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Supporting Information

CO_2-Responsive Surface with Amidine-Terminated Self-Assembled Monolayer for Stimuli-Induced Selective Adsorption

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Experimental section

1. Materials

Ethylene diamine (EA), di-tert-butyl dicarbonate (Boc anhydride), dichloromethane (DCM), Lipoic acid (LA), dimethyl aminopyridine (DMAP), N, N'-dicyclohexylcarbodiimide (DCC), N, N-Dimethylacetamide dimethyl acetal (DMADMA), diethyl ether, sodium hydrogen carbonate ($NaHCO_3$), $HAuCl_4 \cdot 3H_2O$, sodium citrate, oleylamine were purchased from Sigma (Singapore). Ethyl acetate, HCl, anhydrous Na_2SO_4, NaOH and toluene were purchased from Merck (Singapore). Unless otherwise stated, all the other chemicals are reagent grade and used without further purification. Millipore Milli-Q water (Di-water/18 MΩ cm^{-1}) was used in all experiments. The single crystal silicon wafers (100) polished on one side were obtained from Latech Inc. (Singapore).

2. Instruments and characterizations

All nuclear magnetic resonance (NMR) data were measured at room temperature by an Agilent 600-MHz NMR spectrometer. Water contact angle (CA) was measured using the FTA 200 contact-angle system at ambient temperature. A droplet of solution was generated at a very low rate (1μL/s) and detached from the syringe needle tip as soon as it touched the substrate surface. The CA values reported are averages of respective values of several spots on each sample surfaces. Measurements were taken immediately after the formation of NADPA SAM to minimize reaction with atmospheric CO_2. An Autolab PGSTAT 302 potentiostat equipped with a FRA 2 module and GPES/FRA 4.9 software was used for the electrochemical measurements. Cyclic voltammetry (CV) and electrochemical impedance (EIS) measurements were performed in 0.1M KCl Di-water containing 5 mM K3[Fe(CN)6]/K4[Fe(CN)6] (1:1) as a redox probe in a conventional three-electrode cell with Pt foil and Ag/AgCl electrode as well as Au electrode as the counter electrode, reference electrode and working electrode, respectively. The impedance spectra were measured in the frequency range from 100 mHz to 100 kHz at a potential of 0.24 V versus Ag/AgCl (saturated KCl), with a voltage amplitude of 5 mV. A modified Randles circuit is used to fit the obtained impedance data (shown in the inset of Figure 2A). R_{sol}, R_{ct} and W imply the Ohmic resistance due to an electrolyte, charge transfer resistance occurring at the film/solution interface and Warburg impedance, respectively. The ideal capacitor is replaced by a constant phase element (CPE) Q_{dl} due to the roughness and/or porosity on the interface between film and surface. The morphologies of selective-adsorbed Au NPs on amidine-modified surfaces were observed by field-emission scanning electron microscopy (SEM, JEOL JSM6701F) and atomic force microscopy (AFM, MFP-3D-SA, Asylum Research, tapping mode).

3. Synthesis of CO_2-responsive bifunctional molecule

3.1 N-Boc-ethylene diamine (BEDA)

Boc anhydride (5 mL, 22 mmol) in 50 mL dried dichloromethane was added dropwisely over 2 h to an ice cooled mixture of dried 50 mL DCM and EA (6 mL, 90 mmol). The mixture was stirred in ice water for another 2 h, then at room temperature overnight. After removal of DCM by a rotary evaporator, residual liquid was dissolved in 100 mL saturated brine and extracted by ethyl acetate (100 mL × 3). After being dried over anhydrous Na_2SO_4, ethyl acetate was removed by rotary evaporator to get BEDA product. Yield: 81%. ^1H NMR ($CDCl_3$): δ1.44 (s, 9H, $(CH_3)_3C$), 2.66-2.69 (t, 2H, CH_2NH), 3.11-3.13 (t, 2H, CH_2NH_2).

