

Supporting Information

1. More detailed information

1.1. Adsorption energy E_a

E_a represents the adsorption energy. $E_a = E_{atom/thiophene} - (E_{atom} + E_{thiophene})$.

$E_{atom/thiophene}$ represents the energy that the atoms have adsorbed to the surface. E_{atom} represents the energy of the Au atom in vacuum, $E_{thiophene}$ represents the energy of the clean surface.

1.2. Preparation of PTs monomers

In our work, all used chemicals and reagents were bought from Aladdin or Energy Chemical. Then the chemicals and reagents are employed without any purification in advance. Solvents for chemical synthesis and electrochemical were already purified by distillation. CuI (0.2 mol), potassium t-butoxide (1.5 mol), and ethanol (diethylene glycol monoethyl ether, triethylene glycol monoethyl ether, or 2-ethoxyethanol 5 mol) (5 mol) were added to 500 mL pyridine and allowed to stir for 0.5 hour. Then, 3-Bromo thiophene (1 mol) was added and the mixture was heated to 100 °C for 24 hours. After cooling down to room temperature and adding 50mL of CH₂Cl₂, the mixture was washed successively with aqueous HCl (0.5 N), saturated aqueous solution of Na₂CO₃ and water. The organic phase was dried over Na₂SO₄. After filtration, the solvent was only removed under vacuum and the residue was purified by column chromatography

on silica gel (petroleum ether/EtOA=1:2) to give a white compound (yield: 63.1%). Then, we get four thiophene derivatives monomers (shown in Figure S1): (a) 3-ethoxy-2, 5-dimethylthiophene, (b) 3-(2-ethoxyethoxy)-2, 5-dimethylthiophene, (c) 3-(2-(2-ethoxyethoxy) ethoxy)-2, 5-dimethylthiophene, and (d) 3-(2-(2-(2-ethoxyethoxy) ethoxy) ethoxy)-2, 5-dimethylthiophene. The structures of the PTs monomers were further verified by NMR, which are illustrated as Figure S1.

1.3. Initial structure selection

Experimental analysis has proved that the structures of PTs usually have three ways of connection. Thiophene ring and thiophene ring can be coplanar connection and can also be twisted into a certain angle. If thiophene ring and thiophene ring have been twisted into a certain angle, the interaction between thiophene ring and thiophene ring will be reduced. Then, the charge in the main chain will become localized and π electrons conjugation in the main chain will be reduced accordingly, leading to higher relative energy. After the preliminary calculation of the minimum energy structure of PTs in Chemoffice software, the coplanar structure of thiophene ring coplanar connection is energetically superior to the other two non-coplanar structures. In order to meet the requirements of theoretical calculation, we selected the structure of coplanar connection thiophene derivatives as initial structure model. Then we tested S, O and C atoms at different positions in PTs. It is found that the adjacent C of the side chains can serve as the adsorption site that can effectively interact with Au ion, but the C atoms in other positions and other elements had almost no adsorption ability. This adjacent C is

an easily replaceable activation site on the main chain of PTs and has its own advantages in spatial configuration.

1.4. Uv-vis absorption spectrum analysis of PT substrates

The Uv-vis absorption spectrum of the four PT substrates are measured and shown as Figure S6 (H₂O is used as solvent). We have successfully synthesized four kinds of PT substrates for the intensity of the ultraviolet absorption increased evenly with the increase of electrical aggregation laps. PT substrates exhibited absorption peaks at 380nm ~ 400nm and 510nm ~ 540nm, which were consistent with the reference ³². Thus, it can be proved that PT substrates can be stable when prepared by electrochemical polymerization method. Uv-vis absorption spectra during the electropolymerization process of PT substrates indicated that the technology to mass-produce such PT substrates is feasible and manageable. In addition, the initial surfaces morphology of PT substrates are shown in Figure S2 (SEM images) and Figure S3 (AFM images), which are pretty uniform and smooth. Our work represents a further effort novel strategy on controlling the AuNPs morphology toward ultrafine nanoparticles and understanding the electrodeposition processes occurring at Au-PTs interfaces, which are promising in electrocatalysis and electrochemical energy conversion devices.

