Temperature-Controlled Electrochemical Switch Based on Layered Double Hydroxide/Poly(N-Isopropylacrylamide) Ultrathin Films Fabricated via Layer-by-Layer Assembly

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ABSTRACT: In this paper we report the fabrication of layered double hydroxide (LDH) nanoparticles/poly(N-isopropylacrylamide) (pNIPAM) ultrathin films (UTFs) via the layer-by-layer assembly technique, and their switchable electrocatalytic performance in response to temperature stimuli was demonstrated. X-ray diffraction and UV–vis absorption spectroscopy indicate a periodic layered structure with uniform and regular growth of the (LDH/pNIPAM)_n UTFs; an interaction based on hydrogen bonding between LDH nanoparticles and pNIPAM was confirmed by X-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy. Temperature-triggered cyclic voltammetry and electrochemical impedance spectroscopy switch for the UTFs was obtained between 20 and 40 °C, accompanied by reversible changes in surface topography and film thickness revealed by atomic force microscopy and ellipsometry, respectively. The electrochemical on−off property of the temperature-controlled (LDH/pNIPAM)_n UTFs originates from the contraction−expansion configuration of pNIPAM with low−high electrochemical impedance. In addition, a switchable electrocatalytic behavior of the (LDH/pNIPAM)_n UTFs toward the oxidation of glucose was observed, resulting from the temperature-controlled charge transfer rate. Therefore, this work provides a facile approach for the design and fabrication of a well-ordered command interface with a temperature-sensitive property, which can be potentially applied in electrochemical sensors and switching.

1. INTRODUCTION

Stimuli-responsive polymers, also known as “smart” polymers, have attracted substantial research efforts directed to the tailoring of new electronic or catalytic materials, drug delivery/release systems, separation materials, and sensor interfaces.1−4 Such smart species are capable of conformational and chemical changes on receiving an external signal derived from variations in the surrounding environment, such as temperature, chemical composition, and applied mechanical force, or that can be triggered exogenously by irradiation with light or exposure to an electrical and magnetic field.5−8 To design stimuli-responsive materials, two critical problems should be addressed: one is the reversibility of the material alteration, and the other is the function tunability. Although many efforts have been carried out to develop polymer-based smart materials (for instance, thermal sensors,9 pH-controlled switches,10 and magnetic field sensitive actuators11), they generally suffer from poor stability, a long response time, and unsatisfactory sensitivity.

Recently, the incorporation of signal-responsive polymers with inorganic nanoparticles has evoked much attention for the development of hybrid materials with tunable electronic, photonic, and catalytic properties, which are not present in the individual components alone.12−15 In particular, stimuli-controlled electrocatalysis has aroused great interest owing to its application in switchable electronic devices and sensors, signal amplification, fuel cells, and information storage and processing.16−18 The cyclic on−off formation of the charged smart films on electrode surfaces by the external stimuli allows the generation of “command interfaces” that selectively enhance or inhibit electrochemical reactions.19−21 In these cases, the aggregation of smart polymers is normally inevitable due to the disordered structure and the intertwist of cross-linkers, which lead to decreased responsiveness and controllability for electrochemical processes. Therefore, it is highly essential to explore novel materials and approaches for the immobilization and assembly of smart polymers with high stability, reusability, and environmental compatibility.

To solve these problems mentioned above, it is of crucial importance to obtain well-organized structures with a highly arrayed smart polymer in a suitable matrix which can provide a stable microenvironment for promoting extra stimuli sensitivity.

