



# Superhydrophobic titania nanoparticles for fabrication of paper-based analytical devices: An example of heavy metals assays

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## ABSTRACT

A new strategy has been introduced to successfully fabricate the hydrophobic barriers of PADs by using organofluorine-modified superhydrophobic TiO<sub>2</sub> NPs. Superhydrophobic TiO<sub>2</sub>-140 NPs with high-photoactivity can be converted to hydrophilicity by self-degradation of surface organic moieties under full spectrum light irradiation. Superhydrophobic TiO<sub>2</sub>-RT NPs with low-photoactivity exhibits good hydrophobic stability under light irradiation. Thus, combining these features, the PADs have been designed and constructed by photo-induced fabrication of hydrophobic barriers on the surface of the paper. To demonstrate the effectiveness of the constructed PADs, colorimetric detections have been displayed for Fe<sup>3+</sup> and Ni<sup>2+</sup> ions. The synchronous multi-component detections based on the “multi-channel” PADs and the intuitive detections based on the “chemical-symbol-style” PADs are rapid and feasible. A detection range of Fe<sup>3+</sup> and Ni<sup>2+</sup> ions based on the “circle-array” PAD is applicable and reliable in 0.2–6.0 mM and 0.4–4.0 mM, respectively. Thus, these results make it to be believed that this new strategy provides an alternative way to effectively construct the PADs.

## 1. Introduction

At present, water contamination is one of the most serious environmental problems because the continuous increasing of toxic substances in water systems, originated from human activities and rapid industrializations [1–3]. Among them, heavy metals are one kind of the most important pollutants owing to severe pathogenicity to the human body [4]. On this account, it is obligatory to develop water pollution control methods for effective abatement of heavy metals in polluted water. First of all, accurate and rapid analysis of heavy metals is a crucial step [5,6]. Many methods have been developed for qualitative and quantitative analysis of heavy metals in water including atomic absorption spectroscopy (AAS) [7], inductively coupled plasma mass spectroscopy (ICP-MS) and inductively coupled plasma atomic emission spectroscopy (ICP-AES) [8,9], which are expensive and only operable in lab conditions. Therefore, the method for on-site assay of heavy metals is necessary for accurate and rapid analysis in non-lab conditions.

Paper-based analytical devices (PADs) offer a convenient platform for users due to they are inexpensive, disposable, portable as well as easy to be used, stored and transported [10–12]. It has been widely applied for rapid analysis in many fields such as environmental

monitoring, medical diagnosis, and biological hazards detection and so on, by means of some techniques such as colorimetry, chemiluminescence and electrochemistry [13–18]. The PADs based on colorimetry may provide a more intuitive method to quickly identify and quantify the target object in non-lab conditions. Patterning paper with hydrophilic areas and hydrophobic barriers seems to be the major strategy to fabricate PADs, allowing to be applied in the analysis of heavy metals in water [19–21]. However, a major challenge is to effectively fabricate PADs with hydrophobic barriers.

Many techniques have been explored to fabricate PADs, such as photolithography [22–24], inkjet printing [25], wax printing [26–28], direct writing of polydimethylsiloxane (PDMS) [29] or paper cutting [30]. Obviously, painting a coating seems to be a simple and effective way to change the wettability of paper, in which the formation of hydrophobic surface is strongly depended on the composition of coating materials such as wax and PDMS [31–33]. Photolithography based on photoactive coating materials is facile to be carried out in the fabrication of hydrophilic areas and hydrophobic barriers on the paper with a mask. The low-cost and non-toxic materials are always attracting researchers' attention, such as TiO<sub>2</sub>. As we know, TiO<sub>2</sub> owns a large of surface OH groups that can be easily modified to be hydrophobic by a

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hydrophobic molecule [34,35]. Due to the photoactivity of TiO<sub>2</sub> [36–38], this hydrophobic surface may be further transformed into hydrophilic surface under the full range spectrum light irradiation (using a solar simulator with 60.0 mW cm<sup>-2</sup> for 2.0 h or a Xe lamp with 800 mW cm<sup>-2</sup> for 5.0 min) by self-degradation of organic moieties, which seems to be a suitable candidate for photosensitive coating of the PADs [39–41]. It has also been well understood the photodegradation ability of TiO<sub>2</sub> is closely related to its crystallinity. In general, high crystallinity of TiO<sub>2</sub> results in high photoactivity in photodegradation [42,43]. So, the hydrophobic TiO<sub>2</sub> as an alternative coating material may provide a new approach to fabricate hydrophobic barriers of PADs by photolithography [34,35].

In this work, the superhydrophobic TiO<sub>2</sub> NPs with different photoactivities have been applied to construct the PADs. The photoactivity of the as-prepared TiO<sub>2</sub> NPs plays an important role in the fabrication of hydrophilic areas and hydrophobic barriers on the surface of the paper. The patterns on the paper coated by different photoactive TiO<sub>2</sub> NPs exhibit remarkably different features under light irradiation, and the hydrophilic areas are constructed by photo-induced conversion of superhydrophobic TiO<sub>2</sub>-140 to hydrophilic TiO<sub>2</sub> as well as the hydrophobic barriers are kept owing to the higher photostability of low photoactive TiO<sub>2</sub>-RT. Based on these results, we have designed and developed the PADs combined with colorimetry to identify heavy metal ions (Ni<sup>2+</sup> and Fe<sup>3+</sup>) in water and investigated the practicability of these PADs, which showed reliable results in terms of the synchronous multi-components detection, the intuitive detection and the quantitative analysis. Thus, it is believed that this new strategy provides an alternative way to fabricate PADs by simplified photolithography without photomask.