1.5. Simulation methods

First-principles calculations were performed based on the density functional

theory (DFT) as implemented in the Vienna *Ab-initio* Simulation Package (VASP) code³³. We used the projector augmented wave potential, while chose the generalized gradient approximation (GGA) with the parametrization of Perdew-Burke-Ernzerhof (PBE) to treat the exchange correlation interaction. The kinetic energy cutoff for plane wave expansion is set at 550 eV, which is enough for the PT substrates materials we have selected. A vacuum of 25 Å is used along the direction perpendicular to the layer to avoid slab's interaction with their periodic images. Monkhorst-Pack mesh of 3×3×3 is used for integration in reciprocal space. To obtain the optimized structures, the forces on all atoms were minimized to be smaller than 0.01 eV/ Å.

1.6. Details of the electropolymerization

0.1 Mm H₂AuCl₄ and 0.1 M NaClO₄ solution are used as deposition solution of Au nanoparticles, the geometric area of PT substrates (0.5cm²) was controlled by nail polish. Electropolymerization was performed using CHI Model 660E electrochemical analyser in the way of cyclic voltammetry. AuNPs were prepared in two steps: 1. Using Chronoamperometry method, we applied a voltage range from -0.8V ~ +0.89V to ITO electrode. 2. Then we used cyclic voltammetry method to control the potential range from 0.3V ~ -0.04V and the scanning speed is 100 mV/s. Then we set the CV cycle number to 25 in order to obtain the electrochemical deposition.

1.7. Further verification of DFT theory

To further verify our idea, we further calculated the adsorption energy between poly [1-((2, 5-dimethylthiophen-3-yl) oxy)-3, 6, 9, 12-tetraoxatetradecane] (chemistry formula of PTsO5 is shown in Figure S5) and Au ions, the adsorption energy is 1.121 eV and the adsorption energy of PTsO6 is 1.121 eV. The trend was consistent with our preliminary prediction.

1.8. XRD analysis

We also did the XRD during our modification process. Unfortunately, different phases were not found in our deposited AuNPs. The XRD patterns of AuNPs on PTsO1 to 4 are showed in Figure S10. All AuNPs on PTsO1 to 4 samples possess the same characteristic diffraction peaks at 38.2° , 44.4° , 64.6° , and 77.5° , corresponding to the (111), (200), (220) and (311) crystalline planes of the face-centered cubic (fcc) Au phase (JCPDS#04-0784), which confirms that AuNPs has been successfully deposited on PTs and no different phases were found in our deposited AuNPs. In addition, as a typical measure of degree of crystallinity, the intensity of intense (111) plane for AuNPs on PTsO4 to 1 was gradually increasing, implying an increase in degrees of crystallinity. Excluding the peaks of Au, other diffraction peaks belong to In_2O_3 of ITO substrate. They are at 21.5° , 30.6° , 35.5° , 37.7° , 45.7° , 51.0° and 60.7° , which can be directly assigned to the (211), (222), (400), (411), (431), (440) and (622) planes of cubic In_2O_3 phase (JCPDS#06-0416). Finally, AuNPs on PTsO1 to 4 consists of an additional broad diffraction peak at around 25.0° , resulting from the amorphous polythiophene structure.

