Supplementary Information (SI) for Nanoscale.

Fabrication of One-Dimensional Nanostructures Standing Vertically on the Substrate through Layer-by-Layer Deposition

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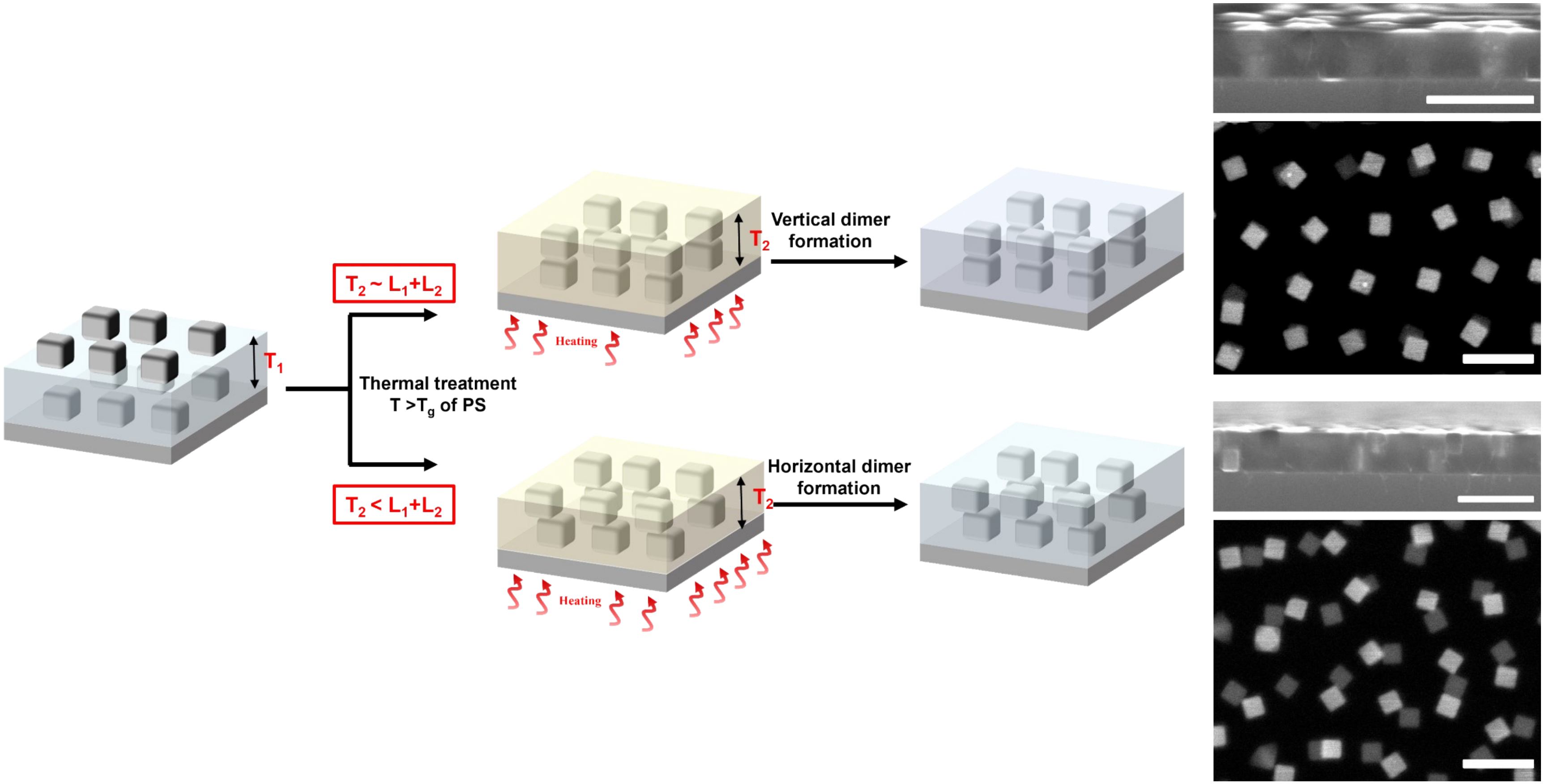
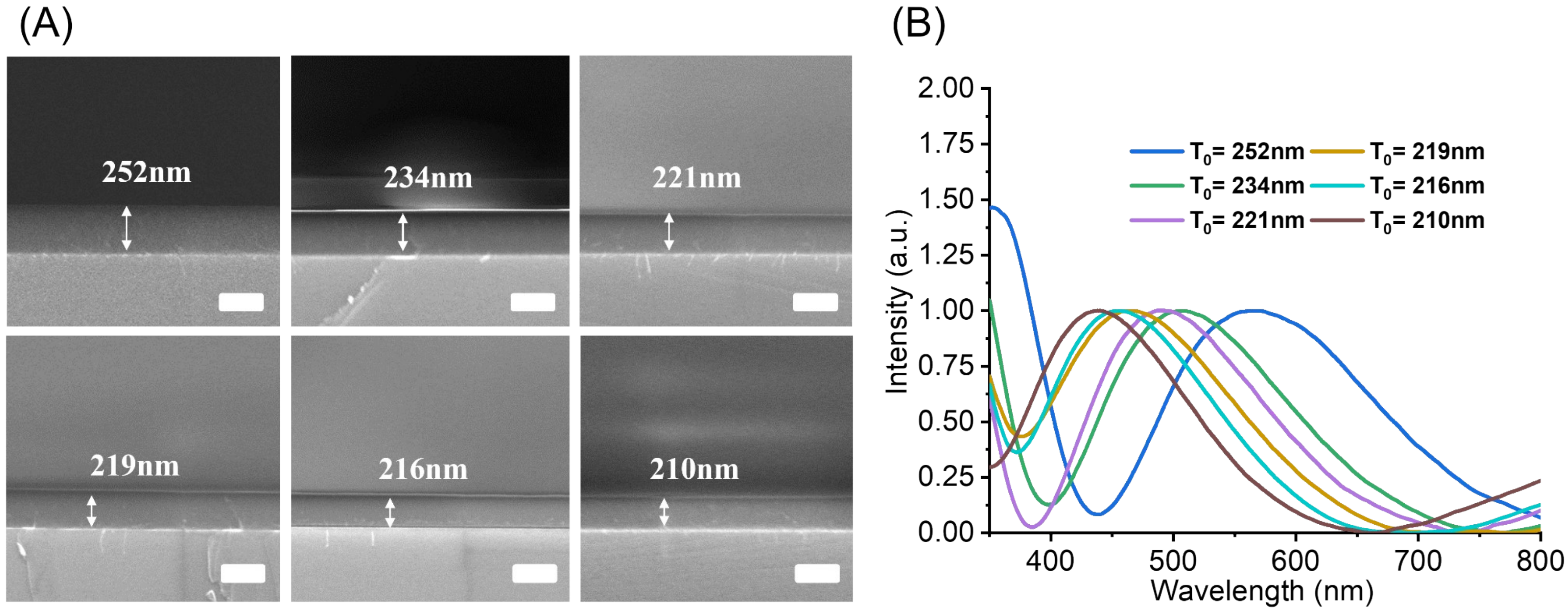
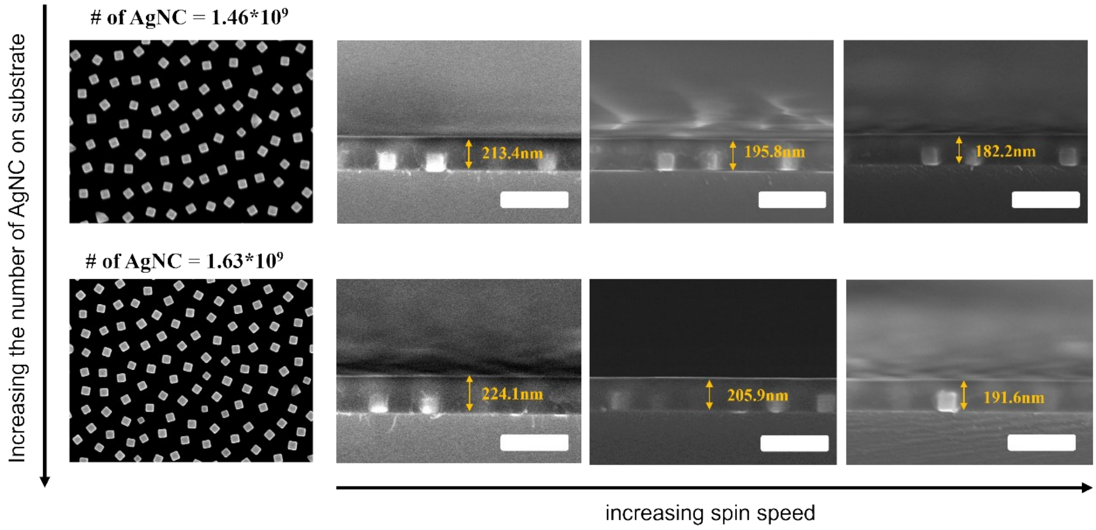


