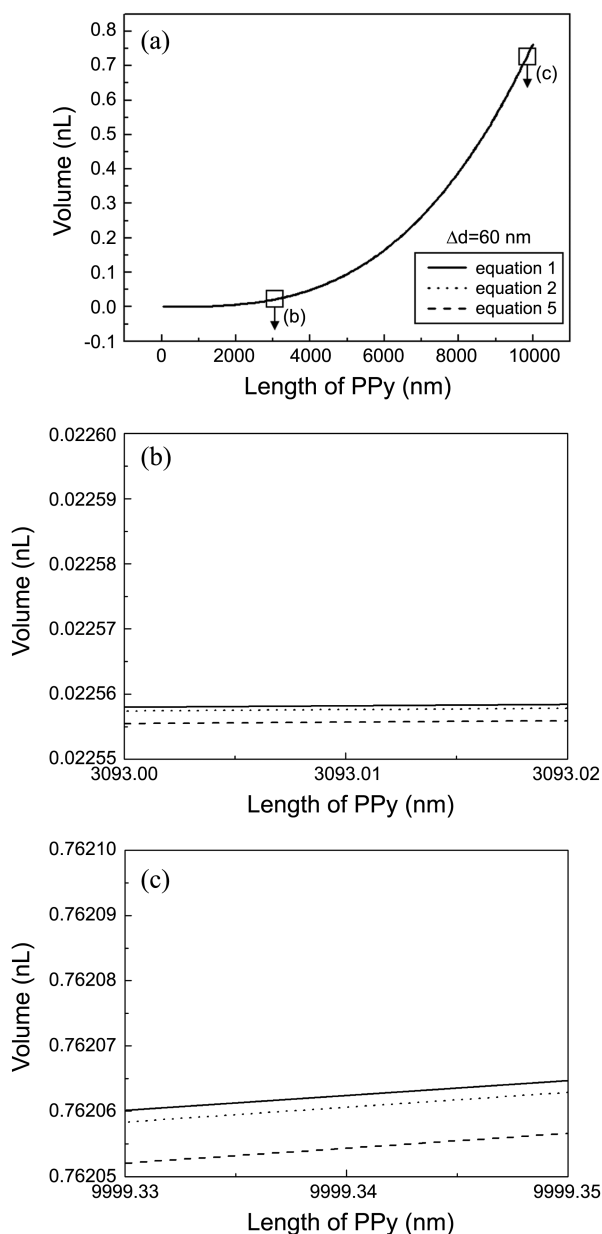


Figure 4. The volume of inner space calculated using equation 1, 2, or 5 in large Δd ($\Delta d = 60$ nm) is increased, as the length of PPy is increased, (a). The difference of volume is also increased with increasing of the length of PPy, which is clearly seen in (b), and (c). The difference of volume at long PPy (distance between lines in (c)) is larger than that at short PPy (distance between lines in (b)).

difference of radius (Δr) or volume (ΔV) in Figure 2 or 5, respectively. Although the difference of radius is decreased as the length of PPy is increased as shown in Figure 2(c), the difference of volume can be increased with increasing of the length of PPy (Figure 5). This apparently opposite trend is mathematically natural result, but shows that small difference of radius can make large volume difference. Eq. (5) newly suggested in this manuscript is much simpler than the previously suggested equations (Eqs. (1) and (2)), and mathemati-

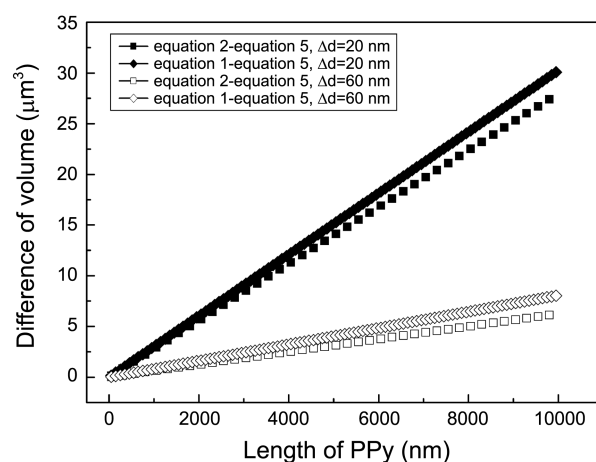


Figure 5. The difference of volume calculated equation 1, 2, or 5 is plotted against to the length of PPy. The difference of volume in small Δd (filled squares or diamonds) is rapidly increased more than the difference of volume in large Δd (empty squares or diamonds), with increasing of the length of PPy.

cally complete equation, because redundant assumption is excluded.

Conclusion

In this paper, we adopted a new approach to obtain new equation which is much simpler than the previous equations. In addition, since this new equation was derived without redundant assumption, the new equation is accurate more than the two previous equations, and acceptable at all lengths of l_{PPy} . The volume and radius of the inner space of the capsule-like superstructure were calculated using three equations and compared with each other. The radii of inner space show small deviation from each to each, however, the volumes of the inner space show large difference as l_{PPy} increases. The assessment of the available volume is very important for practical applications of capsule-like assembled superstructures, such as microencapsulation.

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