

## Supporting Information

### **Plasma polyacrylic acid and hollow TiO<sub>2</sub> spheres modified with rhodamine B for sensitively electrochemical sensing Cu(II)**

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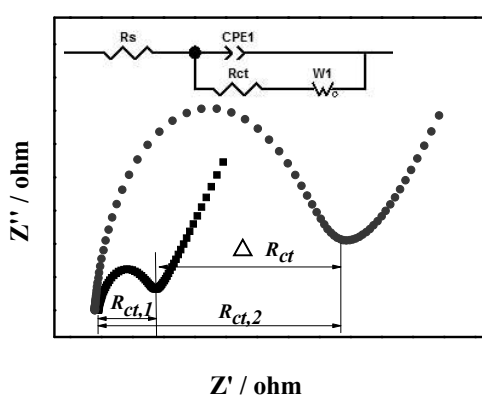
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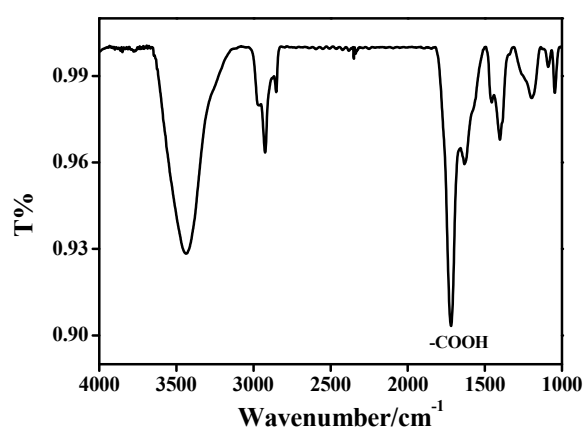
### 1. EIS Nyquist plot and equivalent circuit

The EIS spectrum was analyzed using Zview2 software. A nonlinear least-squares method was used to fit and determine the parameters of the elements in an equivalent circuit (**Fig. S1**). The Randles equivalent circuit, which consists of solution resistance ( $R_s$ ), charge-transfer resistance ( $R_{ct}$ ), constant-phase element (CPE), and Warburg impedance ( $W_o$ ), is shown in the inset of **Fig. S1**.



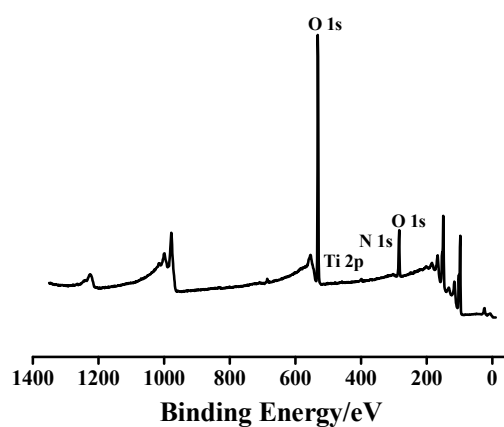
**Fig. S1** EIS Nyquist plots and equivalent circuit

### 2. The FT-IR spectra of $\text{TiO}_2$ @PPAA composite deposited at 20W



**Fig. S2** FT-IR spectra of  $\text{TiO}_2$ @PPAA nanocomposites deposited at 20 W for 1 min

### 3. The XPS spectra of $\text{TiO}_2$ @PPAA composite



**Fig. S3** The survey scan spectra of  $\text{TiO}_2@\text{PPAA}$  composite deposited at 20 W for 1 min

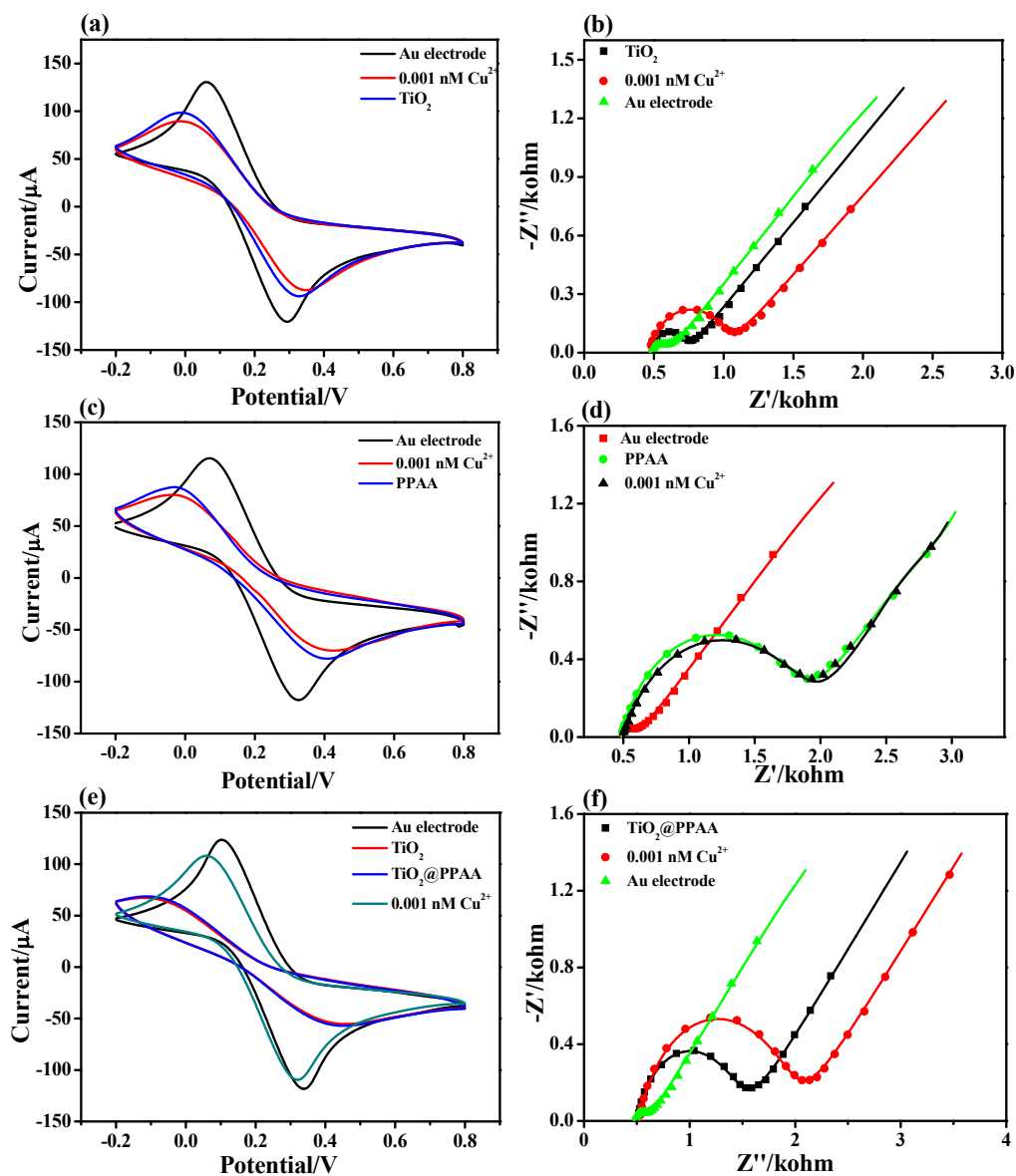
**Table S1** Atomic percentage of  $\text{TiO}_2@\text{PPAA}$  composite for fabrication developed the sensor for detection of  $\text{Cu}^{2+}$