S1 The morphology of dimer nanojunctions in the PS matrix can be controlled through the thickness of the PS matrix after embedding the second layer of AgNC (T_2). For T_2 which is approximately the sum of the sizes of AgNCs in the first layer (L_1) and the second layer (L_2) ($T_2 \sim L_1+L_2$), the morphology of the self-assembled dimer nanojunctions in the substrate was vertical dimer nanojunctions. For the case where T_2 was smaller than L_1+L_2, the morphology of the self-assembled dimer nanojunctions in the substrate was horizontal dimer nanojunctions. The corresponding SEM image was shown on the right. The scale bar was 400 nm.



S2 Study on the relationship between the thickness of PS matrix on the substrate without AgNCs (T_0) and the absorption peak wavelength of Uv-Visible spectrum. (A) The thickness of PS on the substrate can be measured through cross-section SEM images and the corresponding absorption spectra of these substrates with different PS thickness were shown in (B). The scale bar was 400 nm.

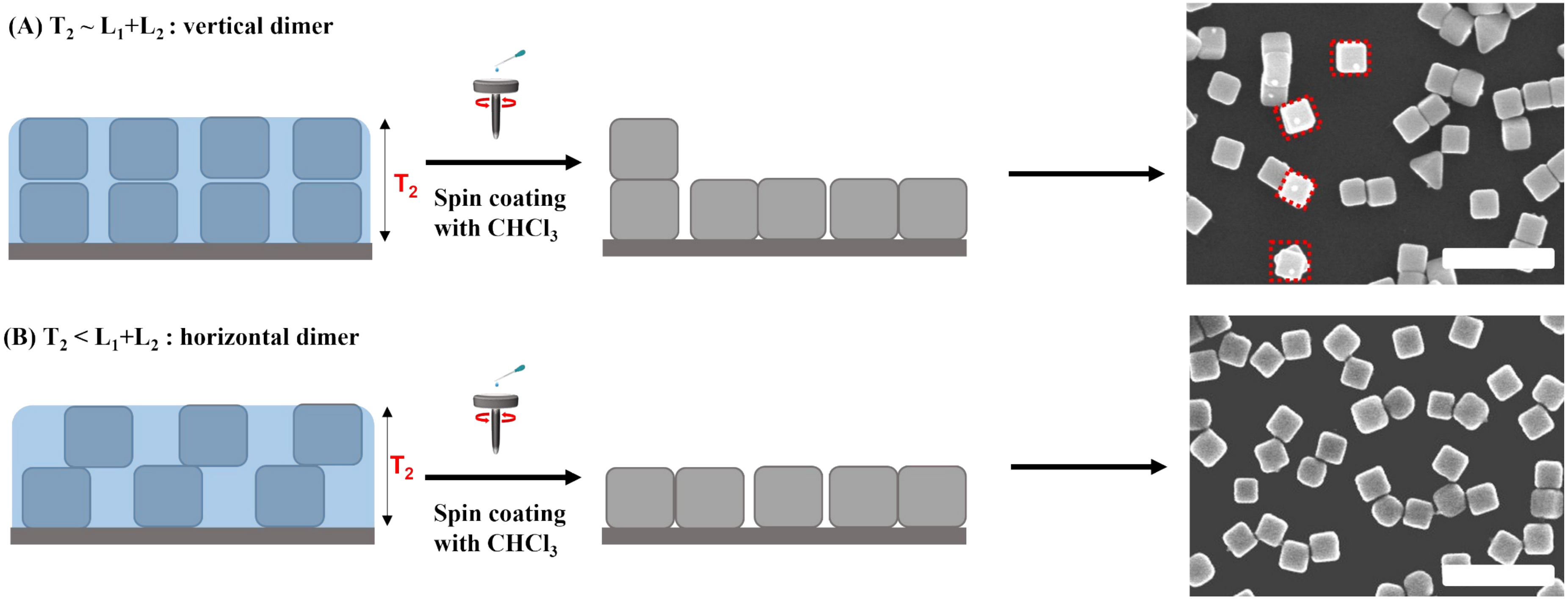


S3 Thickness changes of PS matrix deposited on substrates with different quality of AfNC array on the substrate under different spin speeds. Substrates with AgNC array of two different AgNC concentrations were used to study the effect of the number of AgNC on the substrate on the thickness of PS deposited on it. The results showed that the thickness of the PS matrix deposited on the substrate had an increasing trend as the number of AgNC on the substrate increases and the spin speed decreases, which was due to the increased interaction between PS and AgNCs on the substrate. The scale bar was 400 nm.

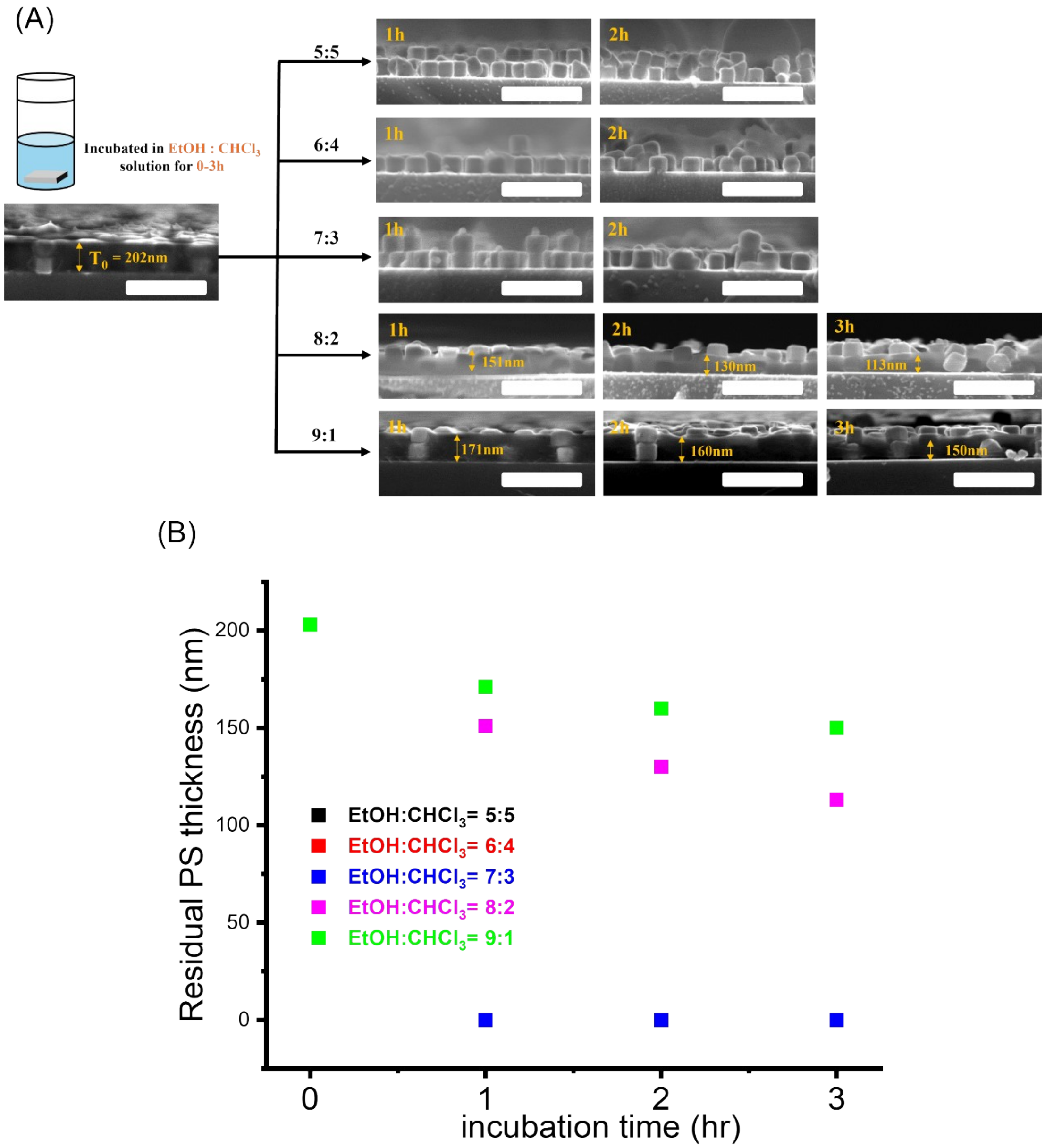
Table S1 the relationship between T_0 (the thickness of PS matrix deposited on the pure substrate) and T_1 (the thickness of PS matrix deposited on the AgNC-substrate with different number of AgNCs on the substrate)