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Layered double hydroxides (LDHs), whose structure can be generally expressed as [M\text{II}_{1-x}M\text{III}_x(OH)_2]\text{(A}^\text{x/y}\text{)\cdot nH}_2\text{O} (M\text{II} and M\text{III} are divalent and trivalent metals, respectively, and A\text{\textsuperscript{x/y} is the interlayered anion}), are one type of important layered materials which represent a large versatility in building up a 2D-organized structure.\textsuperscript{22,23} Recently, LDH-based organic–inorganic functional materials have been widely used in the biology,\textsuperscript{24} optical,\textsuperscript{25} and electrochemical fields.\textsuperscript{26} This gives us impetus to take the challenge of fabricating switchable electrochemical sensors based on a smart polymer and LDH nanoparticles, which exhibit a fine-tuning nanostructure and stimuli-responsive electrochemical behavior. The assembly of a smart polymer within the LDH gallery for the preparation of command interfaces may exhibit the following advantages: first, the intrinsic anisotropy of the LDH matrix imparts a high dispersion and orientation to the polymers, which are expected to show an enhanced extraresponsive property; second, the LDH matrix would improve the stability (optical, thermal, and mechanical) as well as the environmental compatibility of the functional polymers. In this work, temperature-responsive LDH/poly(N-isopropylacrylamide) (pNIPAM) ultrathin films (UTFs) were fabricated by the layer-by-layer (LBL) self-assembly method based on the hydrogen-bonding interaction, which show a reversible on–off transformation in their electrocatalytic performance (Scheme 1). A periodic layered structure vertical to the substrate was obtained via the alternate deposition of LDH nanoparticles and pNIPAM. The resulting UTFs exhibit a reversible transformation in the surface topography, film thickness, and surface wettability by modulating the temperature in the range of 20–40 °C, owing to the contracted and expanded configuration of the polymer. In addition, a temperature-triggered on–off switch for electrolycatalytic oxidation of glucose based on the (LDH/pNIPAM)\textsubscript{\text{\text{\text{\textsuperscript{n}}}}} UTFs was achieved, resulting from the significant change in the charge transfer rate. It is expected that the strategy presented here can be employed to fabricate a variety of intelligent materials based on regular arrangements of smart species within a 2D inorganic matrix.

2. EXPERIMENTAL SECTION

2.1. Reagents and Materials. Polysodium 4-styrenesulfonate (PSS) with a molecular weight of ~70000, N-isopropylacrylamide (NIPAM), and \text{N,N\text{-methylenebis}(acrylamide)} (BIS) were purchased from Sigma-Aldrich Co. The following analytical grade chemicals were used without further purification: NaOH, Co(NO\text{3})\text{2}\cdot 6H\text{2O}, Al\text{-(NO\text{3})\text{2}\cdot 9H\text{2O}}, sodium dodecyl sulfate (SDS), potassium persulfate (KPS), acetone, ethanol, NH\text{3}\cdot H\text{2O}, H\text{2O2}, H\text{2SO4}. Deionized water was used in all the experimental processes.

2.2. Synthesis of a CoAl–LDH Colloidal Suspension. A colloidal LDH suspension was prepared according to the separate nucleation and aging steps (SNAS) method reported by our group.\textsuperscript{27} Typically, 100 mL of solution A (Co(NO\text{3})\text{2}\cdot 6H\text{2O} (0.2 M) and Al(NO\text{3})\text{2}\cdot 9H\text{2O} (0.1 M)) and 400 mL of solution B (NaOH (0.15 M)) were simultaneously added to a colloid mill with a rotor speed of 3000 rpm and mixed for 1 min. The resulting LDH slurry was obtained via centrifugation, washed with water, and then dispersed in 400 mL of deionized water. The aqueous suspension was transferred into a stainless steel autoclave with a Teflon lining. After hydrothermal treatment at 110 °C for 24 h, a stable homogeneous CoAl–LDH suspension with a narrow size distribution was obtained.

2.3. Synthesis of the pNIPAM Polymer. The pNIPAM polymer was synthesized via free radical dispersion polymerization based on the reported method.\textsuperscript{28,29} Briefly, NIPAM (4.304 g), BIS (0.082 g), and sodium dodecyl sulfate (SDS; 0.082 g) were dissolved in 250 mL of deionized water with vigorous stirring at 72 °C in a nitrogen atmosphere. A KPS solution (0.218 g, 50 mL) was added and the resulting solution stirred for 5 h under nitrogen. The reaction mixture was centrifuged, washed three times with deionized water, and then filtrated using a membrane filter (1.2 μm, Millipore) to remove any unreacted monomer and other impurities. The obtained pNIPAM polymer was then exhaustively dialyzed against deionized water (changing the dialysate twice daily for a week).

