Electronic Supplementary Material (ESI) for Molecular Systems Design & Engineering.

Directed Assembly of Metal Nanoparticles in Polymer Bilayers

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Supporting information

Materials

Poly(vinyl pyrrolidone) (PVP, Mw = 55,000, Sigma-Aldrich), polystyrene (PS, Mw =11,500, Polymer Source), poly (methyl methacrylate) (PMMA, Mw = 17,000 and Mw= 7000, polymer Source), thiol-terminated poly(ethylene glycol) (PEG) (M_w=20,000, Laysan Bio) , and 1-dodecanethiol ($C_{12}H_{25}SH$, 98%, Acros Organics)

Fabrication of polymer bilayer nanocomposite

(a) PS layer formation

Silicon substrates were cleaned in a freshly prepared piranha solution (70% (v) concentrated H_2SO_4 and 30% (v) H_2O_2). The substrates were then treated with hexamethyldisilazane vapor to obtain hydrophobic surfaces. Polystyrene was dissolved in a toluene solution (4 wt %) and thin films were prepared by spin coating (600 rpm 4 sec and 2000 rpm 40 sec).

(b) Ag nanocube array formation in air-water interface

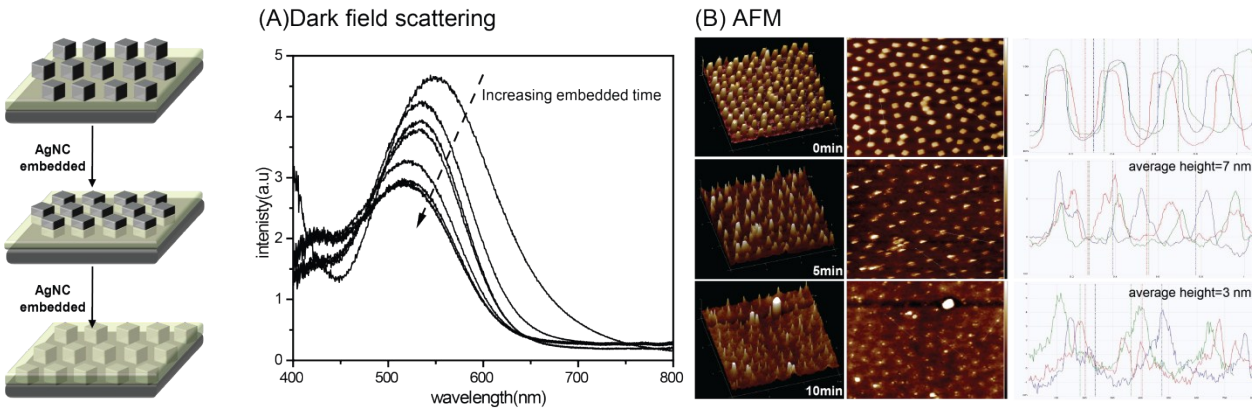
To prepare the composite film, the as-made silver nanocrystals colloidal solution were precipitated in ethanol and then dispersed in $CHCl_3$. The colloidal nanocrystal solution was then added dropwise to the air-water interface of glass petri dish, leaving an isotopically distributed monolayer of silver nanocrystals floating at the air-water interface. Nanocrystal monolayers were then transferred onto the polystyrene films by dip-coating. Nanocube array is then embedded into the underlying PS matrix before the top layer deposition.

