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ARTICLE TYPE

CO₂-Responsive Surface with Amidine-Terminated Self-Assembled Monolayer for Stimuli-Induced Selective Adsorption

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A specific bifunctional molecule containing amidine was prepared to construct CO₂-responsive surface *via* molecular self-assembly. The smart surface undergoes CO₂-responsive switching of surface charges and wettability, leading to distinctively selective adsorption of hydrophobic/hydrophilic molecules.

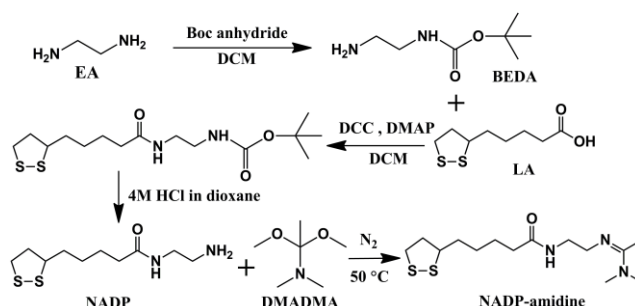
Stimuli-responsive surfaces,¹ also named as “smart” surfaces that undergo reversible transition of surface properties in response to environmental changes, have attracted considerable interest due to their promising applications in diverse fields, such as bioengineering,² switchable wettability,³ controlled lithography,⁴ and drug delivery.⁵ External stimuli typically include electrical potential,⁶ magnetic field,⁷ pH,⁸ light,⁹ temperature,¹⁰ and redox triggers.¹¹ However, acids, bases, and redox reagents can introduce contaminants which are not easy to remove. Light stimuli may cause detriment to biological samples whilst conductive substrates are prerequisite for electrical or magnetic responsiveness.¹² Thus, it is highly desirable to explore the usage of effective and easily removable stimulus. Carbon dioxide (CO₂) is abundant, non-toxic gas and being a key metabolite in cells, it also possesses good biocompatibility and membrane permeability.¹³ Moreover, CO₂ as a trigger enables many switching cycles without the accumulation of by-products.¹⁴ Therefore, CO₂ has been recently exploited as a “green” trigger for artificial smart system.¹² Nevertheless, the majority of these investigations have focused on the CO₂-induced phase behavior of polymers or copolymers in solution.¹⁵ The introduction of CO₂-responsive molecule on substrates to form dynamic surfaces has rarely been investigated and is highly desired.

CO₂-responsive interface may open up exciting feasibilities in the fields of material science and biotechnology such as microfluidics, biochips and separation systems.^{1a} A promising approach towards creation of stimuli-responsive surfaces is to employ highly effective switching entities and through their ordered organization form functional monomolecular films on solid supports.¹⁶ Well-defined molecular monolayer ensures synergetic reorientation of switching units, leading to an amplification of switchable transitions of individual molecule to macroscopically measurable changes in surface properties.^{1a, 16b} The design and synthesis of appropriate building blocks for spontaneous self-assembly of the switching entities is critical in this approach.

In the present work, a bifunctional molecule containing

amidine and disulphide is synthesized for the first time and used for fabrication of a CO₂-switchable surface *via* self-assembled monolayer (SAM) on gold substrates. This fabrication process is advantageous in its simplicity, convenience and represents a new strategy for gas-triggered switching. The as-prepared smart surface is capable of reversible binding with dissolved CO₂ (dCO₂) in water, consequently, undergoes a switching of surface charges and wettability. Moreover, the smart surface exhibits excellent selective adsorption in response to dCO₂ stimuli, using oleylamine (hydrophobic) and citrate (hydrophilic) capped gold nanoparticles (Au NPs) as model targets.