3.2 N-(2-aminoethyl)-5-(1,2-dithiolan-3-yl) pentanamide (NADP)

LA (5 g, 24.2 mmol), BEDA (4.65 g, 29.0 mmol, 160.21), DMAP (0.59 g, 4.84 mmol) was dissolved into 50 mL DCM in a flask and cooled by ice water. DCC (5.98 g, 29.0 mmol) in 50 mL DCM was added dropwisely in 1 h, the reaction mixture was continually stirred at room temperature overnight. After filtration to remove the white precipitate, the organic phase was removed by rotary evaporate. The acquired product was dissolved in 50 mL DCM, and washed subsequently by 0.1 M NaOH (50 mL), brine (50 mL) and water (50 mL). DCM was removed and the product was purified by gel chromatography (methanol/DCM=10/1). To remove the Boc group, 10 mL 4 M HCl in dioxane was added into 3 g product prepared above in a glass vial and the mixture was stirred overnight. 20 mL diethyl ether was added to precipitate the product. The acquired product was dissolved in 50 mL DCM, washed subsequently by 0.1 M NaOH (50 mL) and water (50 mL) to remove HCl. After dried by anhydrous Na_2SO_4, DCM was removed and the final product NADP was collected. Yield: 85%. ^{1}H NMR ($CDCl_3$): δ4.10 (m, 2H, CH_2), 3.53-3.09 (m, 4H, 2 CH_2), 2.41-2.29 (m, 3H, CH and CH_2), 1.87-1.66 (m, 6H, 3CH_2), 1.21 (m, 2H, CH_2).

3.3 NADP-amidine (NADPA)

NADP (3 g, 12.1 mmol), DMADMA (3.2 g, 24.2 mmol) were dissolved in diethyl amine (10 mL) and stirred overnight under N_2 protection. After removal of solvent by rotary evaporator, the reactant was dissolved by 10 mL DCM and washed subsequently by 0.1 M NaOH (10 mL) and water (10 mL). The organic phase was dried over anhydrous Na_2SO_4 and removed. The acquired product was dried in vacuum. Yield: 100%. ^{1}H NMR (D2O): δ4.10 (m, 2H, CH_2), 3.53-3.09 (m, 10 H, 2 CH_2, 2 CH_3), 2.41-2.29 (m, 3H, CH and CH_2), 2.0-1.66 (m, 9H, CH_3 and 3CH_2), 1.21 (m, 2H, CH_2).

4. Fabrication of CO_2-responsive molecular monolayer

The NADPA-modified Au electrode surface was achieved through molecular self-assembly. Prior to use, an Au electrode (diameter 2 mm) were polished with wet alumina powder of successively smaller particle sizes (1.0 and 0.05 μm diameter), and then washed ultrasonically with ethanol and water respectively. Consequently, the Au electrode was electrochemically cleaned by cycling between – 0.4 and 1.6 V vs. Ag/AgCl in 0.5 M sulfuric acid until the formation of three distinct gold oxide peaks and no change during the successive scans. To form the amidine self-assembled monolayer (SAM), the electrochemically cleaned Au electrode was incubated into an ethanol solution containing 10 mM amidine for 12 h. After that, they were thoroughly rinsed with ethanol and DI-water to remove the physically-absorbed chemicals. For silicon wafers modification, the polished silicon wafers were ultrasonicated in acetone and ethanol for 30 min, and then cleaned in freshly prepared "Piranha" solution (30% H_2O_2 and concentrated H_2SO_4, 1:4 Vol) for 10 min to remove organic contaminants. Rinsing with DI-water and drying thoroughly, the cleaned silicon wafers were coated with 5 nm Au deposition by using metal evaporation machine. After such treatments, a thin gold layer formed on the silicon surface for anchoring NADPA SAM.

5. Reversible switching of CO_2-responsive surface

The NADPA-modified Au electrode or silicon wafers were incubated into different concentration of $NaHCO_3$ solution for 10 min, respectively. Following the relationship between the molarity of bicarbonate solutions and the partial pressure of CO_2 as proposed by Wolfbeis and co-workers,[1] the dCO_2 concentration can be calculated from $NaHCO_3$ solution concentration. Thus, when the concentration of $NaHCO_3$ solution varied from 0, 0.5, 1, 2.5, 5, 10 and 20 mM, the dCO_2 concentration is calculated as 1.3, 2.6, 6.5, 13, 26 and 52 atm ($\times 10^{-4}$), respectively. When the immobilization is completed, the substrates are transferred into probe solution after rinsed thoroughly by DI-water for electrochemical and contact angle measurements. Switching of surface properties can be carried out by immersion of NADPA surfaces into DI-water with dCO_2 and bubbling N_2 for 15 min, alternatively.

