Ultrafast generation of the thick poly (ether amine) (PEA) brush on the gold surface and its protein resistance

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**Experimental Section**

**Materials**

(111)-oriented single crystal silicon wafer was purchased from Shanghai Risen Co. Ltd.. The silicon wafers were sliced into square chips of 1 cm×2 cm in size. Poly(ether amine) containing thiol groups (PEA-SH) was synthesized as previous report\(^1\). Poly(propylene glycol) diglycidyl ether (PPO, Mn=640) and \(\beta\)-mercaptoethylamine (MEA) were purchased from Sigma-Aldrich. Jeff amine L100 (Mn=1000) was purchased from Hunstman Co. Ltd. Six proteins conjugated with fluorescein isothiocyanate (FTIC) were bought from Beijing Zoman Biotechnology Co. Ltd. Chloroform, ethanol and other chemicals are of analytical grade except as noted.

**Gold substrate preparation**

The silicon wafers were first treated with a strong acidic oxidizing solution of concentrated sulfuric acid and hydrogen peroxide (\(\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2\) (30%) = 3/1) for 1 h
to obtain clean surfaces. Then the gold film was produced by JGP-560C ultrahigh vacuum multifunction sputtering system. The sputtering time was about 5 min. We also prepared other noble metal surfaces such as silver and copper surfaces.

**Synthesis of PEA-SH**

Graft poly (ether amine) containing thiol-group (gPEA-SH) was synthesized as previous report. 1 1.28 g (2 mmol) PPO640, 1.0 g (1 mmol) Jeffamine L100, 0.077g (1 mmol) β-mercaptoethylamine (MEA) and 10 ml ethanol were added into two-necked flask. The mixture was heated to 80 °C for 24 h under nitrogen. After cooling to room temperature, the mixture was poured into 10 fold anhydrous ether and filtered, dried in vacuum at 40 °C to get PEA-SH. FTIR: 3434 cm⁻¹ (OH), 2891 cm⁻¹ (CH), 1096 cm⁻¹ (C-O-C). GPC: $M_n = 1.6 \times 10^4$, $M_w = 8.1 \times 10^4$, $M_w / M_n = 5.1$.

**The fabrication of PEA brush on gold surface**

The gold surfaces were immersed in gPEA-SH /chloroform solution (1 wt%) for several minutes and then sonicated in pure chloroform for 10 min. Thus we got PEA brush grafted gold surfaces.

**Protein Adsorption Experiments**

The PEA brushes grafted gold surface was dipped in protein solution (2mg/ml) for 2 h and then washed extensively with pure water running for 30 min.

**Characterization**

**Water contact angle measurements (WCA)**

Static contact angles of polymer brush samples were measured with a contact angle meter (model CAM Micro) at room temperatures or certain temperature. The
accuracy of the angle measurement was ± 0.1°. Contact angles were averaged from at least three different spots for each sample.

**Thickness measurements**

Variable angle ellipsometer (W-VASE with Auto Retarder TM, J.A.Woollam Co.) was used to measure thickness of polymer brush on gold samples which can verify the growth of PEA brush. Measurements were taken at 1 mm intervals across each film. The accuracy was 0.5 nm and an incident angle of 70° was used.

**X-ray photoelectron spectroscopy (XPS)**

The polymer brushes on gold samples were analyzed by XPS. XPS experiments were carried out on a PHI-5000C ESCA system (Perkin Elmer) with Al Ka radiation (hn = 1486.6 eV). Generally, the X-ray anode was run at 250W and the high voltage was kept at 14.0 kV with a detection angle at 54°. The pass energy was fixed at 46.95 eV to ensure sufficient sensitivity. The base pressure of the analyzer chamber was about 5 ×10⁻⁸ Pa. The sample was directly pressed to a self-supported disk (10×10mm) and mounted on a sample holder and then transferred into the analyzer chamber. The whole spectra (0~1200 eV) of all the elements with much high resolution were recorded. The data analysis was carried out by using the RBD AugerScan 3.21 software provided by RBD Enterprises or XPS Peak 4.1 provided by Raymund W.M. Kwok.

**Atomic force microscopy (AFM)**

The surface morphologies of PEA brush samples were acquired in taping mode on AFM (Nanoscope III, Digital instruments, USA).
Fluorescence interference microscopy (FIM)

The fluorescence microscope images of the BSA-FITC adsorption was taken by FIM (Olympus BX61, Japan) in dark field. U-MWIBA3 (blue, 460-495nm) was used as the excitation module.

Results

Characterization of PEA brush on Au and Ag surface

![Figure S1 FT-IR spectra of (a) PEA brush grafted to gold (5min), (b) PEA brush grafted to silver (2h), (c) gPEA-SH.](image)
Figure S2 Atomic force microscopy (AFM) image of PEA brush grafted to gold.

Figure S3. XPS spectra of PEA brush grafted to silver surface (graft time is 1h)
Figure S4 Reaction time dependence of PEA brush thickness and water contact angle (WCA) on the silver surface
Figure S5 Fluorescence microscope images of protein adsorption on Au surface and PEA brush (a, Human Albumin-FITC; b, Goat anti Mouse IgG(Whole serum)-FITC; c, Goat anti-rabbit IgG (Whole serum)-FITC; d, Goat anti-Pig IgG-FITC; e, Goat anti-Bovine IgG–FITC)
Figure S6 Fluorescence microscope image of Au@PEA brush after storage in protein BSA-FITC aqueous solution for 30 days.

Reference