The bifunctional molecule with switchable ability and capability to anchor to a surface is designed and synthesized according to the synthesis scheme shown in scheme 1. In brief, one amine group of ethylene diamine (EA) was firstly protected by Boc anhydride in dichloromethane (DCM) to form *N*-Boc-ethylene diamine (BEDA). Following that, BEDA reacted with lipoic acid (LA) using *N,N*-dicyclohexylcarbodiimide (DCC) as a coupling agent. After removal of Boc group by strong acid and HCl by washing with strong base, *N*-(2-aminoethyl)-5-(1,2-dithiolan-3-yl) pentanamide (NADP) was acquired. Finally, amidine was grafted by coupling of NADP with *N,N*-Dimethylacetamide dimethyl acetal (DMADMA) in the presence of strong base to obtain the target molecule NADP-amidine (NADPA). Herein, amidine is chosen as end group in the designed molecule as it exhibits higher nucleophilicity for CO₂ binding and undergoes fully reversible switching,¹⁷ in comparison with amines and diethylamine.¹⁴



Scheme 1 Synthesis route of CO₂-responsive NADP-amidine.

The as-synthesized NADPA possesses a disulphide end which enables its immobilization onto Au substrates *via* strong covalent bonding. NADPA modified substrate appears to be smooth with the root mean square (RMS) roughness about 0.45 nm, indicating

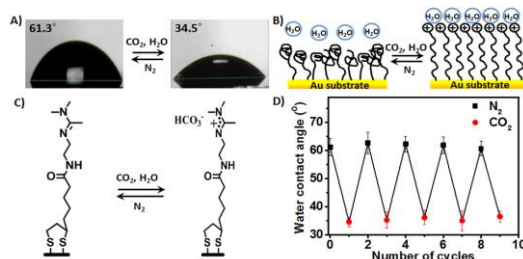


Fig. 1 CO₂-responsive switching of NADPA SAM: A) photographic image of water drop profile on NADPA modified surface before (left) and after (right) the stimuli of dCO₂; B) schematic diagram of stimuli-induced transition of surface wettability; C) changes of chemical structure of amidine; D) reversible switching of water contact angles. The error bars represent the standard error derived from three measurements.

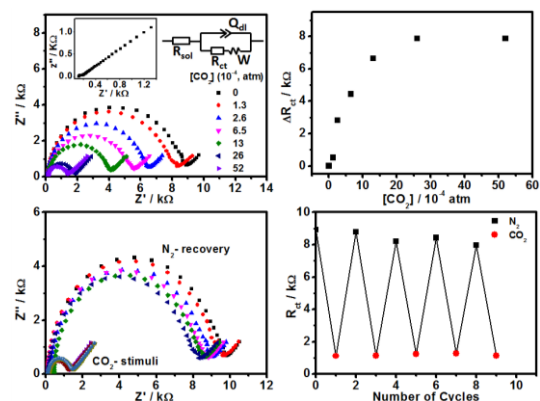


Fig. 2 Electrochemical characterization of CO₂-responsive NADPA SAM: A) impedance spectra of NADPA modified surface in different dCO₂ concentration. Inset: Nyquist plot of bare Au electrode (left) and Randles circuits used for the simulation of impedance data (right); B) interfacial impedance variation upon dCO₂ concentration. Reversible switching on impedance spectra C) and charge transfer resistance D) by alternating contact with dCO₂ and N₂.

a uniform molecular monolayer assembled (Fig. S1, ESI†). As a result, CO₂-responsive functionality is efficiently introduced to the Au substrate *via* a SAM. Switching of surface properties can be triggered when the surface-confined amidines bind with dCO₂. The water contact angle (CA) of the fresh NADPA-modified surface reaches 61.3° (Fig. 1A). This obtained value is in good agreement with a value for entirely amino-terminated surfaces (approximately 60°) reported in previous studies.¹⁸ Upon incubation of the surface with 10 mM NaHCO₃ ($\approx 2.6 \times 10^{-3}$ atm CO₂) solution for 10 min (dCO₂ concentration is calculated from NaHCO₃ concentration as shown in Supporting Information), the CA value is obviously decreased to 34.5°. This implies that the surface experiences a greater degree of hydration. The response time of NADPA SAM towards dCO₂ stimuli is shown in Fig. S2, ESI†. According to the equilibrium reaction of dissolved CO₂ in water ($\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3 \leftrightarrow \text{H}^+ + \text{HCO}_3^-$),¹⁹ the surface-bound amidine can be easily protonated by the released H⁺, resulting into positive-charged amidinium bicarbonates formed. The initially neutral SAM thus becomes positively charged, inducing a greater hydrated transition (Fig. 1B and C). Immersion of the modified surface in water, purged with N₂ for 15 minutes (to remove dCO₂), causes the CA revert back to about value of 61°, suggesting that the surface once again exists in its initial surface state. Furthermore, upon alternative immersions of the surface into aqueous solution containing dCO₂ and water with bubbling N₂, NADPA SAM shows reversible switching of wettability triggered by dCO₂ stimulus or lack thereof (Fig. S3, ESI†). There is no obvious fluctuation of the CA value within the errors and the little difference is coming from experimental error. In comparison with the initial contact angle, a good recovery of 91% can be retained after repeating of 5 cycles (Fig. 1D). The switchable properties of NADPA SAM are derived from its reversible “neutral-charged” transition because of the effective formation and full reversion of conjugation systems in amidines after their reversible protonation/deprotonation in the presence/absence of dCO₂.