2. Figures

2.1. The structure of the PTs monomers were further verified by NMR spectroscopy.

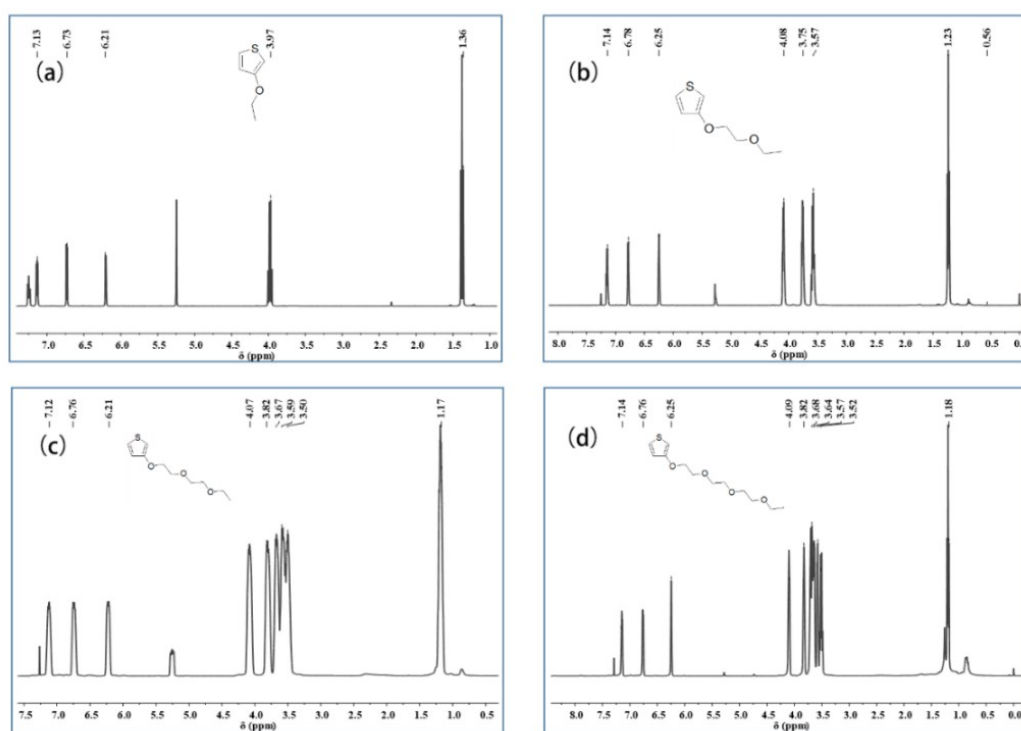


Figure S1. The structure of the PTs monomers were further verified by NMR spectroscopy. The specific peak position and NMR analysis are as follows:(a) NMR image of 3-ethoxy-2, 5-dimethylthiophene): ^1H NMR (CDCl_3 400MHz): δ 7.13 (1H), 6.73 (1H), 6.21 (1H), 3.97 (2H), 1.36(3H).(b) NMR image of 3-(2-ethoxyethoxy)-2, 5-dimethylthiophene: ^1H NMR (CDCl_3 400MHz): δ 7.14 (1H), 6.78 (1H), 6.25 (1H), 4.08 (2H), 3.75 (2H), 3.57 (2H), 1.23(3H). (c) NMR image of 3-(2-(2-ethoxyethoxy) ethoxy)-2, 5-dimethylthiophene: ^1H NMR (CDCl_3 400MHz): δ 7.12 (1H), 6.768 (1H), 6.21 (1H), 4.07 (2H), 3.82 (2H), 3.67 (2H), 3.59 (2H), 3.50 (2H), 1.17(3H).(d) NMR image of 3-(2-(2-(2-ethoxyethoxy)ethoxy)ethoxy)-2,5-dimethylthiophene: ^1H NMR (CDCl_3 400MHz): δ 7.14 (1H), 6.76 (1H), 6.25 (1H), 4.09 (2H), 3.82 (2H), 3.68 (2H), 3.64 (2H), 3.57 (2H), 3.52 (2H), 1.18(3H).

2.2. SEM images of polythiophene derivatives thin film

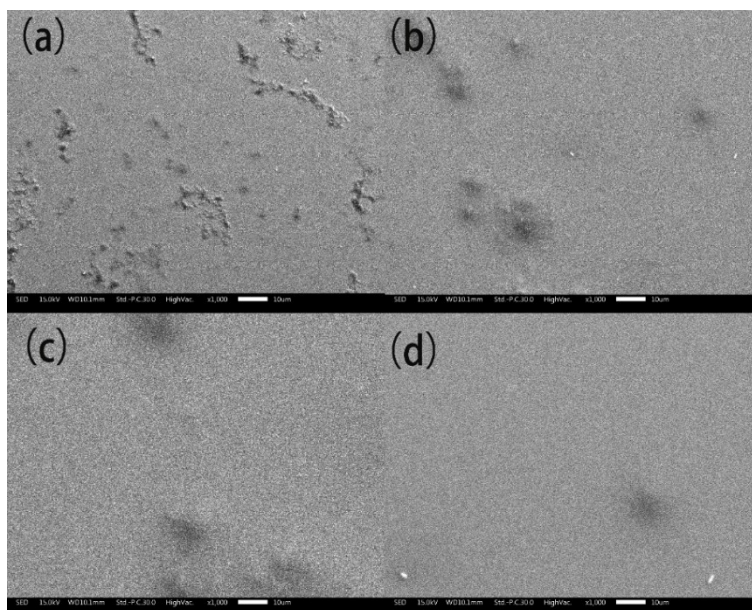


Figure S2. SEM images of polythiophene derivatives thin film deposited electrochemically on ITO electrodes: (a) PTsO1 substrate; (b) PTsO2 substrate; (c) PTsO3 substrate; (d) PTsO4 substrate. Magnification: 1000.

