

## SUPPORTING INFORMATION

### Plasmonic Biomimetic Nanocomposite with Spontaneous Subwavelength Structuring as Broadband Absorbers

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#### Materials

TiN aqueous solutions are prepared with commercially available TiN powders (PlasmaChem) with an average nanoparticle size of 50 nm. We used as-received cationic polyurethane aqueous dispersion (30 vol.%, molecular mass approximately 92,000, from Hepce Chem, South Korea) after diluting in deionized water. Poly(styrene sulfonate) (molecular mass approximately ~100,000 from Sigma-Aldrich) and hydroxypropyl cellulose (molecular mass approximately ~80,000 from Sigma-Aldrich) were used as-received and dissolved in deionized water.

## Supplementary Methods

### Stabilization of TiN Dispersions for LBL Deposition

Aqueous solutions are prepared with commercially available TiN powders (PlasmaChem). Hydroxypropyl cellulose (HPC) was chosen as the stabilizer to prevent aggregation of colloidal particles in the suspension, for HPC can bonded with the native TiO<sub>2</sub> shell on the TiN. [HPC] = 0.79 mg/ml; [TiN] = 0.2 mg/ml. HPC was added into the TiN colloidal solution and stirred overnight. The spectral maximum at the ~700 nm is assigned to the plasmonic absorption of the TiN NPs (Figure S1b). TiN colloids have a passivating oxide layer with 1~2 nm thickness (Figure 1a). The NPs are predominantly cubic in shape with some presence of polyhedral (Figure S1a); their plasmon resonance peak is broad and featureless, which is both expected from polydispersed NPs and desirable for broadband absorbers. However, TiN NPs display poor colloidal stability in aqueous dispersion, which presents a great disadvantage for their processing into structured thin films. The oxide layer on the NPs provides convenient chemical “anchor” for surface functionalization (Figure 1a). Thus, we were able to disperse these NPs in presence of hydroxypropyl cellulose (HPC) that is expected to form a hydrogen bonded film on the surface reducing the attractive interactions between the NPs and increasing the interparticle repulsion. The formation of 7~13 nm HPC film on TiN NPs can be observed in TEM images (Figure 1b). These colloiddally stable negatively charged NPs are denoted here as TiN-HPC.

### PU/TiN/PSS composite coating made by LBL

The uniform coating was made by layer by layer (LbL) assembly method, in which substrates were sequentially dipped into a diluted solution of Polyurethane (PU), a dispersion of

concentrated HPC stabilized TiN NPs and a diluted solution of polystyrene sulfonate (PSS) with each step followed by rinsing with deionized water and drying with compressed air. [PU] = 1%, [PSS] = 1%, HPC stabilized [TiN] = 0.5 mg/ml. This deposition cycle constitutes a pair of layers, and can be repeated as many times as necessary to obtain the desirable thickness. The desired TiN content in the composites was attained by controlling the dipping time of a substrate to achieve the required deposition density and height of the self-assembled out-of-plane superstructures of TiN NPs on the surface.

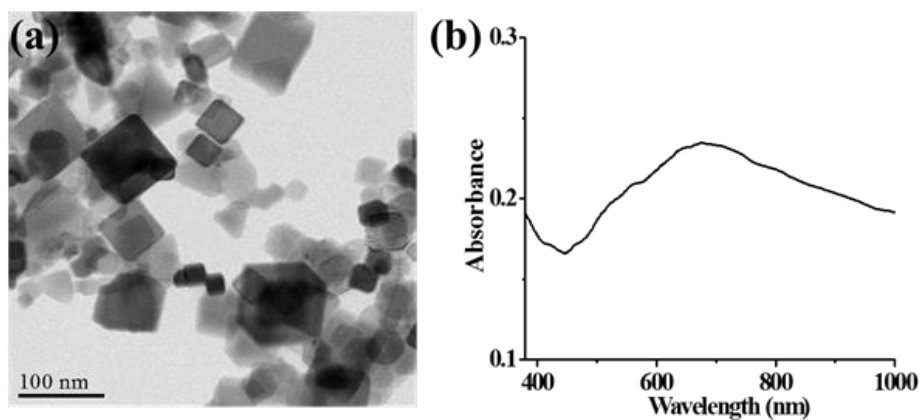
LBL films were obtained by sequential exposure of glass substrates to dispersion of TiN-HPC. In the absence of HPC surface modification, rapid sedimentation of TiN in the bulk of the dispersion occurred during the deposition and uniform films could not be obtained. The complementary LBL components included positively charged polyurethane, PU, and negatively charged poly(styrene sulfonate), PSS (pH=7). The use of additional negatively charged component, *i.e.* PSS, facilitated and accelerated the deposition of the composite films because the native charge of TiN-HPC is small, zeta potential is -7.4 mV, (pH=7).