The interfacial electrical properties of solid/liquid interface are investigated by electrochemical impedance spectroscopy (EIS). Figure 2A shows the Nyquist plots of NADPA modified Au electrode before and after contacting with the different concentration of dCO₂. After modification with NADPA SAM, charge transfer resistance R_{ct} increases dramatically from 150 Ω to 8.93 k Ω compared to the bare electrode. NADPA SAM is thus successfully assembled onto the electrode as it prevents redox probe ($\text{Fe}(\text{CN})_6^{3-/4-}$) from approaching the surface. Based on EIS

data, NADPA coverage of the electrode surface is estimated to be about 98.3% according to the following equation,²⁰

$$\theta = 1 - R_{\text{ct}}^{\text{bare}} / R_{\text{ct}}^{\text{SAM}}$$

where θ is the coverage fraction of the electrode, $R_{\text{ct}}^{\text{bare}}$ and $R_{\text{ct}}^{\text{SAM}}$ are the values of charge transfer resistance of the bare and the SAM electrodes. Meanwhile, a 5.7% decrease of R_{ct} was found even with dCO₂ as low as 1.3×10^{-4} atm, showing the high sensitivity of NADPA surface to dCO₂ stimuli. It is also found that increasing concentrations of dCO₂ causes a gradual decrease in the semicircle diameter, suggestive of an improved charge transfer process. This is probably contributed by the synergistic effect of (i) hydration and (ii) protonation by formation of positive-charged amidinium bicarbonates on surface which facilitates the charge transfer between the negative charged redox probes and the electrode *via* electrostatic interaction. The gradual decrease of R_{ct} with dCO₂ concentration indicates it is feasible to dynamically change the surface properties and charges by altering the concentration of dCO₂. When the concentration of dCO₂ reaches 26×10^{-4} atm, a much lower charge transfer resistance can be obtained ($R_{\text{ct}} \approx 1.73$ k Ω , vs 8.93 k Ω with no dCO₂). Negligible change of R_{ct} is observed with the further increase of dCO₂ to 52×10^{-4} atm, which provides an evidence for a fully charged surface (Fig. 2B). Conversely, after transferring the electrode into water, purged with N₂ for 15 min, the charge transfer resistance reverts to its initial value (Fig. 2C). Figure 2D shows an excellent switching of surface electrical properties between high R_{ct} (average 8.45 k Ω) and low R_{ct} (average 1.18 k Ω) by alternating dCO₂/purging N₂ for 5 consecutive times. Therefore, the change of surface properties of NADPA SAM is reversible in response to dCO₂ stimuli, which is consistent with our contact angle measurements. These properties suggest that the as-prepared CO₂-responsive surface is likely a good candidate for bioelectronics applications due to its ability to convert the stimuli of dCO₂ effectively into electrochemical signals.