2.3. AFM images of polythiophene derivatives thin film

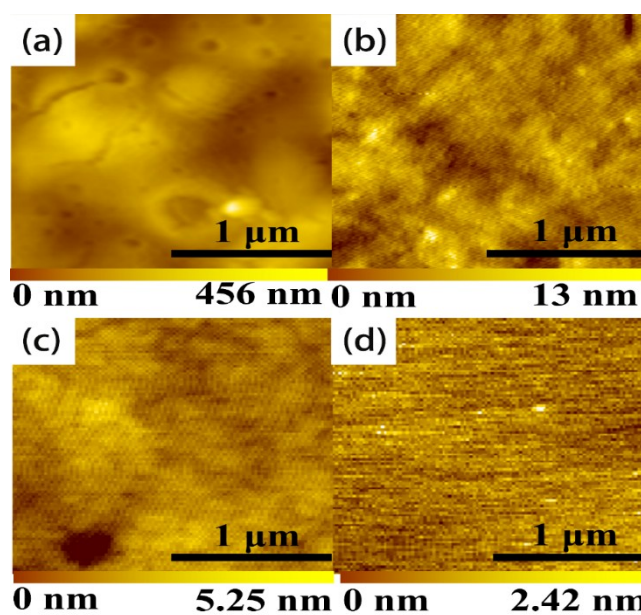


Figure S3. AFM images of polythiophene derivatives thin film deposited electrochemically on ITO electrodes: (a) PTsO1 substrate; (b) PTsO2 substrate; (c) PTsO3 substrate; (d) PTsO4 substrate.

2.4. Schematic histogram of Au particle size distribution

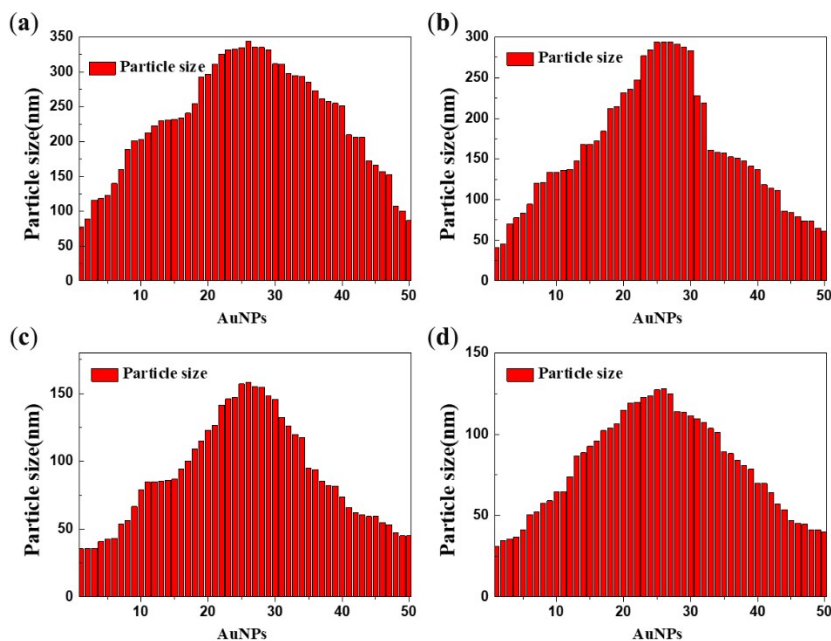


Figure S4. Schematic histogram of Au particle size distribution: (a) PTsO1 substrate; (b) PTsO2 substrate; (c) PTsO3 substrate; (d) PTsO4 substrate.

