

Electronic Supporting Information

Assembly of Gold Nanoparticles on Like-Charge Graphene Oxide for Fast Release of Hydrophobic Molecules

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Experimental Section

Materials:

Graphite powder (99.9995%) with particle diameter of 2-14 μm was purchased from Alfa Aesar (U.S.A.). The poly (allylamine hydrochloride) (PAH, M.W.=15 kDa) was purchased from Sigma-Aldrich Inc. (Germany). The commercial polyelectrolyte was used without further purification. Paclitaxel (PTX) (>99.0% purity) was purchased from Beijing Huafeng United Technology Co., Ltd. Chloroauric acid tetrahydrate ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$), trisodium citrate dihydrate, methanol, dichloromethane (DCM) and NaCl were all of analytical reagents. Dialysis tubings with a molecular

weight cutoff of 14 kDa for the drug release were purchased from Beijing Jingke Hongda Co., Ltd. Pure water with a resistivity of 18.2 MΩ·cm at 25 °C was used in all experiments.

Preparation of GO

GO was prepared using a modified Hummers' method.¹ Briefly, graphite powder (1.0 g) and NaCl (50.0 g) were milled at 350 rpm for 2 h by stainless steel balls (357.0 g) in a QM-3SP4 planetary ball mill (China). After removing the balls, the mixture was washed with water to remove NaCl for 3 times. The graphite flakes were air dried at 25 °C and then added to concentrated H₂SO₄ (23.0 mL), kept stirring for 12 h at 0 °C by ice-bath. Then KMnO₄ (6.0 g) was added while keeping the temperature less than 20 °C. The mixture was stirred at 40 °C for 30 min and then stirred at 90 °C for 90 min. Water (46.0 mL) was then added and the mixture in an oil-bath was stirred at 105 °C for 25 min. Subsequently, water (140.0 mL) and 30% H₂O₂ solution (10.0 mL) were added to terminate the reaction. The color of the mixture was yellow. To remove residual H₂SO₄, the product was washed with water for about 10 times and centrifuged (16654 g, 20 min) until the pH value reached 7.0. Finally, the suspension in water was treated with a FS-1200pv ultrasonic wave piezoelectric vibrator (China) at 1.2 kW for 1 h. The concentration of the final GO suspension was 14.6 mg·mL⁻¹.

Preparation of AuNPs

According to Frens' method,² 0.01 wt% chloroauric acid (50.0 mL) was heated to boiling under vigorous stirring, followed by pouring 1.0 wt% trisodium citrate

solution (0.5 mL). The mixture was heated to boiling, appearing violet within 1 ~ 3 min. The concentration of AuNPs solution was $2.9 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$.

Preparation of GO+PTX

3.6 mL PTX in methanol ($2.3 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$) was added dropwise to 4.5 mL GO suspension in water ($1.6 \text{ mg}\cdot\text{mL}^{-1}$) under rapid stirring. The mixture was stirred for 30 min, sonicated for 30 min and stirred for 30 min, respectively. Concentrated to 4.5 mL by rotary evaporation to remove the methanol, the mixture was dialyzed for 48 h to remove free PTX molecules, followed by filtration through a membrane with pore diameter of 0.45 μm to remove large PTX particles.

Release profiles of PTX from GO+PTX

In a typical process, the GO+PTX nanosheets in suspension (1.0 mL) were put in a dialysis tubing with a molecular weight cutoff of 14 kDa immersed in 15.0 mL phosphate buffered saline (PBS) (pH=7.4) solution under stirring. At each predetermined time interval, the tubing was moved to another 15.0 mL fresh PBS (pH=7.4) solution under the same condition. 5.0 mL DCM was used to extract the released PTX in the PBS solution. The concentration of PTX from GO+PTX released into PBS solution was quantitatively determined by UV spectra based on a working curve (absorbance at 230 nm against concentration of PTX in DCM).

Assemblies of (GO+PTX)/(PAH/AuNPs)/PAH nanocapsules

When the (GO+PTX) nanosheets in suspension (1.0 mL) were used as core, the nanocapsules were assembled by adsorption of PAH, AuNPs and PAH, respectively. Each adsorption cycle included 15 min incubation in $2 \text{ mg}\cdot\text{mL}^{-1}$ polyelectrolyte

solutions containing NaCl or 30 min in AuNPs solutions, washing followed by centrifugation (6139 g, 5 min) for the first adsorption cycle or (5438 g, 5 min) for 2 - 3 adsorption cycles and washing procedures. The washing procedures included three centrifugation steps and redispersion in water. After the last centrifugation, 0.5 mL water was added and sonicated for 10 s to disperse the capsules pellets against aggregation before the next adsorption.

Release profiles of PTX from (GO+PTX)/PAH and (GO+PTX)/(PAH/AuNPs)/PAH nanocapsules under NIR light irradiation

In a typical protocol, 0.2 mL (GO+PTX)/PAH suspension was put in a dialysis tubing with a molecular weight cutoff of 14 kDa immersed in 10.0 mL PBS (pH=7.4) solution under stirring, irradiated by a low energy lamp rather than high intensity laser to produce NIR light. The light passed through a cutoff filter of 800 nm with the intensity of about $40 \text{ mW}\cdot\text{cm}^{-2}$. At each predetermined time interval, the tubing was moved to another 10.0 mL fresh PBS (pH=7.4) solution under the same conditions. Then 3.0 mL DCM was used to extract the released PTX in the PBS solution. The concentration of PTX in (GO+PTX)/PAH nanocapsules released into PBS solution was quantitatively determined by UV spectra based on a working curve.