# of AgNC	Fitting formula : $T_1 = A + BT_0$		
	A	B	R^2
1st layer AgNC: 100 nm			
1.46×10^9	8.8	1.092	0.994
1.63×10^9	16.1	1.109	0.998

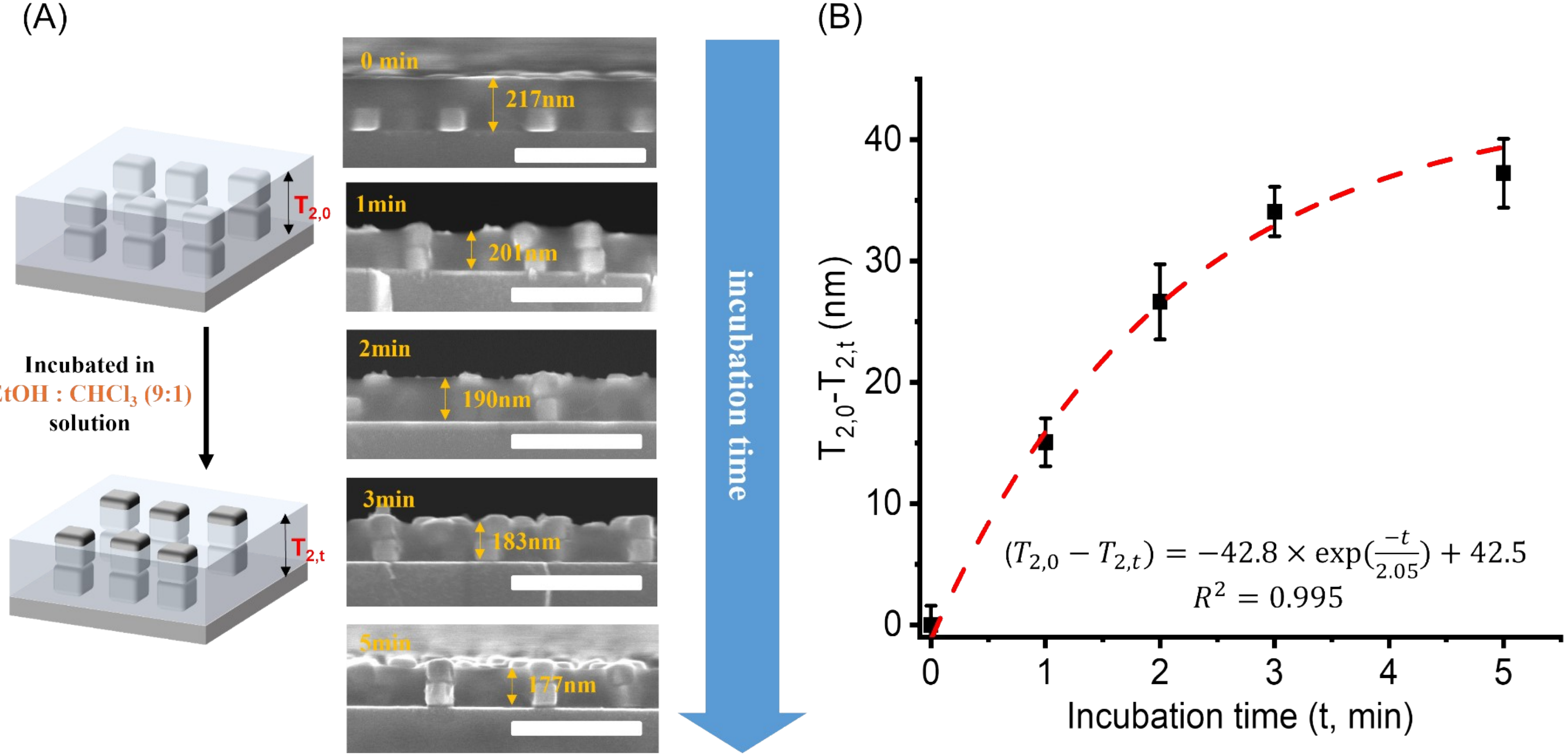
# of AgNC	Fitting formula : $T_1' = A + BT_0$		
	A	B	R^2
1st layer AgNC: 100 nm / 2nd layer AgNC: 100 nm			
2.6×10^9	34.7	1.223	0.980
2.7×10^9	29.4	1.317	0.978
2.8×10^9	44.4	1.215	0.985
3.0×10^9	80.5	1.189	0.980



