

**Chemiluminescence excited photoelectrochemistry aptamer-
device equipped with tin dioxide quantum dots/reduced
graphene oxide nanocomposie modified porous Au-paper
electrode**

**Yanhu Wang,^a Jinneng Xu,^a Chao Ma,^a Shuai Li,^a Jinghua Yu,^a Shenguang Ge^b and
Mei Yan,^{*a}**

Abbreviations

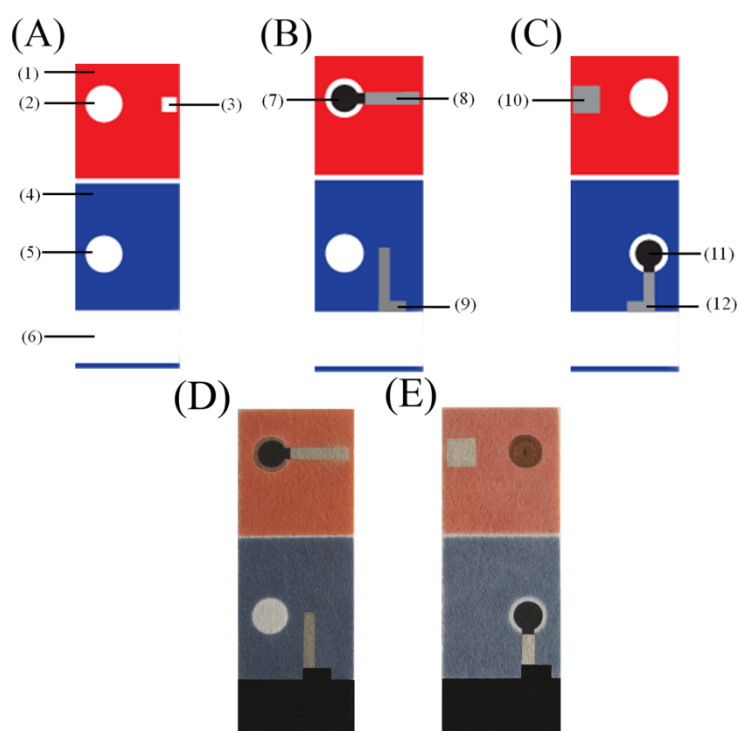
PEC	photoelectrochemical
PSC	paper supercapacitor
μ -PADs	microfluidic paper-based analytical devices
PPECD	paper-based photoelectrochemical device
AuNPs	gold nanoparticles
CL	chemiluminescence
Au-PWE	Au-paper working electrode
DMM	digital multi-meter
SnO ₂ QDs	tin dioxide quantum dots
RGO	reduced graphene oxide
SnO ₂ QDs/RGO	tin dioxide quantum dots/reduced graphene oxide nanocomposie
Fe ₃ O ₄ @AuNPs	ferroferric oxide@ gold nanoparticles
GOx	glucose oxidase
PIP	p-iodophenol
SSDNA1	capture aptamer
SSDNA2	signal aptamer
ATP	adenosine triphosphate
CB	conduction-band
VB	valence-band

Fabrication of this PPECD

Wax was used as the paper hydrophobization and insulation agent in this work. Wax-printing is a rapid, efficient, and inexpensive method that has been used in most applications of microfluidic paper-based analytical devices [1-4]. The shape of the hydrophilic working zones was designed with Adobe illustrator CS4. The configuration of the wax patterns for this PPECD (Scheme S1) comprised a PEC tab (the red area, Scheme S1A(1), 20.0 mm × 22.0 mm), and a supercapacitor tab (the blue area, Scheme S1A(4), 20.0 mm × 35.0 mm). Between each tab, the unprinted line was defined as fold line due to the difference of flexibility between the printed and unprinted area after baking. Afterwards, the wax-screen-printed paper was placed in an oven set at 130 °C for 150 s, and then the wax melted and penetrated the thickness of the paper to form the hydrophobic and insulating patterns. The square zone on the PEC ta named as “via hole” (Scheme S1(3)) was used for the addition of carbon nanotube and AuNPs composite to make both side of PEC tab conductive. Then, the circuit components, including two carbon electrodes, one silver pad, and three silver wires, were screen-printed on the as-prepared wax-penetrated paper sheets.