(c) Second layer deposition

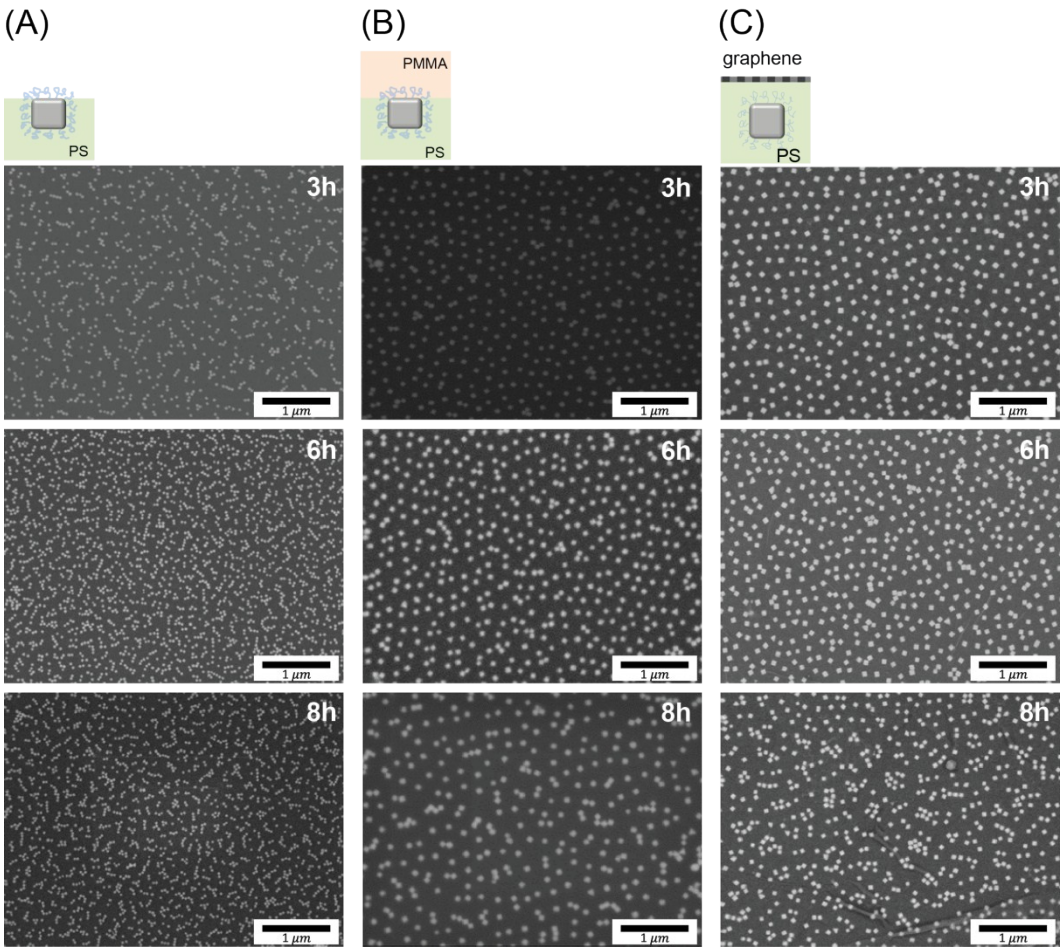
For PMMA as top layer, PMMA was dissolved in a acetonitrile solution (4 wt %) and thin films were prepared by spin coating (600 rpm 4 sec and 2000 rpm 40 sec) on PS-AgNC array substrate.

For graphene as top layer, the monolayer graphene transfer includes (1) etching the Cu support in a 0.25 M $FeCl_3$ solution, (2) rinsing in DI water, (3) transferring onto the PS-AgNC array substrate.

The kinetic of self-assembly AgNCs in bilayers was tested by thermal annealing (T > Tg of polymer matrix).



S1 AgNCs array embedded into polystyrene (PS) layer at thermal treatment temperature= 110^{o}C. (A) dark field scattering spectra of AgNCs array embedded in PS matrix with different of thermal treatment time which shows the dark field spectra without shifting after 15 min thermal treatment. (B) AFM images and height of AgNCs exposed on the top of PS. After 10 min thermal treatment, only average of 3 nm AgNC exposed on the top of PS.