2.4. Fabrication of the (LDH/pNIPAM)\textsubscript{\text{\text{\text{\textsuperscript{n}}}}} UTFs. The (CoAl–LDH/pNIPAM)\textsubscript{\text{\text{\text{\textsuperscript{n}}}}} UTFs were fabricated by the LBL assembly technique. Prior to assembly, ITO substrates were cleaned by sonication in a series of solvents, acetone, ethanol, and deionized water, for 10 min each. Quartz glass was first cleaned in concentrated NH\text{3}\cdot H\text{2O}/30% H\text{2O2} (7:3) and concentrated H\text{2SO4} for 30 min each to make the substrate surface hydrophilic and negatively charged. The substrate was dipped in a colloidal suspension of LDH nanoplatelets (0.1%) for 10 min followed by washing thoroughly, and then the substrate was treated with 100 mL of pNIPAM aqueous solution (0.1%) for 10 min. The (LDH/pNIPAM)\textsubscript{\text{\text{\text{\textsuperscript{n}}}}} UTFs were fabricated by alternate deposition of LDH nanoplatelets and pNIPAM for n cycles. The resulting films were finally rinsed with water and dried at ambient temperature. As comparison samples, the (CoAl–LDH/PSS) UTFs were fabricated by a similar assembly procedure in a sequence of LDH suspension (0.1%) and poly(styrenesulfonate) (PSS; 0.1%) aqueous solution.

2.5. Sample Characterization. X-ray diffraction (XRD) patterns were recorded by a Rigaku XRD-6000 diffractometer using Cu Ka radiation (λ = 0.15418 nm) at 40 kV and 30 mA. The UV–vis absorption spectra were collected in the range of 190–600 nm on a Shimadzu U-3000 spectrophotometer, with a slit width of 1.0 nm. The morphology of the films was investigated using a scanning electron microscope (Zeiss SUPRA 55) with an accelerating voltage of 20 kV and a NanoScope IIIa atomic force microscope from Veeco Instruments. The Fourier transform infrared (FTIR) spectra were obtained using a Vector 22 (Bruker) spectrophotometer with 2 cm\textsuperscript{-1} resolution. X-ray photoelectron spectroscopy (XPS) measurements were performed using an ESCALAB 250 instrument (Thermo Electron) with Al Ka radiation. The determination of thickness for the films was carried out using a spectroscope ellipsometer (Angstrom Advanced Inc. PHE-102) at an angle of 70° within the spectral range of 300–1000 nm. The modeling and fitting of the ellipsometric spectra were performed using the software provided by the manufacturer. Static water contact angles of UTFs were measured using a sessile drop at three different points of each film sample using a commercial drop shape analysis system (DSA100, Krüss GmbH, Germany) at ambient temperature. The volume of the water droplets used for measurement was 2 μL. The electrochemical measurements were performed using a CHI 660C electrochemical workstation (Shanghai Chenhua Instrument Co.). A conventional three-electrode system was used, including a modified indium tin oxide (ITO) glass as the working electrode, a
platinum foil as the auxiliary electrode, and a saturated Hg/HgCl₂ electrode as the reference electrode.

3. RESULTS AND DISCUSSION

3.1. Structural and Morphological Characterization of the (LDH/pNIPAM)ₙ UTFs. The XRD pattern and FTIR spectrum (Figure S1A,B, Supporting Information) of the CoAl–LDH powder sample indicate a well-defined nitrate-containing LDH with high crystallinity. The scanning electron microscopy (SEM) image reveals a narrow size distribution (100–120 nm) for the individual CoAl–LDH hexagonal nanoplatelets (Figure S1C). A clear Tyndall light scattering was observed (Figure S1D), and the well-dispersed colloidal suspension was transparent and stable without any precipitation when stored in an N₂ atmosphere for more than one month. Temperature-sensitive polymer pNIPAM was synthesized via polymerization of the NIPAM monomer. The FTIR spectra of NIPAM and pNIPAM are shown in Figure S2 (Supporting Information), from which the disappearance of vinyl absorption bands (3078 cm⁻¹ for –C=H and 1628 cm⁻¹ for C=C) demonstrates the successful synthesis of pNIPAM via free radical dispersion polymerization. The changes in transmittance of the pNIPAM solution upon increasing the temperature in the range from 20 to 40 °C show that pNIPAM is a thermoresponsive polymer in water (Figure S3, Supporting Information). The (LDH/pNIPAM)ₙ UTFs were fabricated by alternate assembly of the CoAl–LDH suspension with pNIPAM aqueous solution. UV–vis absorption measurements for the (LDH/pNIPAM)ₙ UTFs with various bilayer numbers are shown in Figure 1. The intensity of the characteristic absorption band of pNIPAM at 193 nm correlates linearly with the bilayer number, n (Figure 1, inset), demonstrating a stepwise and regular film growth procedure. Taking into account the abundant amide groups in pNIPAM and a large number of hydroxy groups on the surface of the LDH nanoplatelets, multiple hydrogen-bonding interactions between pNIPAM and LDH may occur, which will be further discussed in the next section.