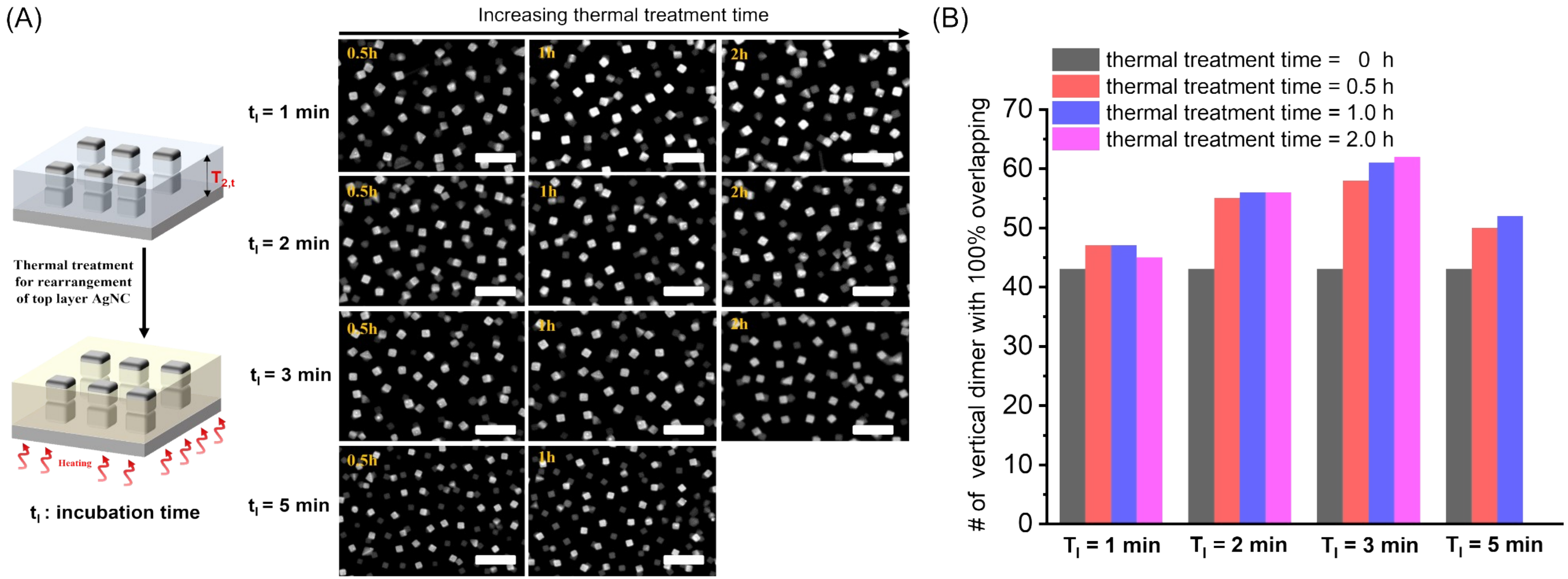
S4 Removal of PS matrix on dimer nanojunction substrate through the spin coating process. During the removal process, the two different morphologies of the dimer nanojunctions on the substrate can lead to changes on the distribution of AgNCs on the substrate after the PS matrix was removed. For substrate with horizontal dimer nanojunctions, the interaction between AgNCs in the dimer nanojunction was weak, causing the second layer of AgNC to move to the substrate or be removed together with the PS matrix through the spin-coating process as shown in (B). However, after removing the PS matrix, the substrate with vertical dimer nanojunctions can leave a small portion of exposed dimer nanojunctions on the substrate as shown in (A), which was due to the stronger interaction of the dimer nanojunctions in the vertical morphology than in the horizontal morphology. The red dashed square represented the position where the vertical dimer nanojunctions appeared. The scale bar was 400 nm.



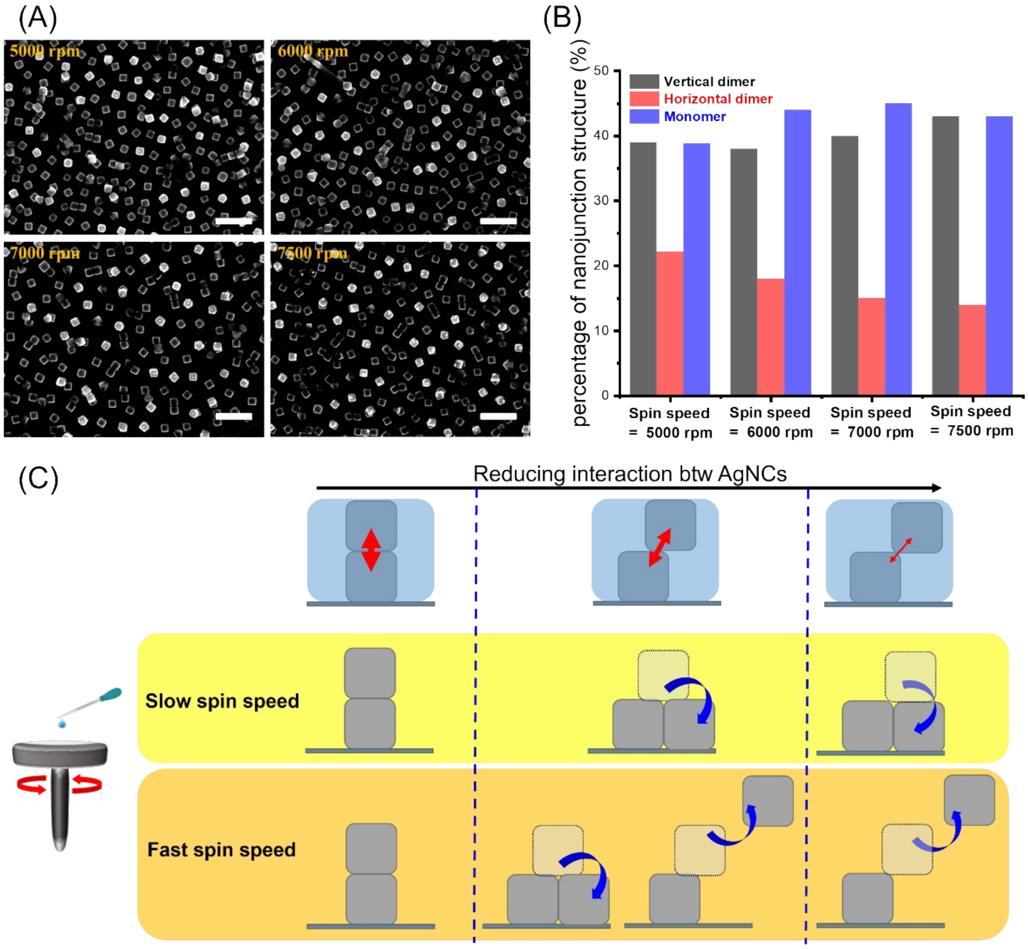
S5 Removal of PS matrix on dimer nanojunction substrate through incubated in mixed solvents. The substrate with vertical dimer nanojunctions was immersed in a mixed solvent composed of different ratios of EtOH: $CHCl_3$ to remove the PS matrix on the substate. Among them, $CHCl_3$ was a good solvent for removing PS matrix and EtOH was a poor solvent for removing PS matrix. For solvents with a lower ratio of EtOH: $CHCl_3$ (= 5:5 ~ 7:3), the PS matrix was completely removed within 1 hour. For solvents with a higher ratio of EtOH: $CHCl_3$ (= 8:2 ~ 9:1), due to the decrease in solubility of PS, it can be observed that with the increase of incubated time, the thickness of the PS matrix in the substrate tended to decrease within 2 hours of immersing, which can be observed through the cross-sectional SEM images, as shown in (A). Changes in the thickness of residual PS in the substrate with incubation time under the mixed solvents with different ratios of EtOH: $CHCl_3$, as shown in (B). The scale bar was 400 nm.



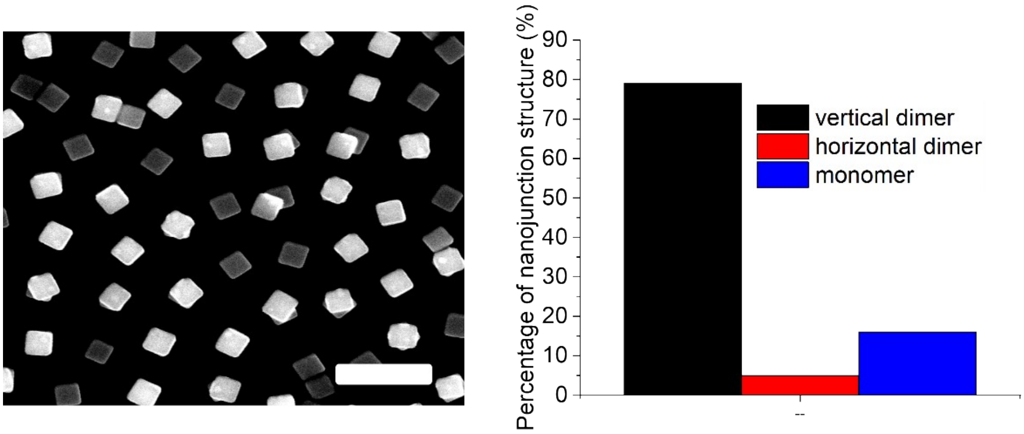
S6 Changes in PS thickness on the substrate when the substrate was immersed in a mixed solvent with the ratio of EtOH: $CHCl_3$ = 9:1. By measuring the corresponding cross-sectional SEM image, the thickness of PS matrix on the substrate can be observed after immersing for 1 ~ 5 minutes, as shown in (A). (B) Decrease in PS thickness ($T_{2,0}$-$T_{2,t}$) on the substrate showed an exponential saturation growth with incubation time. The scale bar was 400 nm.