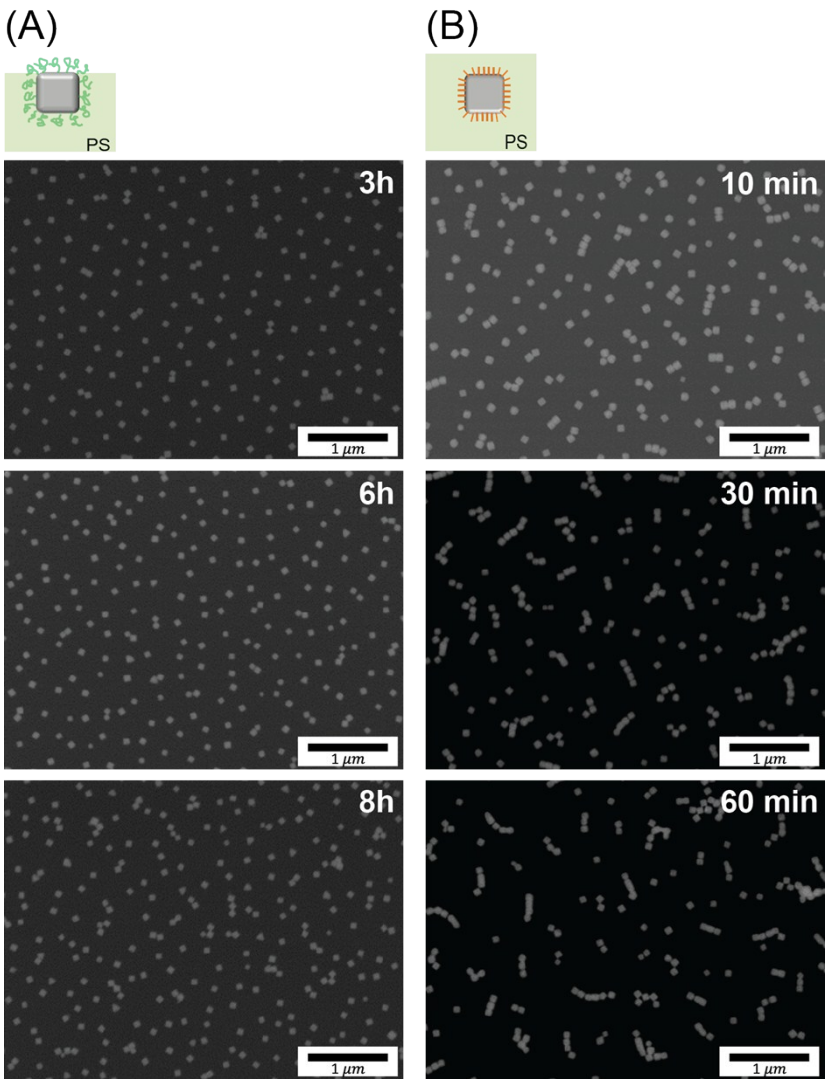


S2 Time dependent PVP coated AgNCs assembled in PS (A), PS-PMMA (B), and PS-graphene(C). The number of AgNCs in embedded chain is used to present the assembled rate by analyzing the SEM images with “Particle Image Characterization Tool (PICT)” program.

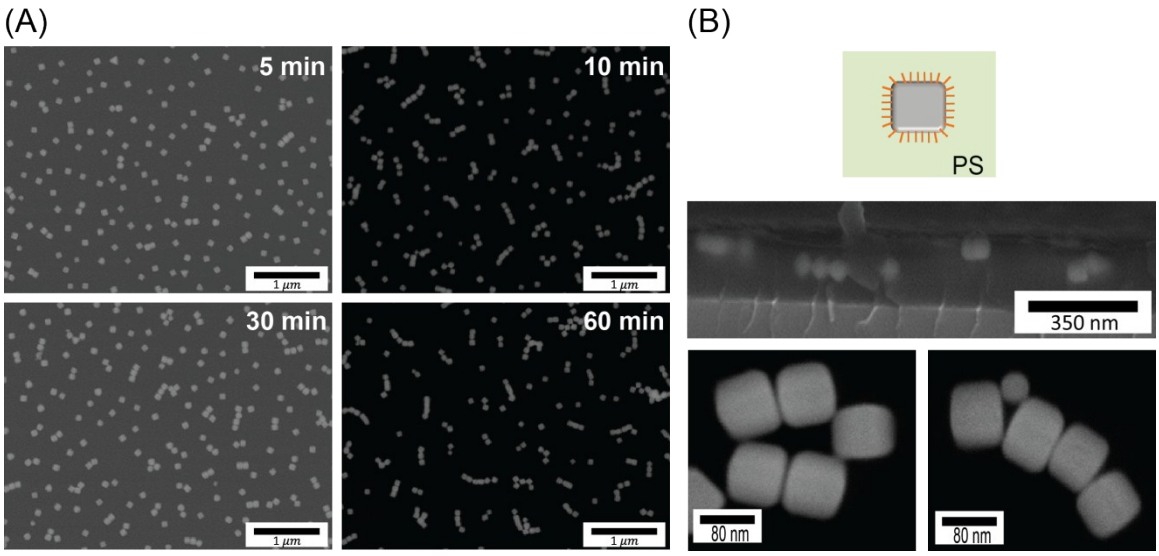
S3 calculation of viscosity of polymer layer

We use two equations to theoretically calculate the viscosity of PS and PMMA at thermal treatment. (1) Masuko and Magilll mode: the relationship between the viscosity of polymer and temperature. $\log\left(\frac{\eta}{\eta_0}\right) = A[\exp\left\{\frac{B(Tg-T)}{T} - 1\right\}]$, here we use A = 15 and B = 6. (2) Mark-Houkink equation: the relationship between intrinsic viscosity and molecular weight of polymer. $[\eta_0] = 4.1035 \times 10^{-4} \times {M_n}^{0.58}$ PMMA and $[\eta_0] = 1.28 \times 10^{-4} \times {M_n}^{0.70}$