2.5. Chemical structure of polythiophene derivatives

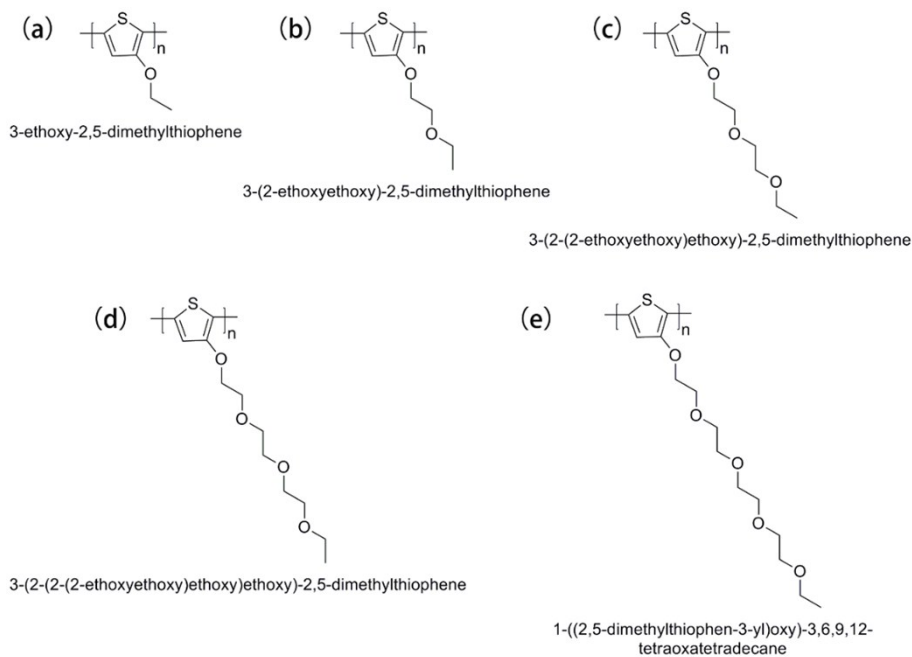


Figure S5. Chemical structure of polythiophene derivatives: (a) PTsO1 substrate; (b) PTsO2 substrate; (c) PTsO3 substrate; (d) PTsO4 substrate and (e) Chemical structure of Poly [1-((2, 5-dimethylthiophen-3-yl) oxy)-3, 6, 9, 12-tetraoxatetradecane], namely PTsO5.

2.6. Uv-vis absorption spectra during the electropolymerization process of PT substrates

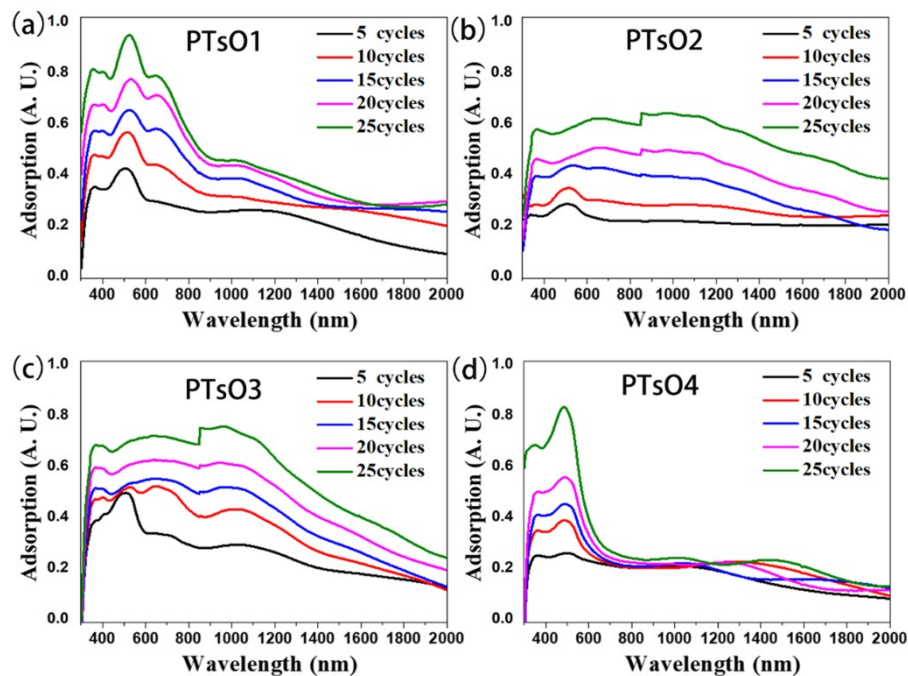


Figure S6. Uv-vis absorption spectra during the electropolymerization process of PT substrates: (a) PTsO1; (b) PTsO2; (c) PTsO3; (d) PTsO4.