## **Characterization**

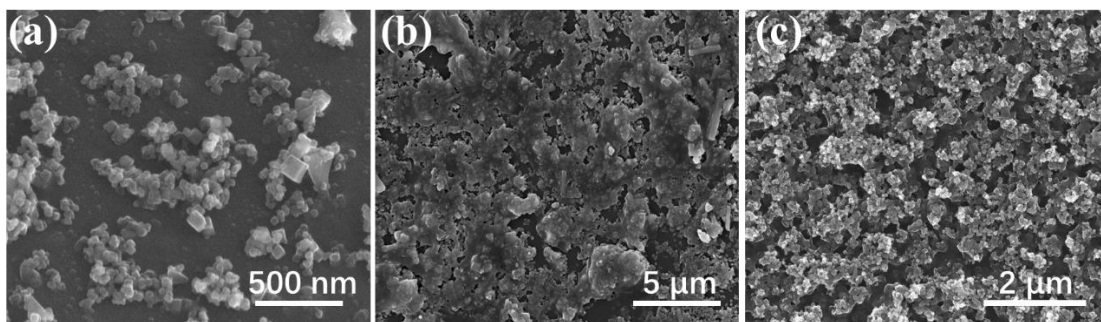
Scanning electron microscopy (SEM) images were recorded by FEI NOVA Nanolab scanning electron microscopy (SEM). Transmission electron microscopy (TEM) images were collected by a JEOL 3011. The absorbance spectra were collected by Agilent 8453 UV-visible Spectroscopy. The spectrophotometer was equipped with the 150 mm integrating sphere. The sample was mounted on the rotating shaft in the center of the integrating sphere. In one series of experiments, the samples, (PU/TiN/PSS)<sub>N</sub> film on glass was covered on the back with a black tape, which

blocked any transmitted light. In this experiment, only reflected light intensity  $R$  was detected. In the second set of measurements, the black tape was removed and the detected signal has contributions from both transmitted and reflected lights,  $T+R$ . The absorbance  $A$  was calculated as  $A=1-[T+R]$ . The thickness was obtained by stylus profilometer (MicroFig. Measuring Instrument SURFCORDER, ET-4000, Kosaka Laboratory Ltd). Temperature plotted with respect to time was obtained Flir A655sc. As the incident is not homogenous (dash circle in **Figure 6**), the coating area of the samples were placed under the center of the light illumination (dash rectangle in **Figure 6**).

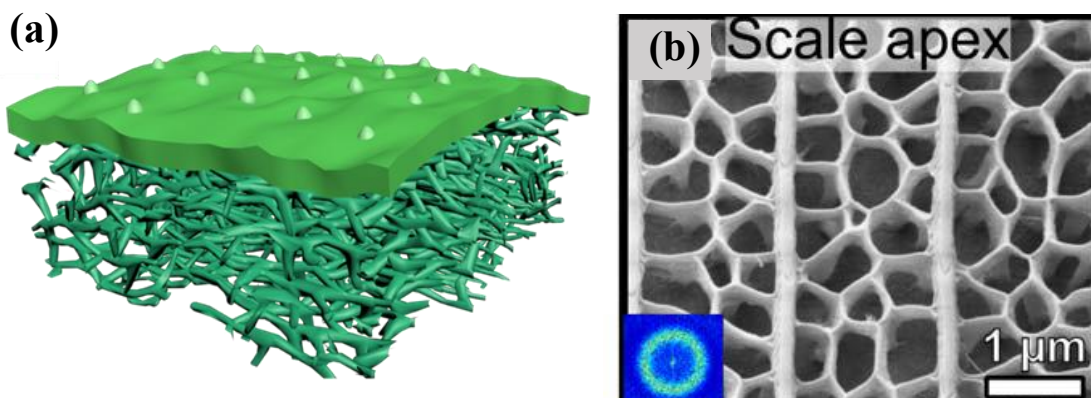
## Supplementary Figures



**Figure S1.** (a) TEM image of the TiN NPs. The NPs are predominantly cubic in shape with some presence of polyhedral with an average NP size of 50 nm and broad size distribution with some of the particles as large as 300 nm and (b) the absorbance of TiN NPs.



**Figure S2.** (a) Angle-view SEM image of typical TiN clusters formed during LBL process. (b) The top-view SEM image of the surface LBL ended with PSS/PU layers. (c) The typical top-view SEM image of  $(PU/TiN/PSS)_N$  ( $N \geq 4$ ).



**Figure S3.** (a) The schematic illustrations of the surface structure of elytrons of *Cyphochilus* beetles (Ref. Science 2007, 315, 348). As known, the elytrons of ultra-white *Cyphochilus* beetles are component a dense complex network of chitin. (b) SEM image of a scale from the wings of the matt black region of the butterfly *Pachliopta aristolochiae* (Ref. Science Advances 2017, 3(10), e1700232) The inset in the lower left corner shows the 2D Fourier power spectrum of the corresponding nanohole array indicating randomness of the shapes of the pores and out-of-plane features.

The dense complex network of fibers or pores induces high reflection in a broad wavelength range and results in an intense white with very little material. Similarly, the prepared LBL-based (PU/TiN/PSS)<sub>N</sub> consists of a highly hierarchical structure, the composite islands and continuous layers with pronounced structuring at both meso- and nanoscales. The highly hierarchical structure can give rise to strong scattering and prolong the light path, leading to strong interaction between light and matter. Consequently, the (PU/TiN/PSS)<sub>N</sub> achieves high absorbance.