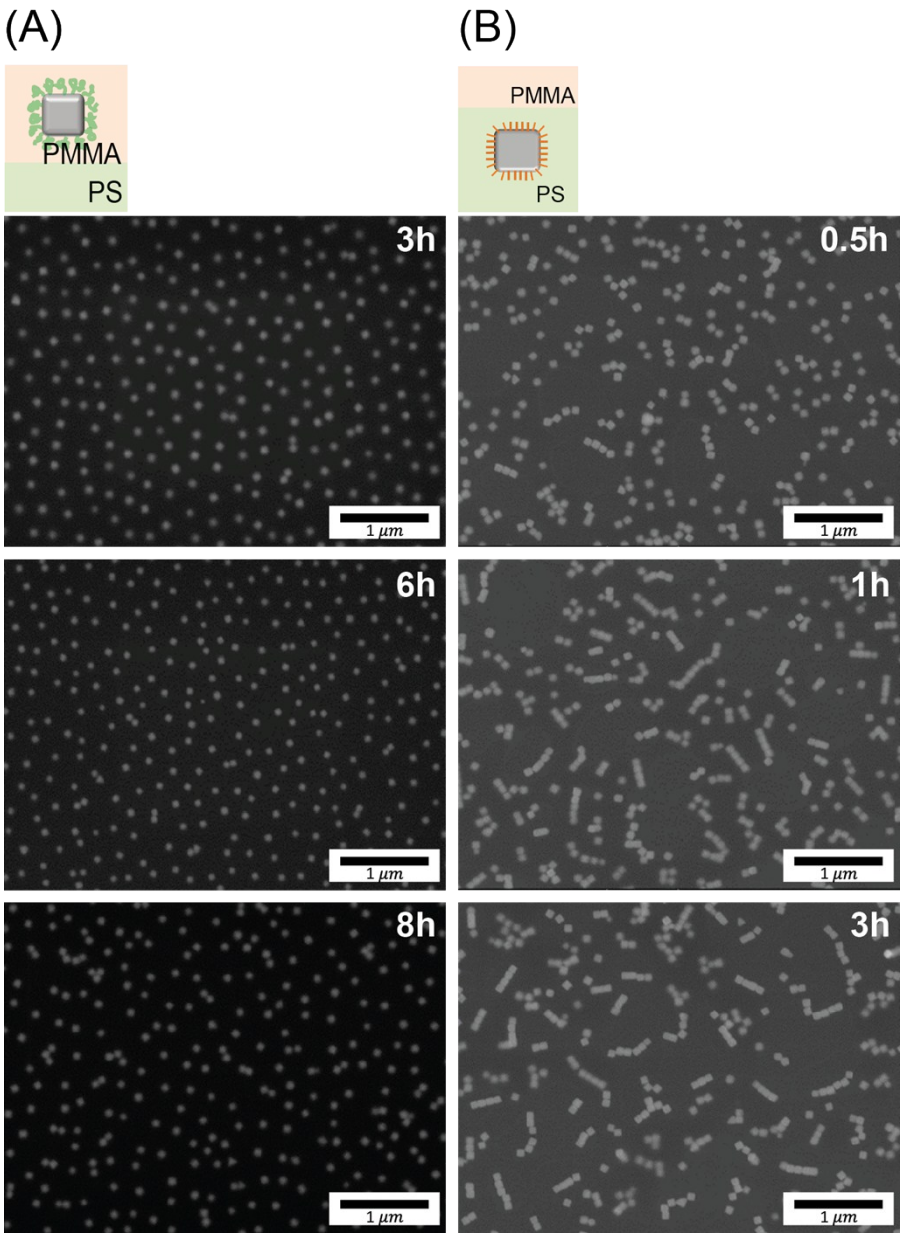
	Mn	Tg (°C)	Thermal treatment temp. (°C)	Viscosity ($Pa \cdot S$)
PMMA	17000	110	110	2.58 X10^4
	17000	110	130	3.00 X10^3
	7000	95	130	163
PS	11500	105	130	576