6. Stimuli-induced selective adsorption of model targets on smart surface

In order to investigate the ability of NADPA surface for selective adsorption triggered by dissolved CO_2, hydrophobic oleylamine-capped and hydrophilic citrated-capped gold nanoparticles (Au NPs) were used as model targets. The citrate-capped Au NPs with 20 nm and oleylamine-capped Au NPs with 13 nm were synthesized according to the reported method, respectively.[2] The NADPA-modified surfaces were incubated in 3.6 nM citrated-capped and oleylamine-capped Au NPs solutions for 5 min, respectively and then the substrates were thoroughly washed and dried for subsequent characterizations. Another group of NADPA modified surfaces were firstly treated by 10 mM $NaHCO_3$ solution for 10 min, after washing by DI-water, then were dipped in 3.6 nM citrated-capped Au NPs and oleylamine-capped Au NPs solution for 5 min, respectively. After the same procedures of washing and drying, SEM and AFM characterizations were carried out.

Figures

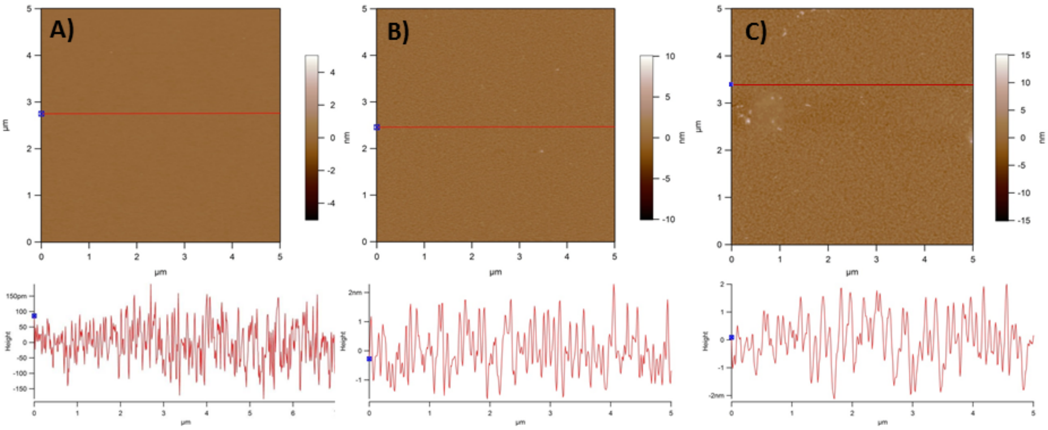

Fig. S1 AFM images (top) and height profiles (bottom) of (A) bare silicon substrate, (B) 5 nm Au-coated silicon substrate and (C) NADPA modified Au substrate.

Compared with the height profile of Au-coating silicon wafer, the average height increase after NADPA modification is around 0.6 nm, indicating a uniform molecular monolayer assembled.

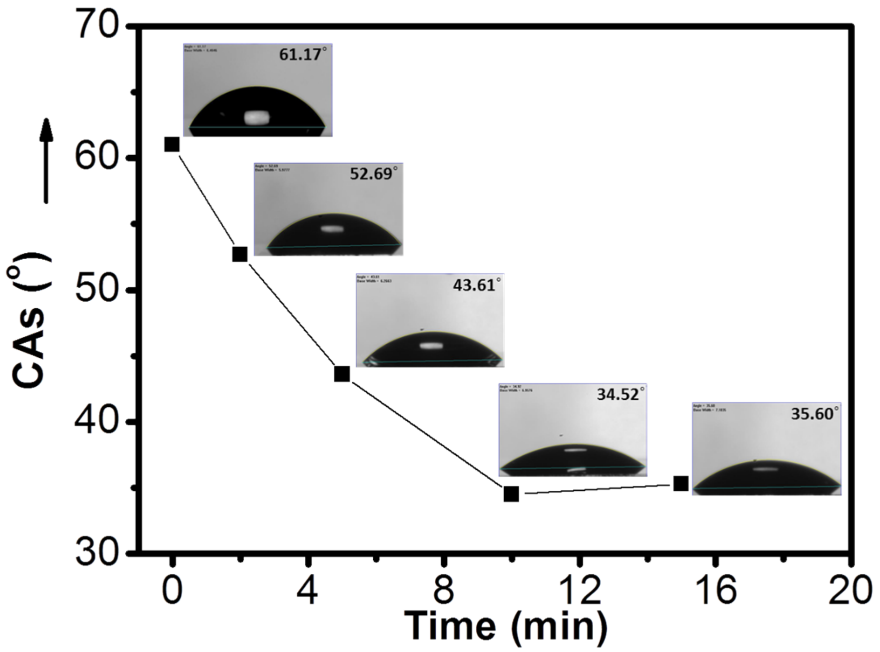

Fig. S2 The response time of water contact angle of NADPA-SAM towards the stimuli of dCO_2.