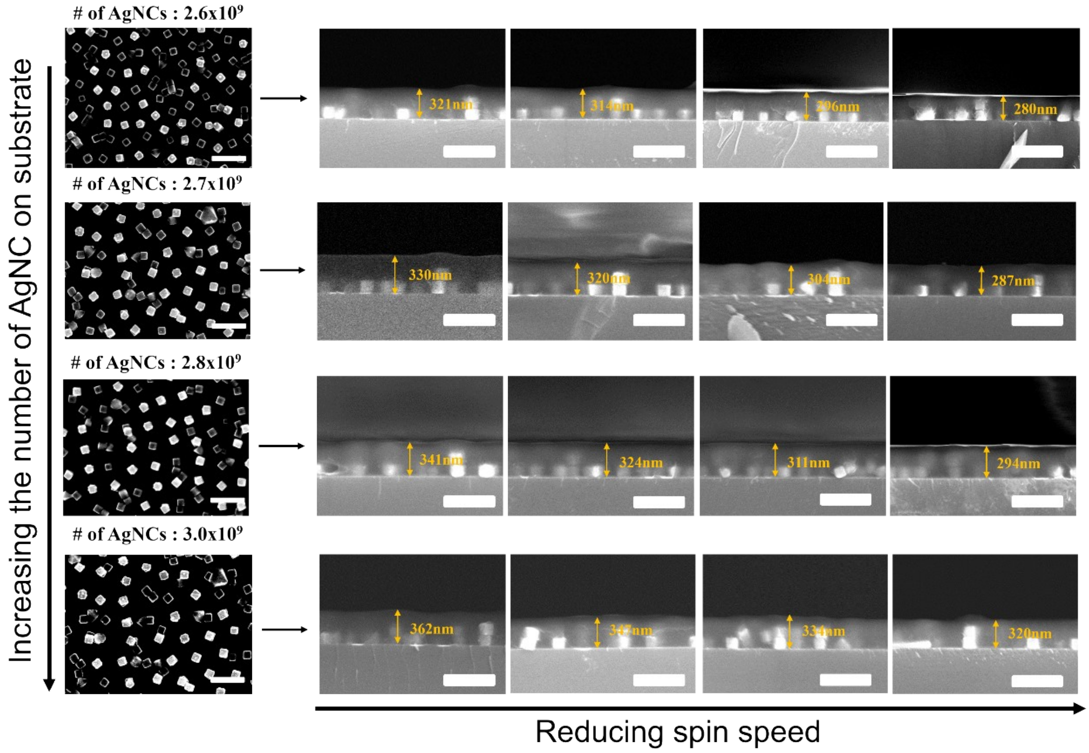
S7 The vertical dimer nanojunctions were rearranged under thermal treatment after the substrate was immersed into a mixed solvent for 1~5 minutes. (A) Immersed the substrate into a mixed solvent (EtOH: $CHCl_3$ = 9:1) for 1~5 minutes and observed the changes in the dimer nanojunctions on the substrate under different thermal treatment times, as shown in the corresponding SEM images. These SEM images can be used to analyze the change in the number of vertical dimer nanojunctions on the substrate as shown in (B). The number of 100% overlapping vertical dimer nanojunctions between two AgNCs in a substrate area of 13.02 μm2 was used to characterize the results of AgNC rearrangement under thermal treatment, as shown in the corresponding SEM images on the right. The scale bar was 400 nm.



S8 Exposed dimer nanojunctions were formed on the substrate through spin-coating process after the dimer nanojunctions were rearranged under thermal treatment for 1 hour. (A) SEM images of dimer nanojunctions formed by removing PS matrix on the substrate under pure $CHCl_3$ at different spin speeds. The corresponding SEM images can be used to analyze the percentage of vertical dimer nanojunctions on the substrate, as shown in (B). The change of AgNC distribution on the substrate can be attributed to the competition between the interaction between AgNCs in the dimer nanojunction and the centrifugal force during spin-coating, as shown in (C). The scale bar was 400 nm.



S9 Tuning the quality of exposed dimer nanojunctions on the substrate. By controlling the relative number of AgNC in the first and second layers, the amount of exposed vertical dimer nanojunctions on the substrate can be close to 80 %. The left side was the corresponding SEM image, and the right side was the analysis result of SEM image. The scale bar was 400 nm.



S10 Thickness changes of PS matrix deposited on substrates with different quality of exposed dimer nanojunctions under different spin speeds. Substrates with exposed dimer nanojunctions of four different qualities were used to study the effect of the number of AgNC on the substrate on the thickness of PS deposited on it. The results showed that the thickness of the PS matrix deposited on the substrate had an increasing trend as the number of AgNC on the substrate increases and the spin speed decreases, which was due to the increased interaction between PS and AgNCs on the substrate. The scale bar was 400 nm.

Set :

The length of AgNC =102 (nm)

The area of single AgNC = 10404 (nm^2)

The volume of single AgNC = 1061208 (nm^3)

The length of Si substrate = 10^7 (nm)

The area of Si substrate = 10^{14} (nm^2)

The surface coverage of third layer AgNCs = 9.43%

The area of third layer AgNCs in substrate

= The surface coverage of third layer AgNCs x The area of Si substrate

= 9.43% x 10^{14} (nm^2) = 9.43 x 10^{12} (nm^2)

The # of third layer AgNCs in substrate

= The area of third layer AgNCs in substrate / The area of single AgNC

= 9.43 x 10^{12} (nm^2) / 10404 (nm^2) =9.063 x 10^8

The total volume of AgNCs in substrate

=The # of third layer AgNCs in substrate x The volume of single AgNC

= 9.063 x 10^8 x 1061208 (nm^3) = 9.617 x 10^{14} (nm^3)

The excluded thickness from excluded volume (L)

= The total volume of AgNCs in substrate / The area of Si substrate

= 9.617 x 10^{14} (nm^3) / 10^{14}(nm^2) = 9.617 (nm)

The perfect thickness of vertical trimer

= The sum of length of each layer AgNC

= 102 + 102 + 102 = 306 (nm)

The actual thickness of vertical trimer (T_2')

= The perfect thickness of vertical trimer + 5 (nm) (ligand spacing between AgNCs in nanojunction + ligand spacing between 1st AgNC and the substrate)