The XRD pattern (Figure 2A) for the obtained (LDH/pNIPAM)₁₀ UTF displays a peak at 2θ = 11.4° attributed to the (003) reflection of the LDH structure. The absence of any nonbasal reflections (h, l ≠ 0) compared with the LDH powder sample indicates a preferred orientation of LDH platelets with the ab plane parallel to the substrate (the broad peak at 2θ = 15–30° is assigned to the amorphous reflection of the quartz substrate). The top view SEM image of the UTF exhibits a smooth and continuous surface (Figure 2B); high magnification of the film (Figure 2C) shows that the LDH nanoplatelets are densely packed on the substrate plane with good c orientation, consistent with the XRD result. The side view of the SEM image (Figure 2D) displays a uniform layered architecture, with a thickness of ~132 nm for the (LDH/pNIPAM)₁₀ UTF on the quartz substrate. Moreover, the thickness of the (LDH/pNIPAM)ₙ UTFs as a function of the bilayer number (n) (Figure S4, Supporting Information) illustrates an approximately linear increase, from which an augment of ~15 nm was obtained per LDH/pNIPAM bilayer unit. Furthermore, no delamination or peeling occurred on cross-cutting the film surface, indicating a strong adhesion of the film to the substrate (Figure S5, Supporting Information).

The interaction between LDH and pNIPAM was studied by means of XPS and the FTIR technique. After the combination of LDH and pNIPAM via LBL assembly, the binding energy of Co (2p) in CoAl–LDH shifts from 780.9 to 781.6 eV (Figure 3A), indicating a decrease in the electron density of Co. Concomitantly, a decreased binding energy of N 1s (–NH in pNIPAM) from 400.2 to 399.6 eV was observed (Figure 3B), implying an increase in the electron density of the N atom. The XPS results indicate the formation of hydrogen bonding between pNIPAM and LDH, which was further verified by the strong suppression of the lattice vibration of the LDH matrix at 618 cm⁻¹ as well as the presence of a hydroxyl vibration at 800–1000 cm⁻¹ from FTIR spectra (Figure S6, Supporting Information). A combination study based on XPS and FTIR has also been used to confirm the existence of hydrogen bonding in clay–polymer composite materials in previously reported work.²⁶,²⁸

3.2. Temperature-Responsive Expansion–Contraction of the (LDH/pNIPAM)ₙ UTFs. The temperature-triggered variation in the surface topography for the (LDH/pNIPAM)₁₀ UTF was investigated by atomic force microscopy (AFM). The root-mean-square (rms) roughness of the surface topography decreases from 86.5 nm (Figure 4A) to 43.5 nm (Figure 4B)
during the heating process from 20 to 40 °C and increases to 84.3 nm (Figure 4C) again after cooling treatment to 20 °C. Moreover, the rms of the UTF at 20 and 40 °C for five heating−cooling cycles shown in Figure 4D indicates a rather good reversibility of the surface topography change. In addition, Figure 5 displays the reversible variation in film thickness based on ellipsometry measurements for the (LDH/pNIPAM)10 UTF at 20 and 40 °C. The thickness of the UTF is ∼136 nm at ∼20 °C, and it decreases to ∼66 nm at 40 °C. The transition between the expansion and contraction states can be repeated even for 10 cycles. Interestingly, similar to the changes in the thickness, a variation in the contact angle of the surface (∼82° at 40 °C and ∼64° at 20 °C) can be performed reversibly (Figure S7, Supporting Information). The results above indicate that the (LDH/pNIPAM)10 UTF exhibits a reversible variation in the surface topography, thickness, and surface wettability, which originates from the expansion−contraction of pNIPAM chains induced by temperature stimuli.