2.7. Synthetic route and chemical formula of PTs

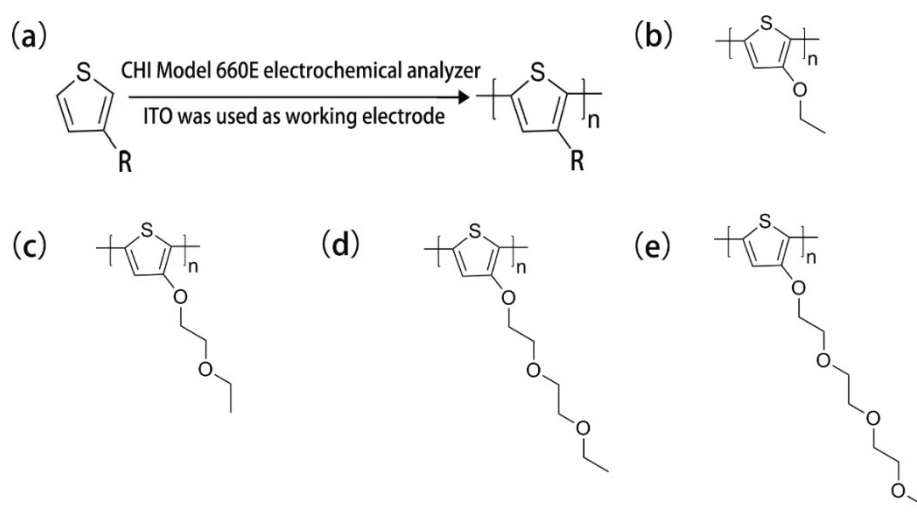


Figure S7. (a) Synthetic route of PT substrates, (b) chemical formula of PTsO1; (c) chemical formula of PTsO2; (d) chemical formula of PTsO3; (e) chemical formula of PTsO4.

2.8. Cyclic voltammety curve during the electropolymerization process of PT substrates

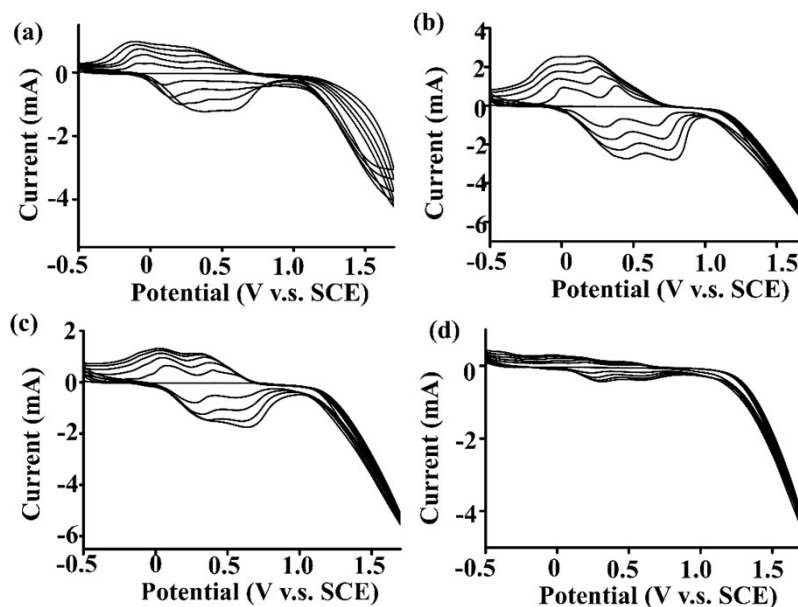


Figure S8. UV polymerization curves: (a) PTsO1 substrate; (b) PTsO2 substrate; (c) PTsO3 substrate; (d) PTsO4 substrate