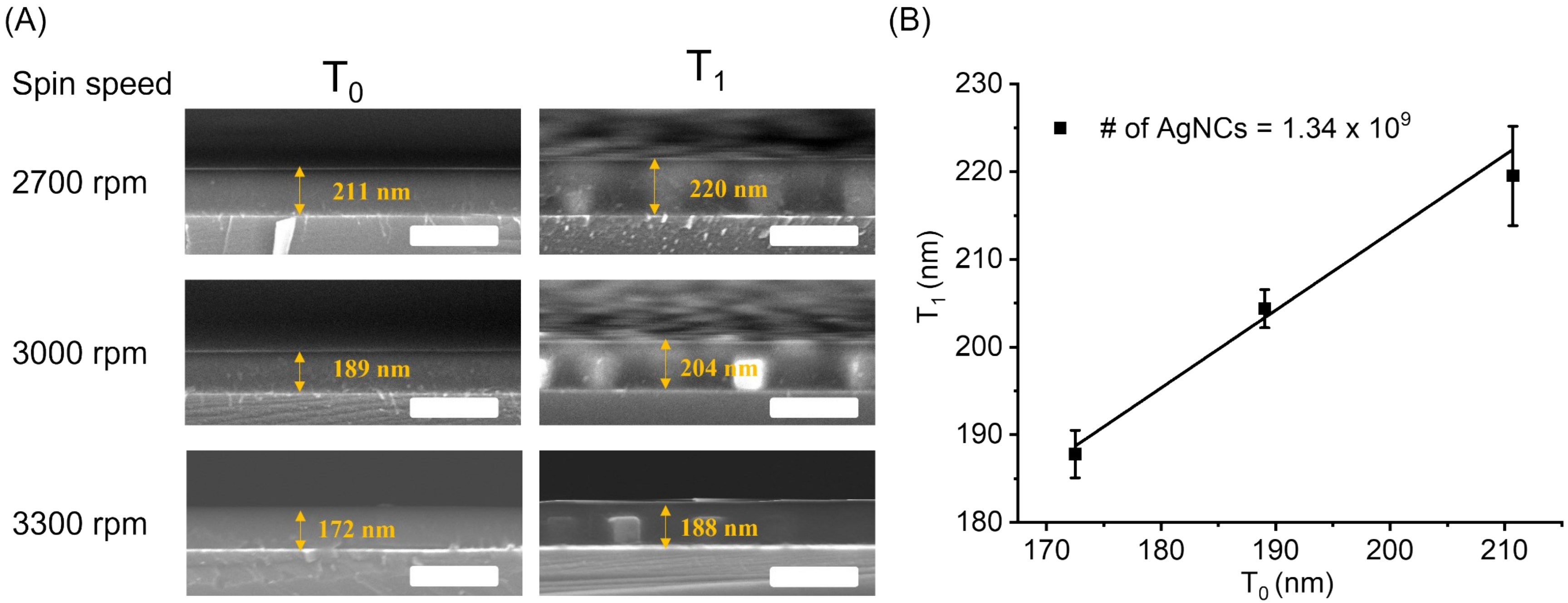
= 306 + 5 = 311 (nm)

The targeted thickness without excluded thickness (T_1')

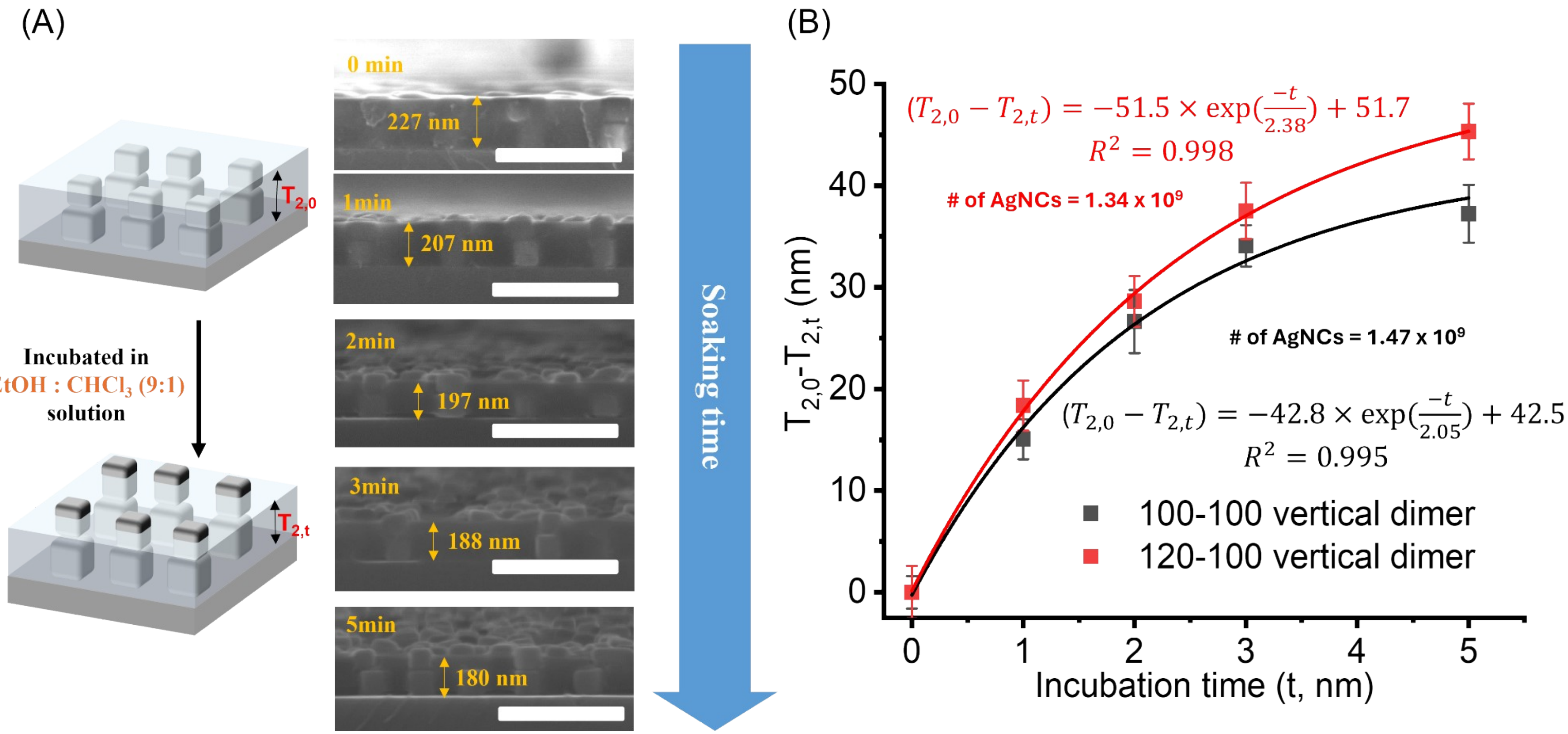
= The actual thickness of vertical trimer – The excluded thickness from excluded volume

= 311 – 9.6 = 301.4 (nm)