3.3. Electrochemical On−Off Behavior of the (LDH/pNIPAM)n/ITO Electrode. The electrochemical response of (LDH/pNIPAM)n UTF modified ITO electrodes toward temperature stimuli was investigated. In this work, the (LDH/pNIPAM)n/ITO with n = 10 was chosen as the optimal electrode to study the temperature response behavior (Figure S8, Supporting Information). Figure 6A shows the cyclic voltammograms (CVs) of (LDH/pNIPAM)10/ITO as a function of temperature in 0.1 M NaOH solution at a scan rate of 0.1 V s⁻¹. As the temperature increases from 20 to 40 °C, a progressive increase in both the anodic and cathodic peak currents is observed, and the plot of the anodic peak current vs temperature (Figure 6B) demonstrates two stable state at 20 and 40 °C. Moreover, the CV responses toward a temperature change between 20 and 40 °C are fully reversible (inset of Figure 6B). In addition, the temperature-dependent electrochemical properties of the electrode were further studied by electrochemical impedance spectroscopy (EIS), which provides more information about the interfacial impedance change. The semicircle diameter of the EIS spectrum equals the electron transfer resistance (Rct), which controls the electron transfer kinetics of the redox probe at the electrode interface. Figure 7A

Figure 3. (A) Co 2p orbital XPS spectra for (a) LDH and (b) the (LDH/pNIPAM)10 UTF. (B) N 1s orbital XPS spectra for (a) pNIPAM and (b) the (LDH/pNIPAM)10 UTF.

Figure 4. Surface topography change of the (LDH/pNIPAM)10 UTF recorded by AFM images at various temperatures: from (A) 20 °C to (B) 40 °C and (C) back to 20 °C. Before AFM measurement, the film was immersed in water for 1 h. The scanned area was 5 μm × 5 μm for all images. (D) Reversible variation of rms for the (LDH/pNIPAM)10 UTF at 20 and 40 °C.

Figure 5. Reversible variation of the film thickness based on ellipsometry measurements for the (LDH/pNIPAM)10 UTF at 20 and 40 °C.
shows the typical EIS spectrum for the (LDH/pNIPAM)_{10}/ITO with the presence of 5 mM [Fe(CN)_{6}]^{3-/4-} in 0.1 M KCl solution in the temperature range of 20–40 °C. The diameter of the semicircle in the EIS response becomes smaller with increasing temperature, indicating an enhanced interfacial charge transfer of the electrode at high temperature. Analogously, two steady states at 20 and 40 °C for $R_{et}$ of the electrode are observed (Figure 7B) with rather good reversibility (inset of Figure 7B). The results demonstrate that the (LDH/pNIPAM)_{10}/ITO electrode exhibits electrochemical on–off behavior at 40 and 20 °C, which may be attributed to fast–slow interfacial charge transfer induced by the contraction–expansion transition of the pNIPAM in the UTF. To further reveal the mechanism of the temperature stimuli electrochemical response of the (LDH/pNIPAM)_{n}/ITO electrode, a comparison study was carried out. The temperature-dependent electrochemical property of the (CoAl–LDH/
PSS)\textsubscript{10} UTF modified ITO electrode was examined under identical conditions. No obvious change in both the CV (Figure S9, Supporting Information) and EIS spectrum (Figure S10, Supporting Information) was observed upon increasing the temperature from 20 to 40 °C, indicating that PSS shows no temperature-responsive behavior. It thus can be concluded from the above comparison study that pNIPAM in the transition between contracted and expanded configurations plays a key role in determining the electron transfer rate of the (CoAl-LDH/PSS)\textsubscript{10}/ITO electrode. Therefore, the electrochemical on–off behavior of this electrode is attributed to the variation in impedance and the resulting electron transfer rate under two different conditions, which is generated by the temperature-controlled configuration transition of pNIPAM.