This result was obtained by incubation of the NADPA modified surface into 10 mM $NaHCO_3$ (≈ 2.6×10^{-3} atm CO_2) solution for different time.

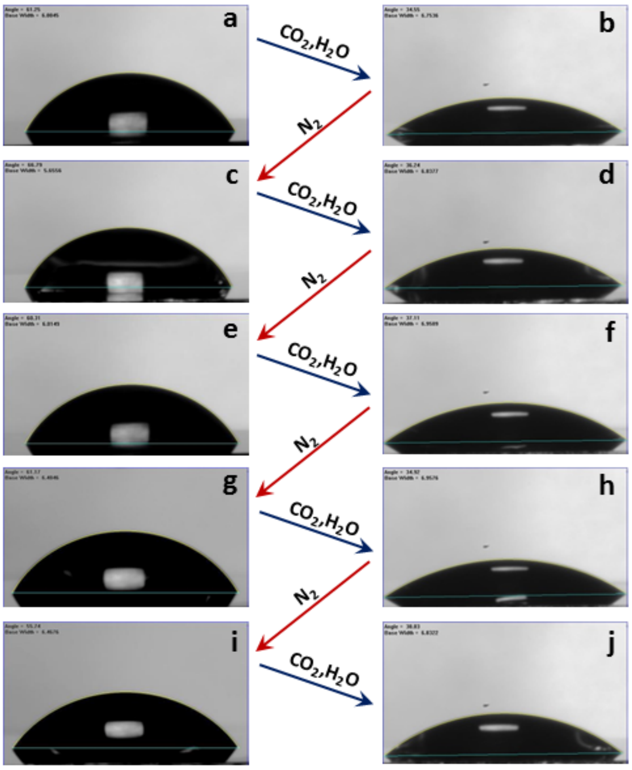

Fig. S3 Photographic image of switching water drop profile on NADPA modified surface by alternative interaction with dCO_2 (b, d, f, h, j) and purging N_2 (a, c, e, g, i).

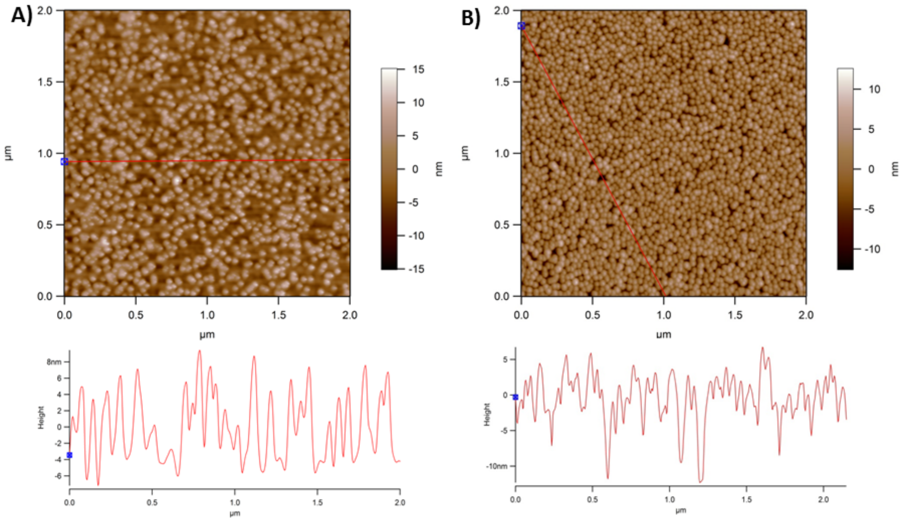

Fig. S4 AFM images of the adsorption of (A) oleylamine-capped Au NPs on amidine-terminal surface and (B) citrate-capped Au NPs on amidium-terminal surface. The bottom pictures are the height profiles of (A) oleylamine-capped Au NPs film and (B) citrate-capped Au NPs film along with the red line in the AFM images.

Height profiles of either oleylamine- or citrate-capped Au NPs film on NADPA surface show good consistency with their particle size of approximately 13 and 20 nm respectively.

References

(1) Ali, R.; Lang, T. M.; Saleh, S. M.; Meier, R. J.; Wolfbeis, O. S. *Anal. Chem.* **2011**, *83*, 2846.
(2) a) Frens, G. *Nature-Phys. Sci.* **1973**, *241*, 20; b) Polavarapu, L.; Xu, Q. H. *Nanotechnology* **2009**, *20*, 185606.