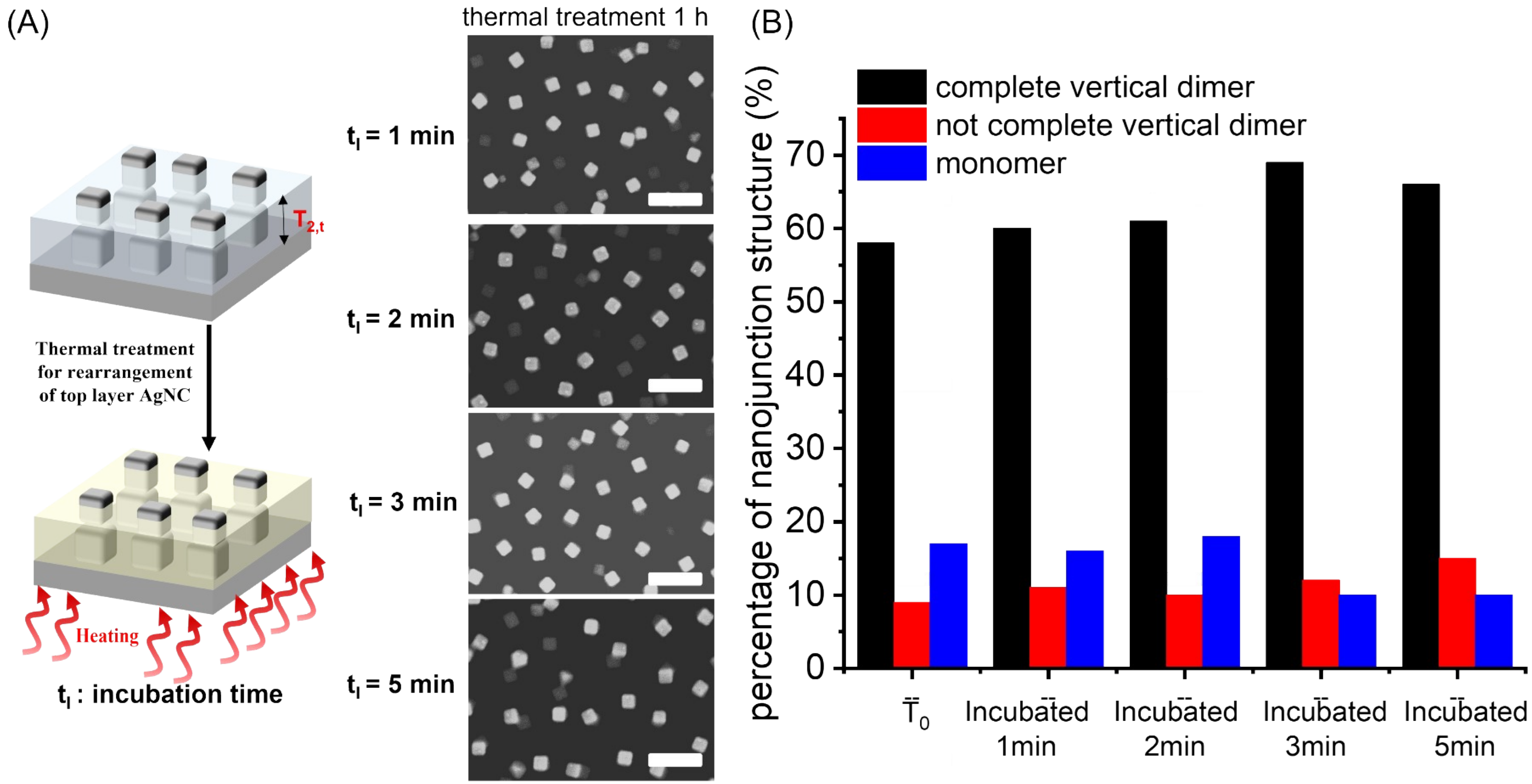
S11 Calculated the thickness of PS deposited on a substrate with exposed vertical dimer nanojunctions (T_1') and the thickness of the PS matrix desired to form vertical trimer nanojunctions (T_2').



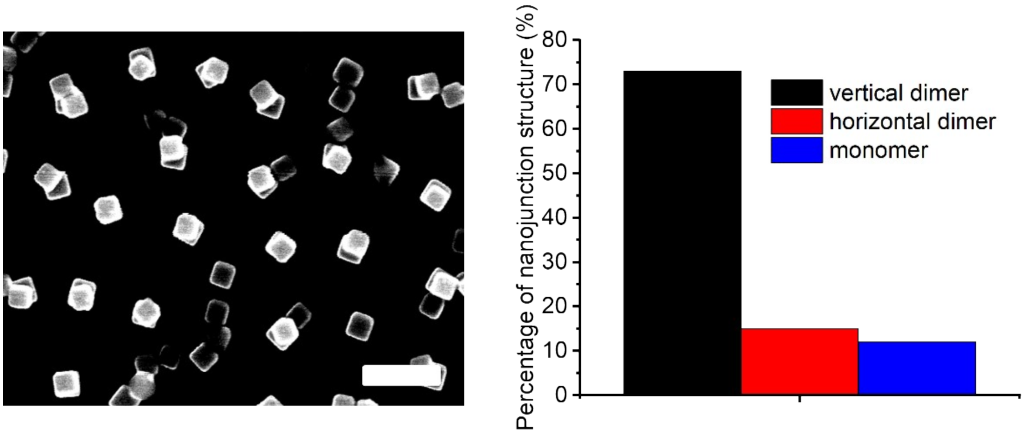
S12 Thickness changes of PS matrix deposited on substrates with and without 1st layer AgNC (L_1 = 120 nm) under different spin speeds. Substrates with 1st layer of AgNC concentration = 1.34 x 10^9 /cm^2 were used to study the effect of spin speed on the substrate on the thickness of PS deposited on it. The results showed that the thickness of the PS matrix deposited on the substrate had an increasing trend as the spin speed decreases, which was due to the decrease the centrifugal force during the spin coating. The scale bar was 400 nm.



S13 Changes in PS thickness on the substrate when the substrate was immersed in a mixed solvent with the ratio of EtOH: $CHCl_3$ = 9:1. Here, the vertical dimer nanojunctions in PS matrix were composed of 120 nm AgNC (first layer) and 100 nm AgNC (second layer). By measuring the corresponding cross-sectional SEM image, the thickness of PS matrix on the substrate can be observed after immersing for 1 ~ 5 minutes, as shown in (A). (B) Decrease in PS thickness ($T_{2,0}$-$T_{2,t}$) on the substrate showed an exponential saturation growth with incubation time (red squares) which was similar to the phenomenon observed with vertical dimer nanojunctions composted of two layers of 100 nm AgNC (black squares). The scale bar was 400 nm.



S14 The vertical dimer nanojunctions composed of 120 nm AgNC (first layer) and 100 nm AgNC (second layer) were rearranged under thermal treatment after the substrate was immersed into a mixed solvent for 1~5 minutes. (A) Immersed the substrate into a mixed solvent (EtOH: $CHCl_3$ = 9:1) for 1~5 minutes and observed the changes in the dimer nanojunctions on the substrate after thermal treatment for 1 hour, as shown in the corresponding SEM images. These SEM images can be used to analyze the change in the number of vertical dimer nanojunctions on the substrate as shown in (B). The scale bar was 400 nm.



S15 Exposed dimer nanojunctions were formed on the substrate through spin-coating process after the dimer nanojunctions were rearranged under thermal treatment for 1 hour. The amount of exposed vertical dimer nanojunctions on the substrate can be close to 75 %. The left side was the corresponding SEM image, and the right side was the analysis result of SEM image. The scale bar was 400 nm.

<u>Set :</u>
The length of first layer AgNC =122 (nm)
The length of second layer AgNC =102 (nm)
The length of third layer AgNC =82 (nm)

The area of third layer single AgNC = 6724 (nm^2)
The volume of third layer single AgNC = 551368 (nm^3)
The length of Si substrate = 10^7 (nm)
The area of Si substrate = 10^{14} (nm^2)

The surface coverage of third layer AgNCs = 9.2%

The area of third layer AgNCs in substrate
= The surface coverage of third layer AgNCs x The area of Si substrate
= 9.2% x 10^{14} (nm^2) = 9.2 x 10^{12} (nm^2)

The # of third layer AgNCs in substrate
= The area of third layer AgNCs in substrate / The area of single AgNC
= 9.2 x 10^{12} (nm^2) / 6724 (nm^2) = 1.368 x 10^9

The total volume of AgNCs in substrate
=The # of third layer AgNCs in substrate x The volume of single AgNC
= 1.368 x 10^9 x 551368 (nm^3) = 7.542 x 10^{14} (nm^3)