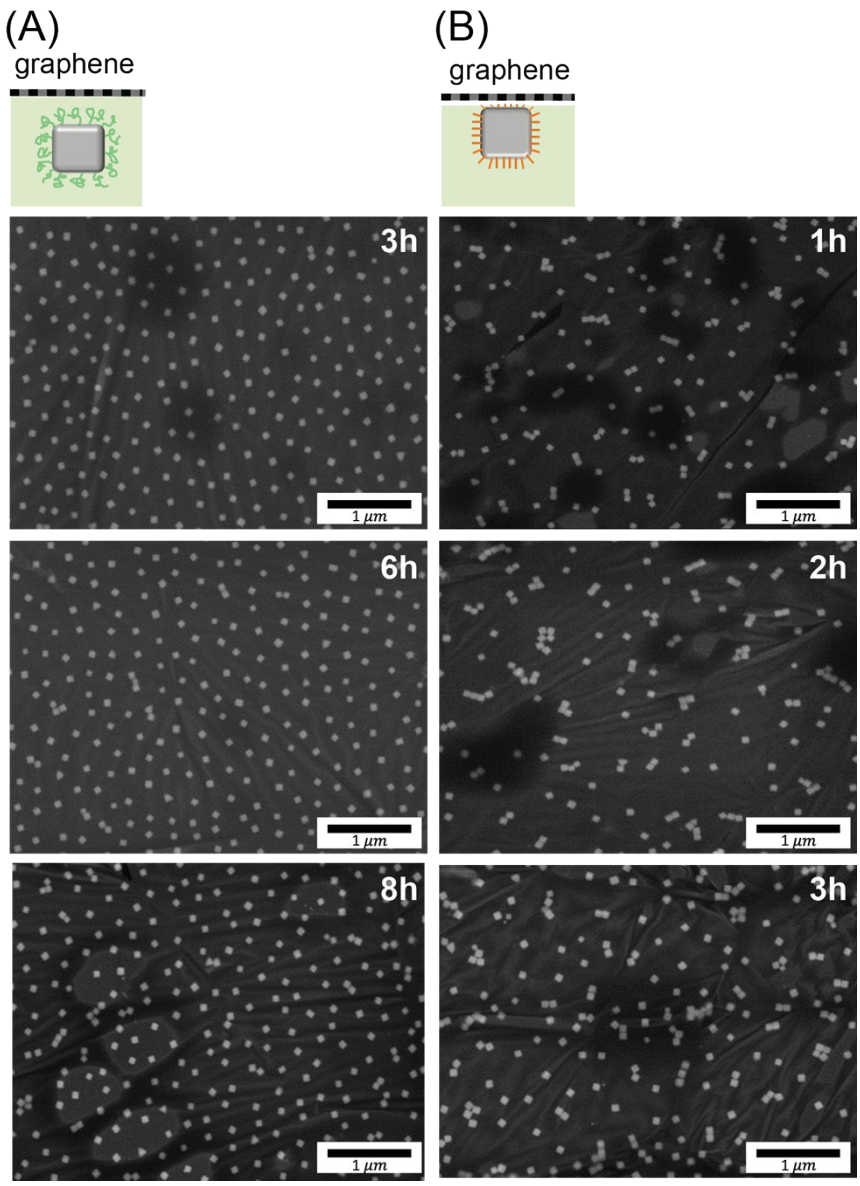
S4 Time dependent assembled in PS with different ligand shell on AgNC, PEG-SH coated AgNCs in (A) and 1-dodecanethiol coated AgNC in (B). The number of AgNCs in embedded chain is used to present the assembled rate by analyzing the SEM images with “Particle Image Characterization Tool (PICT)” program.



S5 (A) Time dependent 1-dodecanethiol coated AgNC assembled in PS at 110^{o}C (embedded temperature) (B) cross sectional SEM shows the AgNCs are pushed into PS layer and formation face-to-face assembled orientation during the embedded process.



S6 Time dependent assembled in PS-PMMA with different ligand shell on AgNC, PEG-SH coated AgNCs in (A) and 1-dodecanethiol coated AgNC in (B). The number of AgNCs in embedded chain is used to present the assembled rate by analyzing the SEM images with “Particle Image Characterization Tool (PICT)” program.



S7 Time dependent assembled in PS-graphene with different ligand shell on AgNC, PEG-SH coated AgNCs in (A) and 1-dodecanethiol coated AgNC in (B). The number of AgNCs in embedded chain is used to present the assembled rate by analyzing the SEM images with “Particle Image Characterization Tool (PICT)” program.