3.4. Temperature-Responsive Electro catalysis of the (LDH/pNIPAM)\textsubscript{10}/ITO Electrode. The electrocatalytic oxidation of glucose was chosen as a model reaction for investigating the temperature-controlled electrocatalytic behavior of the (LDH/pNIPAM)\textsubscript{10}/ITO electrode. Figure 8A shows the current–time curves corresponding to the electrocatalytic oxidation of glucose at 20 and 40 °C. With the successive addition of glucose, gradual increases in the amperometric signals are observed at both 40 and 20 °C (Figure 8A). Moreover, the amperometric signals increase gradually upon increasing the temperature from 20 to 40 °C (Figure S11, Supporting Information), accompanied by continuous enhancement of response sensitivity. The output signal intensity is substantially stronger at 40 °C in comparison with that at 20 °C. Compared with the detection limit (24.4 μM) and sensitivity (1.22 μA mM\textsuperscript{-1} cm\textsuperscript{-2}) at 20 °C, the (LDH/pNIPAM)\textsubscript{10}/ITO electrode exhibits a much lower detection limit (8.7 μM) and largely enhanced sensitivity (5.01 μA mM\textsuperscript{-1} cm\textsuperscript{-2}) at 40 °C (Figure 8B). Furthermore, its CV behavior at 40 and 20 °C (Figure S12, Supporting Information) also demonstrates a significantly improved intensity and sensitivity at 40 °C, which is in good agreement with the current–time results. The largely enhanced electrocatalytic current as well as sensitivity for the oxidation of glucose at 40 °C is attributed to the low impedance resulting from the effective electric contact between the LDH layer and the contracted polymer. The results indicate that the fine-tuning 2D-ordered nanostructure supplied by LDH nanoplatelets is favorable for the configuration transition of a smart polymer, giving rise to the on–off command based on the charge transport rate of electrode.

In addition, the interference test of the (LDH/pNIPAM)\textsubscript{10}/ITO electrode was examined by adding NaCl or NaNO\textsubscript{3} with various concentrations into the supporting electrolyte. The CV response of the (LDH/pNIPAM)\textsubscript{10}/ITO electrode toward glucose (4 mM) shows no obvious change with the interference of sodium salt (Figure S13, Supporting Information). Moreover, the (LDH/pNIPAM)\textsubscript{10}/ITO electrode exhibits good reversibility on the basis of 10 cycling tests at 20 and 40 °C, with a relative standard deviation (RSD) of 0.6% and 0.7% (Figure S14, Supporting Information), respectively. The long-term stability and environmental compatibility of the (LDH/pNIPAM)\textsubscript{10}/ITO electrode were studied by storing the electrode at room temperature and monitoring its CV response toward 4 mM glucose every 15 days at 20 and 40 °C (Figure S15, Supporting Information). After 45 days, the current maintained ~98% of its initial value. The good stability and long service life of the electrode are related to the ordered stacking of pNIPAM within the LDH matrix, which guarantees its practical applications.

4. CONCLUSIONS

In summary, the (LDH/pNIPAM)\textsubscript{10} UTFs with a temperature-induced on–off property in the electrochemical response were successfully fabricated on ITO electrodes via LBL assembly. The structural and morphological studies illustrate that the UTFs display reversible contraction–expansion transition by temperature stimuli. More significantly, the UTFs exhibit reversible temperature-dependent CV and EIS on–off behavior. In addition, the temperature-controlled activated–deactivated electrocatalytic behavior toward the oxidation of glucose for the (LDH/pNIPAM)\textsubscript{10} UTF was observed at 40 and 20 °C. The mechanism of switchable electrochemical behavior of the UTFs was explored by a comparison study, which is attributed to the contraction–expansion transition of pNIPAM with low–high impedance. Therefore, the novel strategy in this work can be effectively used for the fabrication of command UTFs with prospective applications in switchable electronic sensors, controlled electroanalysis, and information storage–readout devices.

ASSOCIATED CONTENT

Supporting Information

Characterization of the LDH material (Figure S1), FTIR spectra (Figures S2 and S6), transmittance of the pNIPAM solution (Figure S3), side view of the SEM images (Figure S4), UTF tested for adhesion (Figure S5), water contact angle (Figure S7), CVs of the (LDH/pNIPAM), UTF modified ITO electrodes (Figure S8), CVs of the (LDH/PSS)\textsubscript{10}/ITO electrode (Figure S9), EIS of the (LDH/PSS)\textsubscript{10}/ITO electrode (Figure S10), current–time curves of the (LDH/pNIPAM)\textsubscript{10}/ITO electrode (Figure S11), CVs of the (LDH/pNIPAM)\textsubscript{10}/ITO electrode (Figure S12), interference test (Figure S13), stability test (Figure S14), and long-term stability test (Figure S15). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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