The release profiles of PTX from (GO+PTX)/(PAH/AuNPs)/PAH nanocapsules into PBS solution were measured following the protocol described above.

Characterization techniques

Fourier Transform Infrared (FT-IR) spectroscopy

FTIR spectra were collected by using a VERTEX-70 FTIR spectrometer (Bruker, Germany).

Ultraviolet-Visible (UV-Vis) spectrophotometer

UV-Vis-NIR absorption spectra of AuNPs and UV-Vis absorption spectra of PTX were recorded with quartz cells on a HP-8453 diode array spectrophotometer (Agilent, U.S.A.) with a resolution of 2 nm.

Transmission Electron Microscopy (TEM)

The TEM samples were prepared by dropping 5 μ l of capsule suspensions onto copper grids covered with holey carbon-supported films. Transmission electron microscopy (TEM) images were obtained with JEM-1011 (Jeol, Japan) under an accelerating voltage of 100 kV.

Atomic Force Microscopy (AFM)

GO+PTX and the capsules with GO+PTX as template core were both observed by atomic force microscopy (AFM) with Nanoscope IIIA (Digital Instrument, U.S.A.) in tapping mode.

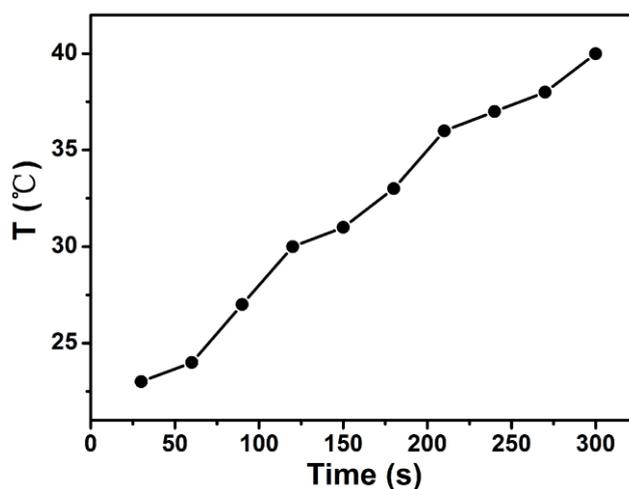


Fig. S1 The relationship between solution temperature and the NIR irradiation time.

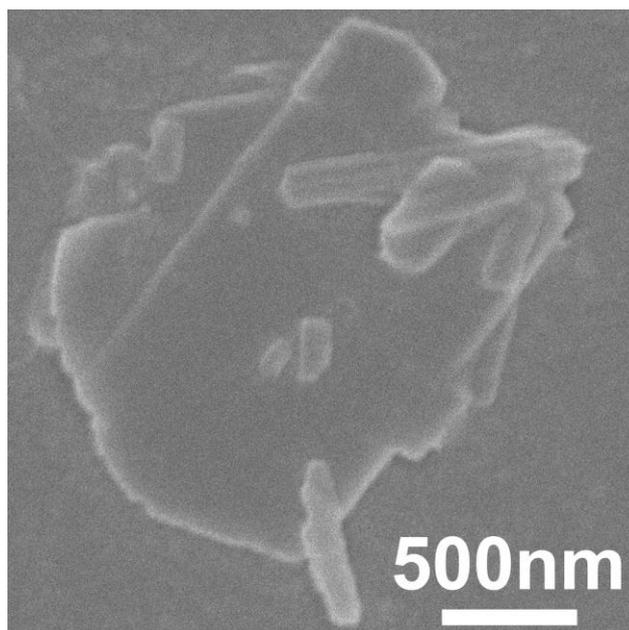


Fig. S2 The SEM micrograph of the (GO+PTX)/(PAH/AuNPs)/PAH nanocapsule.

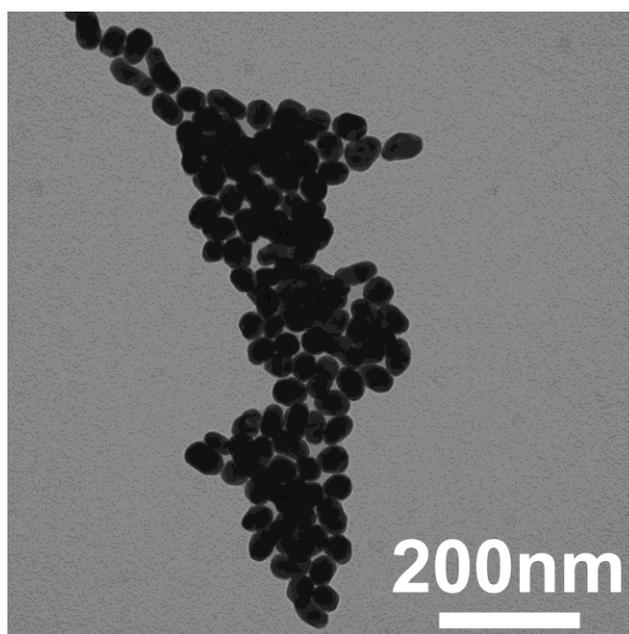


Fig. S3 The TEM micrograph of AuNPs.

References:

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(b) W. S. Hummers Jr and R. E. Offeman, *J Am Chem Soc*, 1958, **80**, 1339.
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