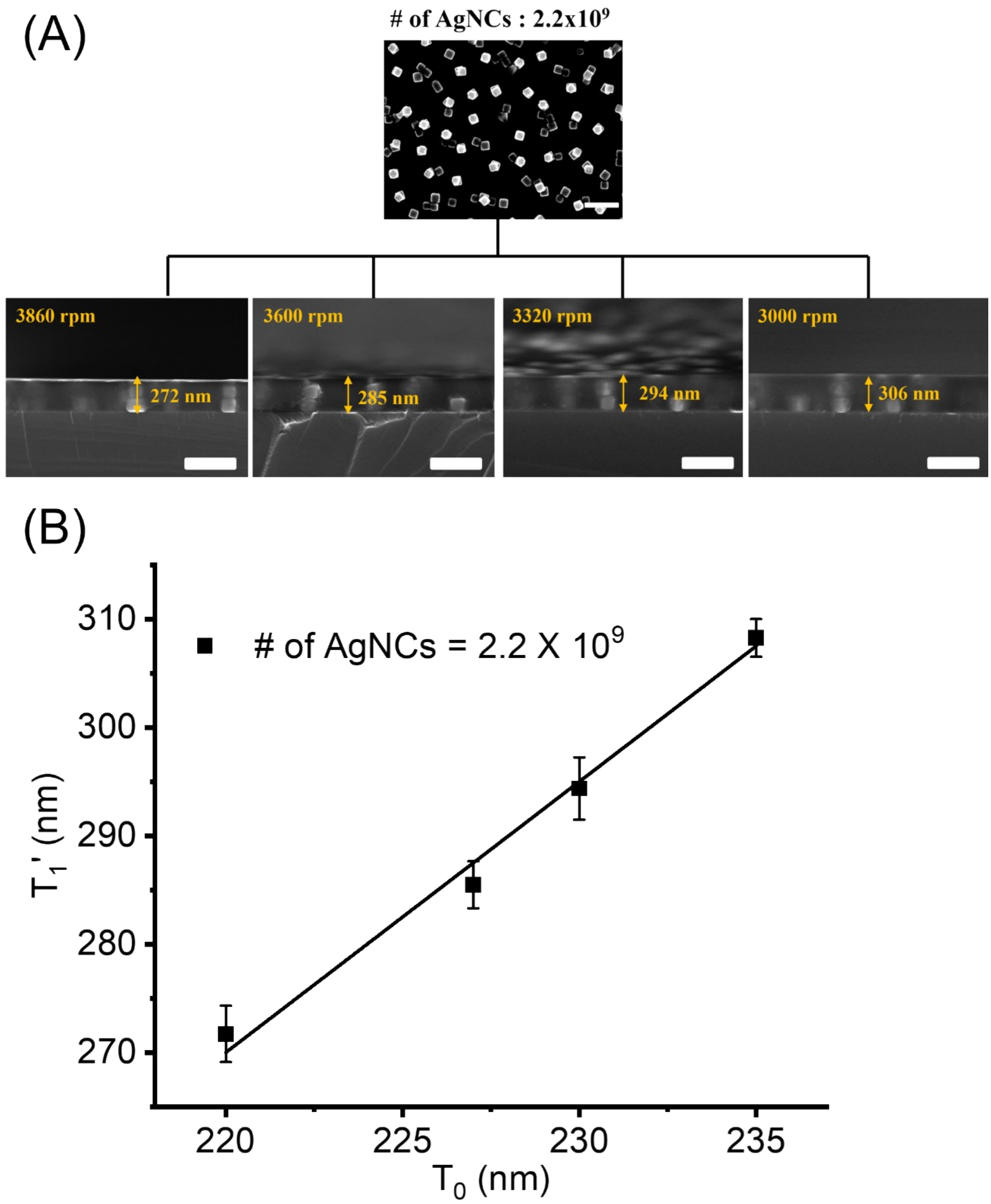
The excluded thickness from excluded volume (L)
= The total volume of AgNCs in substrate / The area of Si substrate
= 7.542 x 10^{14} (nm^3) / 10^{14}(nm^2) = 7.542 (nm)

The perfect thickness of vertical trimer
= The sum of length of each layer AgNC
= 122 + 102 + 82 = 306 (nm)

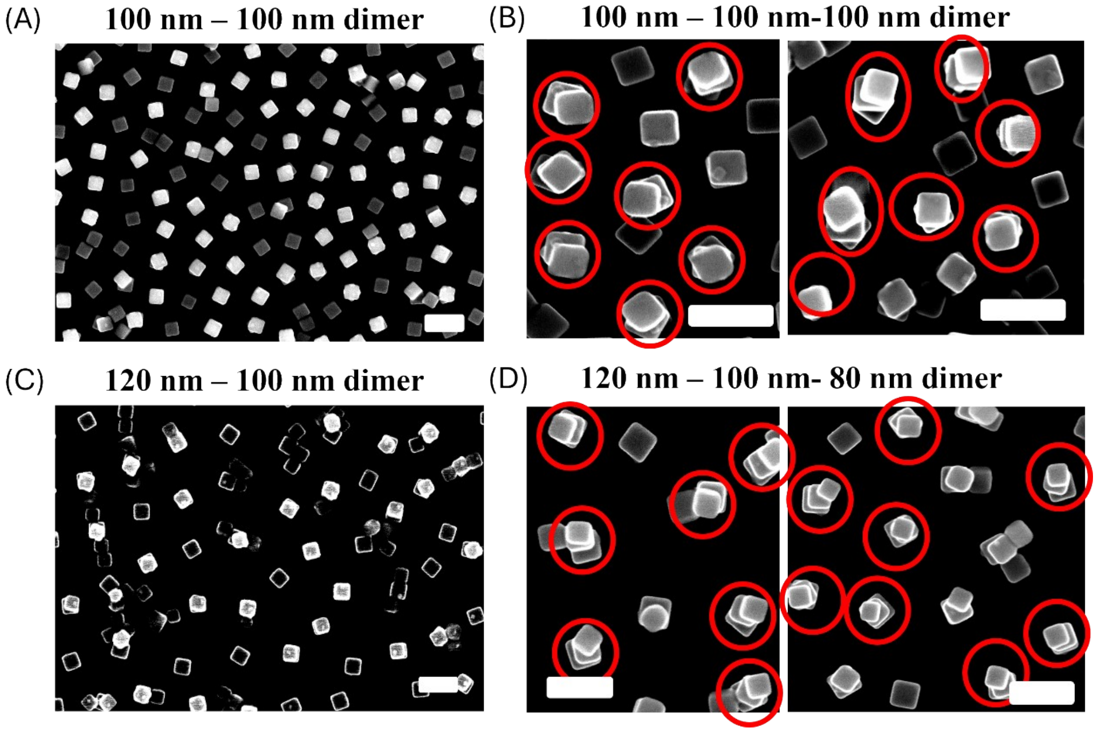
The actual thickness of vertical trimer (T_2')
= The perfect thickness of vertical trimer + 5 (nm) (ligand spacing between AgNCs in nanojunction + ligand spacing between 1st AgNC and the substrate)
= 306 + 5 = 311 (nm)

The targeted thickness without excluded thickness (T_1')
= The actual thickness of vertical trimer - The excluded thickness from excluded volume
= 311 – 7.5 = 303.5 (nm)

S16 Calculated the thickness of PS deposited on a substrate with exposed vertical dimer nanojunctions (T_1') and the thickness of the PS matrix desired to form vertical trimer nanojunctions (T_2')



S17 Thickness changes of PS matrix deposited on substrates under different spin speeds. Substrates with exposed dimer nanojunctions composed of 120 nm AgNC (first layer) and 100 nm AgNC (second layer) were used to study the effect of spin speed on the thickness of PS deposited on it. The results showed that the thickness of the PS matrix deposited on the substrate showed an increasing trend as the spin speed decreases, which was due to the increase in centrifugal force during spin-coating as spin speed increases. The scale bar was 400 nm.



S18 Top-view SEM images for analysis the one-dimensional nanostructure. (A) vertical dimer nanojunction (100 nm AgNC -100 nm AgNC). (B) vertical trimer nanojunction (100 nm AgNC-100 nm AgNC - 100 nm AgNC). (C) vertical dimer nanojunction (120 nm AgNC -100 nm AgNC). (B) vertical trimer nanojunction (120 nm AgNC-100 nm AgNC - 80 nm AgNC). The red circles represent vertical trimer nanojunctions. The scale bar was 200 nm.