2.9. Charge density difference of PTs before and after the adsorption of Au ions.

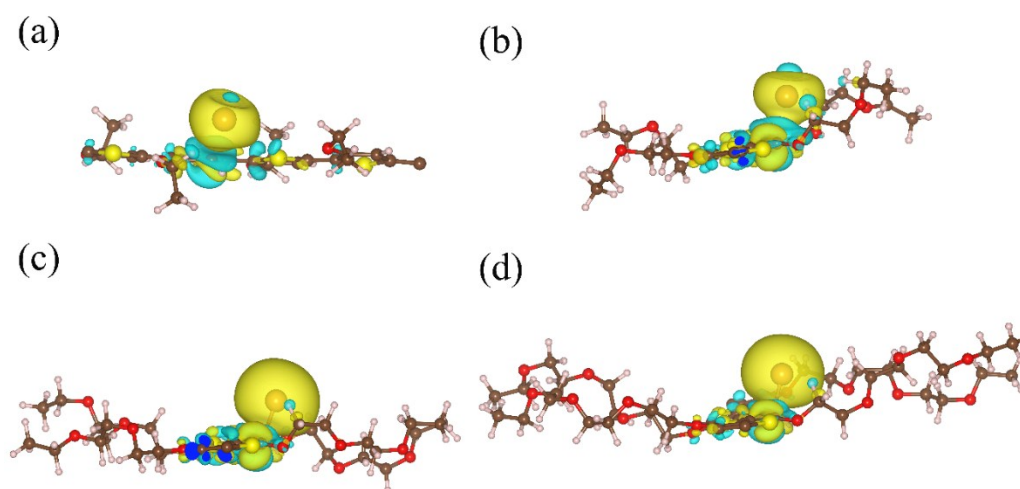


Figure S9. Charge density difference of PTs before and after the adsorption of Au ions. (a) PTsO1; (b) PTsO2; (c) PTsO3; (d) PTsO4. The golden, yellow, red, brown and gray spheres represent the Au, S, C, O, and H atoms, respectively.

2.10. XRD pattern of AuNPs on PTsO1 to 4.

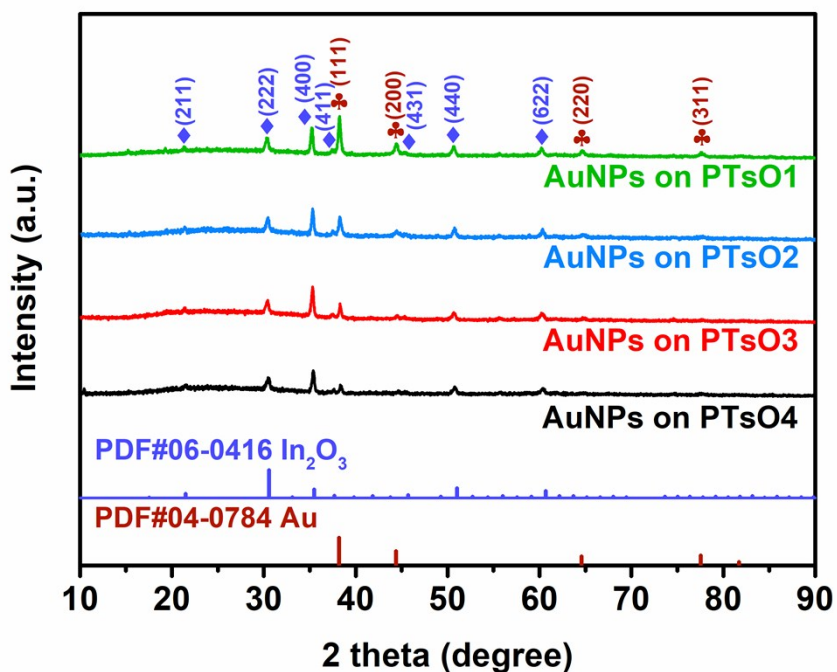


Figure S10. X-ray diffraction patterns of AuNPs on PTsO1 to 4. The standard XRD patterns of In_2O_3 (PDF#06-0416) and Au (PDF#04-0784) were inserted as background.

3. Tables

Table S1. Particle size of AuNPs on PT substrates.

	PTsO1	PTsO2	PTsO3	PTsO4
Particle size Aver.(μm)	0.23	0.14	0.09	0.08

Table S2. Adsorption energy between PTs and Au ions.

	PTsO1	PTsO2	PTsO3	PTsO4
Adsorption energy (eV)	0.841	0.919	1.117	1.120

Acknowledgments

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