## 2. Experimental

### 2.1. Materials and methods

Tetrabutyl titanate (TBT, 98%), NaOH (96%), acetic acid (99.5%), sodium acetate (99%), Mn(NO<sub>3</sub>)<sub>2</sub> (50%), Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (99%), Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (98%), Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (99%), Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (99%), Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (99%), NaNO<sub>3</sub> (98%), Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (98%), Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (98.5%), Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (98%), 1,10-phenanthroline (99%), NaF (98%), ammonium hydroxide (25%), PEG400, absolute ethanol (99.7%), cyclohexane (99.5%) and methyl orange were obtained from Sinopharm Chemical Reagent Co., Ltd. Poly(acrylic acid) 50% solution and dimethylglyoxime (98%) were purchased from Aladdin Chemical Reagent Co., Ltd. 1H, 1H, 2H, 2H-pre-fluorooctyltriethoxysilane (PTES, 97%) was obtained from J&K Chemical Ltd. All chemicals and materials were used without further treatment. Deionized water was used throughout all the experiments. All devices were fabricated using the commercially-available rice paper from Taoji rice paper Co., Ltd. Full spectrum irradiation experiments were performed with a solar simulator CHF-XM-500 W with 60.0 mW cm<sup>-2</sup> of light intensity or xenon lamp Perfect light PLS-SEX300 with 800 mW cm<sup>-2</sup> light intensity. HP Laser jet M1216nfh was used to print the patterns of the PADs and captured the images of the colorimetric assays. Camare (Canon EOS 550D) was used to take the experiment photographs.

### 2.2. Preparation of the TiO<sub>2</sub> NPs and the superhydrophobic coating

The superhydrophobic TiO<sub>2</sub> NPs were synthesized by co-hydrolysis and condensation of TBT and PTES via a two-phase reaction method. In a typical synthesis, PTES (0.45 g, 0.88 mmol) was added to a 50 mL of cyclohexane solution containing 6 mL of TBT (17.6 mmol) under stirring at room temperature for 0.5 h. 15 mL of deionized water was then introduced and the two-phase solution was continuously stirred at room temperature for 1 h until a gel formed. After that, the gel mixture was placed into an autoclave and aged at the desired temperature for 15 h.

The as-obtained white precipitates were collected by centrifuging, washed with ethanol for three times, and the residues were re-dispersed in absolute ethanol by ultrasonication to prepare superhydrophobic coating (concentration is about 18 mg mL<sup>-1</sup>). According to the different aging temperature at room temperature, 50 °C, 80 °C and 140 °C, the samples was labeled as TiO<sub>2</sub>-RT, TiO<sub>2</sub>-50, TiO<sub>2</sub>-80 and TiO<sub>2</sub>-140, respectively (Fig. S1). The details of characterizations for the as-prepared superhydrophobic TiO<sub>2</sub> NPs are shown in the Supporting information (Figs. S2–S4).

### 2.3. Design and fabrication of the “multi-channel” paper-based analytical device (MC-PAD)

A coating technique was used to create the MC-PAD. Before coating the white TiO<sub>2</sub> suspension on the surface of white paper, the three-channel pattern was printed onto the paper to define the hydrophobic and hydrophilic areas by using a commercial printer (model: HP Laser jet M1216nfh). The hydrophilic areas included sample reservoir and detection reservoir with diameters of 7 and 4 mm, respectively. The area out-of-pattern was treated by TiO<sub>2</sub>-RT and the sample channels were treated by TiO<sub>2</sub>-140 NPs. The hydrophobic area outside the three-channel pattern was made by the TiO<sub>2</sub>-RT coating paint which prevented water solution leakage through the device. The zones at the sample channels were covered by the TiO<sub>2</sub>-140 coating paint to get temporary protected channel, which prevented the indicators in the detection reservoirs to enter the sample reservoir. All the hydrophobic areas were covered three times with the corresponding coating paint. To cure coating, the MC-PAD was dried completely in air after each painting step. Finally, three kinds of indicators were added into the detection reservoir, respectively.

### 2.4. Design and fabrication of the “chemical-symbol-style” paper-based analytical device (CSS-PAD)

Paper was employed to prepare CSS-PAD by coating TiO<sub>2</sub>-RT and TiO<sub>2</sub>-140 suspension paint on different areas. A piece of paper was soaked in TiO<sub>2</sub>-RT coating paint for 0.5 min and dried completely in air. After three times of the same procedure, a hydrophobic area was obtained on the surface of the paper. The patterns of chemical symbols of Fe and Ni were written using a pen loaded a special “ink” of TiO<sub>2</sub>-140 suspension paint for three times. The paper was then irradiated with a solar simulator, and the zones with chemical symbols were transformed to hydrophilicity. The so-patterned CSS-PAD was further immersed in an aqueous solution containing certain metal indicator and dried in air. In order to observe it clearly, computer-generated chemical symbols were first printed on the paper.

### 2.5. Design and fabrication of the “circle-array” paper-based analytical device (CA-PAD)

The same procedure was used to fabricate the CA-PAD according to the preparation of the CSS-PAD. The paper was first soaked in TiO<sub>2</sub>-RT coating paint, and then TiO<sub>2</sub>-140 suspension paint was coated fully in the circle on the surface of the paper. After irradiation treatment, the circular zone was transferred to hydrophilicity. The so-patterned CA-PAD was further immersed in an aqueous solution containing certain metal indicator and dried in air.

### 2.6. Indicators [21,44]

The Fe assay: a solution of Fe indicator was prepared by the following procedure. 2.4 g of NaOH and 4.2 g of Hydroxylamine hydrochloride were mixed in 20 mL of deionized water under stirring to form hydroxylamine solution. Then, a buffer solution (6.3 M, pH = 4.5) composed of 4.7 mL of acetic acid and 3.616 g of sodium acetate was added to the above solution. Finally, 28 μL of poly(acrylic acid)

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