Different steps	Atomic %		
	C 1s	O 1s	N 1s
$\text{TiO}_2@\text{PPAA}$	32.6	64.69	2.14
$\text{TiO}_2@\text{PPAA-EDC/NHS}$	69.92	13.13	16.95
$\text{TiO}_2@\text{PPAA-RhB}$	52.4	44.53	3.07

**Table S2** The fitting values of the Randles Equivalent Circuit elements for the assembly process of *h*-TiO<sub>2</sub>@PPAA-RhB electrochemical sensor before and after the detection of Cu<sup>2+</sup>.

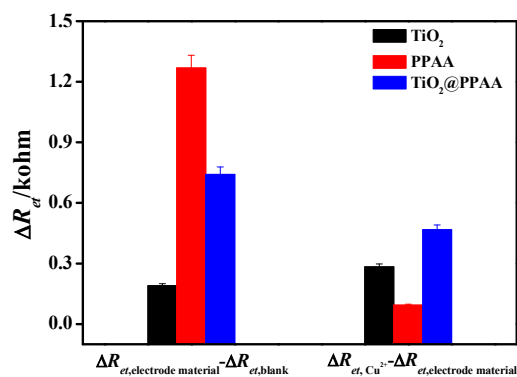
Modified electrodes	$R_s(\Omega)$	$R_{et}(\Omega)$	CPE( $\mu$ Mho)/n
Au	594.8	50.21	1.95/0.982
<i>h</i> -TiO <sub>2</sub> /Au	583.6	139.9	3.76/0.839
<i>h</i> -TiO <sub>2</sub> @PPAA/Au	533.3	426.8	5.52/0.80
<i>h</i> -TiO <sub>2</sub> @PPAA-EDC-NHS/Au	533.2	354.2	66.38/0.563
<i>h</i> -TiO <sub>2</sub> @PPAA-RhB/Au	546.5	797.2	4.491/0.80
<i>h</i> -TiO <sub>2</sub> @PPAA-RhB-Cu <sup>2+</sup> /Au	554.4	1510	2.415/0.857

#### 4. The different developed sensor for detection $\text{Cu}^{2+}$

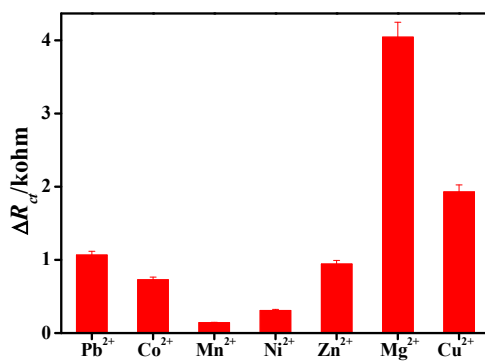


**Fig. S4** CV and Nyquist plots of  $h\text{-TiO}_2/\text{Au}$  (a-b), PPAA/Au (c-d) and  $h\text{-TiO}_2@\text{PPAA}$

(e-f) for directly detection of  $1 \text{ pM } \text{Cu}^{2+}$ .



**Fig. S5** The values of  $\Delta R_{et}$  about the different modified electrodes with  $\text{TiO}_2$ , PPAA and  $\text{TiO}_2@PPAA$  toward the direct adsorption of  $\text{Cu}^{2+}$ , respectively.



**Fig. S6** The values of  $\Delta R_{et}$  about the direct adsorption of  $\text{Pb}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Cu}^{2+}$  using the  $\text{TiO}_2@PPAA$  nanofilm as the electrode materials.