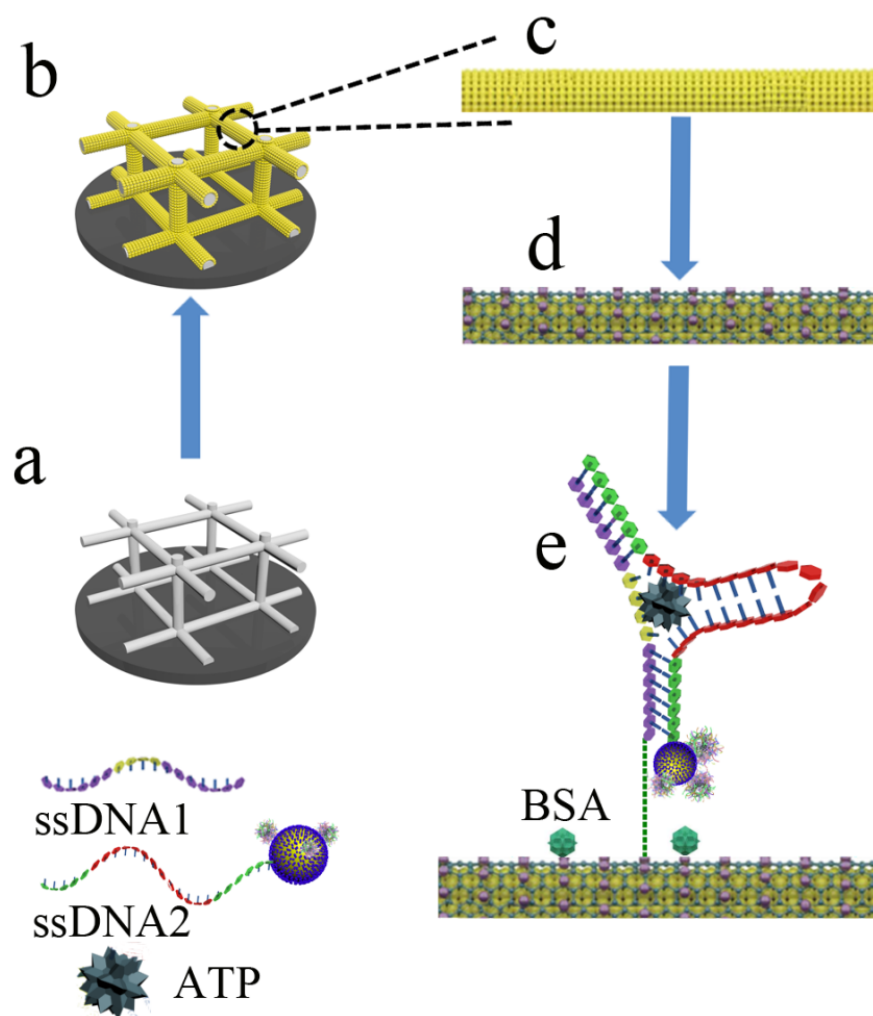
Meanwhile, the all-solid-state paper supercapacitor was assembled directly on the unprinted rectangular area of the supercapacitor tab through a simple two-step approach, that is, drawing of the thin film graphite electrodes on both sides of the unprinted rectangular paper zone by a graphite pencil, and the soaking and solidification of the unprinted rectangular area in the H₂SO₄-Poly(vinyl alcohol) (PVA) gel electrolyte. The drawing method would be suitable for macroscopic fabrication of graphite layer onto paper surface. Typically, the two thin film graphite electrodes for the paper supercapacitor were fabricated through pencil drawing on both sides of the unprinted rectangular area. This drawing was repeated three times to form a uniform coating. After that, the

thin film graphite electrode was immersed into the hot solution of H₂SO₄-PVA gel electrolyte for 10 min and picked out. The reason for the immersion in the hot solution was that, after it cooled down, the solution would become a little viscous, which would not be in favor of the thoroughly soaking of H₂SO₄-PVA gel electrolyte into the unprinted paper zone. The unprinted rectangular area soaked with H₂SO₄-PVA gel electrolyte functioned as both separator and electrolyte, which can minimize the total thickness and simplify the fabrication process. Then, the all-solid-state paper supercapacitor was obtained after the evaporation of the excess water. And the greater suitability of the H₂SO₄-PVA gel electrolyte for flexible and all-solid-state energy storage devices has been well-demonstrated [5].