Taking advantage of their stimuli-induced surface properties, we further investigated the ability of NADPA SAM to selectively adsorb hydrophobic/hydrophilic molecules corresponding to dCO₂ stimuli. Oleylamine- and citrate-capped gold nanoparticles (Au NPs) are chosen as model targets because they exhibit opposite surface wettability (e. g. hydrophobic oleylamine and

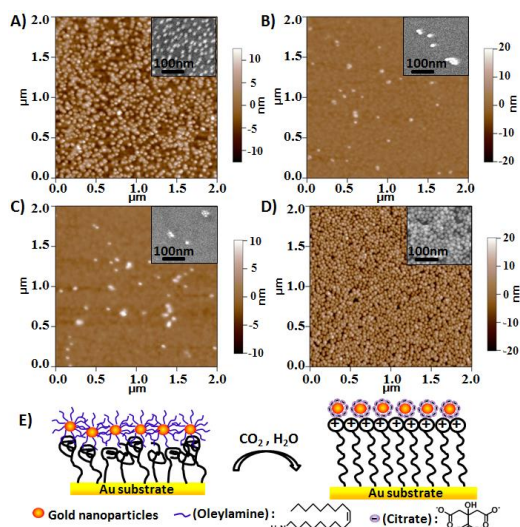


Fig. 3 AFM images of adsorption of oleylamine-capped Au NPs (A, C) and citrate-capped Au NPs (B, D) on NADPA modified surface before (A, B) and after (C, D) interaction with $d\text{CO}_2$ (Inset: corresponding SEM images). (E) Schematic illustration of selective adsorption of oleylamine- and citrate-capped Au NPs on NADPA surface upon $d\text{CO}_2$ stimuli.

hydrophilic citrate), and distinctive surface charges (e. g. neutral oleylamine and negative citrate). In the absence of $d\text{CO}_2$ stimuli, well-dispersed oleylamine-capped Au NPs on the NADPA modified surface is observed by both AFM and SEM images (Fig. 3A), while negligible adsorption of citrate-capped Au NPs is present (Fig. 3B). Conversely, after immersion of NADPA surface in 10 mM NaHCO_3 solution, adsorption of oleylamine-capped Au NPs on the substrate weakens significantly, while the protonated NADPA surface facilitates the capture of a large amount of citrate-capped Au NPs (Fig. 3C and D). Height profiles of either oleylamine- or citrate-capped Au NPs film on NADPA surface demonstrate a monolayer composed of well-ordered Au NPs on substrates (Fig. S4, ESI†). The underlying adsorption mechanism is proposed that before interaction with $d\text{CO}_2$, NADPA SAM is neutral and less hydrophilic, in this state, selective adsorption of oleylamine-capped Au NPs via hydrophobic interactions is dominant. Upon exposure to $d\text{CO}_2$, adsorption of citrate-capped Au NPs is significant as NADPA SAM becomes greater hydrophilic in nature whilst adsorption of oleylamine-capped Au NPs is unfavored (Fig. 3E). Therefore, the selective adsorption towards Au NPs with different wettability can be easily achieved on NADPA SAM by controlling the switchable surface properties by $d\text{CO}_2/\text{N}_2$. These results provide a feasibility of CO_2 -responsive surface combined with an online system such as lab-on-a-chip for stimuli-induced separation of molecules with different wettability and surface charges.

In conclusion, using CO_2 as a “green” gas-stimulus, herein, we present a novel strategy of utilizing a specific bifunctional molecule containing amidine to construct CO_2 -responsive surface via SAM on Au substrates. The “smart” surface based on molecular switching is capable of undergoing reversible switching of surface charges and wettability, leading to distinctively selective adsorption on the smart surface. These findings may have the potential to be used for a wide range of applications including microfabrication of smart template for microfluidics and bioseparation, or microengineering of

switching elements for sensors and actuators, or grafting on nanoparticles for stimuli-responsive nanomaterials.

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- † Electronic Supplementary Information (ESI) available: Experimental section, Fig.S1-S3. See DOI: 10.1039/b000000x/
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TOC

A novel amidine-based bifunctional molecule is designed and synthesized for fabrication of CO₂-responsive surface via self-assembled monolayer on Au substrates. Controlling reversible transition of surface charges and wettability upon stimuli of dissolved CO₂ in water, the selective adsorption of hydrophobic/hydrophilic molecules can be easily achieved.

TOC Figure