Scheme S1 Schematic representation of this PPECD. (A) Wax patterns of this PPECD: (1) the PEC tab, (2) paper sample zone, (3) via hole, (4) the supercapacitor tab, (5) paper auxiliary zone, (6) unprinted paper for paper supercapacitor; (B) the PPECD after screen-printing of circuit components: (7) carbon working electrode, (8) (9) silver wire; (C) the reverse side of (B): (10) silver pad, (11) carbon counter electrode; (D) picture of this PPECD: (13) modified Au-PWE, (17) paper supercapacitor.

Construction of the paper working electrode



Scheme S2 Schematic diagram of the fabrication of the 3D-μ-PPECD.

Characterizations of this PSC

Fig. S1A shows the SEM image of thin film graphite electrode that displayed a stacked multilayer structure of graphitic flakes. The edge structures of flakes could be observed obviously in most regions, which is beneficial for electrochemical capacitance [5]. The accurate areal capacitance (AC) of this PSC was calculated by the galvanostatic charge/discharge measurements (LANDIAN Battery Testing System, China) using $AC=I/[A(\Delta V/\Delta t)]$ [5, 6], where I is the current

applied, $\Delta V/\Delta t$ is the slope of the galvanostatic discharge curve, and A is the area of the thin film graphite electrode. Fig. S1B showed the typical result of galvanostatic charge-discharge of this PSC, indicated a good capacitive behavior. In addition, no significant changes in the areal capacitance values of this PSC were observed during 100 charge-discharge cycles, indicated the suitability for the high throughput application in our future work based on the reuse of this PSC (Fig. S1C). These results indicated that this PSC was fabricated as expected using this novel fabrication strategy.

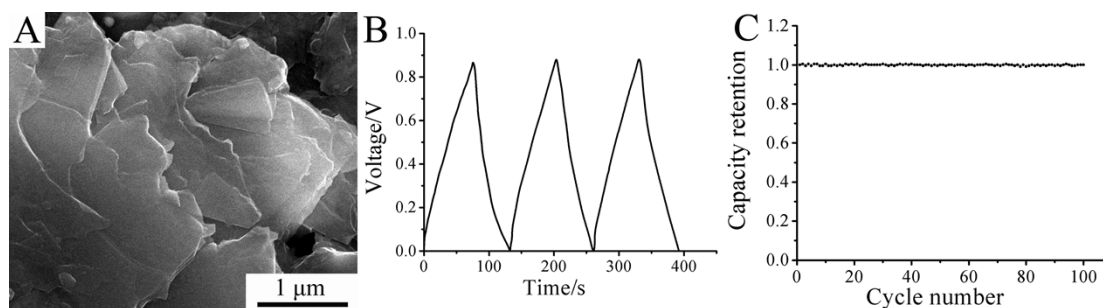


Fig. S1 (A) SEM images of the resulted graphitic film electrode on paper, (B) Galvanostatic charge-discharge curves of this PSC; (C) Durability test of this PSC by measuring 100 charge-discharge cycles.

Assay results for ATP in human serum samples

In order to evaluate and validate the applicability, sensitivity and accuracy of this PPECED with real samples, eleven replicate determinations of ATP in spiked human serum samples were carried out under the optimal conditions. The spiked human serum samples were prepared through adding different amounts of ATP (10 pM to 50 nM) into the human serum samples. The results were shown in Table S1. The recoveries of ATP in human serum samples were obtained in the range of 97.8–103.4%. Thus, the analyzed values of ATP in human serum samples can be

accepted. We believe this ability to detect ATP in real sample would therefore offer a potential approach for diagnosis applications.

Table S1 Assay results for ATP in human serum samples.

Samples	The concentration of ATP (pM)			
	Added*	Founded	RSD (%)	Recovery (%)
Sample-1	10 pM	10.34 pM	3.7	103.4
Sample-2	100 pM	98.72 pM	4.1	98.72
Sample-3	5 nM	5.08 nM	3.8	101.6
Sample-4	20 nM	19.56 nM	3.2	97.8
Sample-5	50 nM	51.57 nM	4.3	103.14

* Average of eleven measurements.

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