

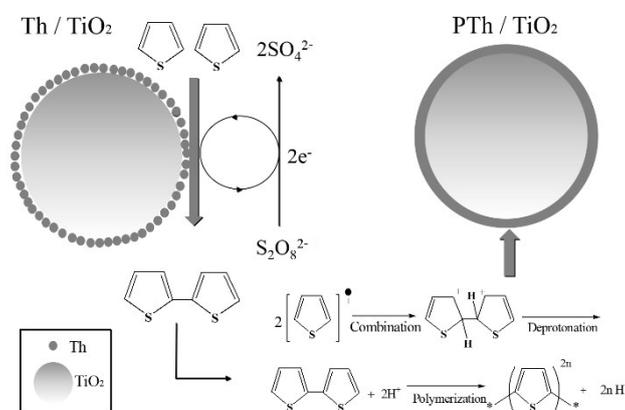
**Supplementary information for:**

**Facile Synthesis of Polythiophene/TiO<sub>2</sub> Particle Composite in Aqueous Medium and Its Adsorption Performance for Pb (II)**

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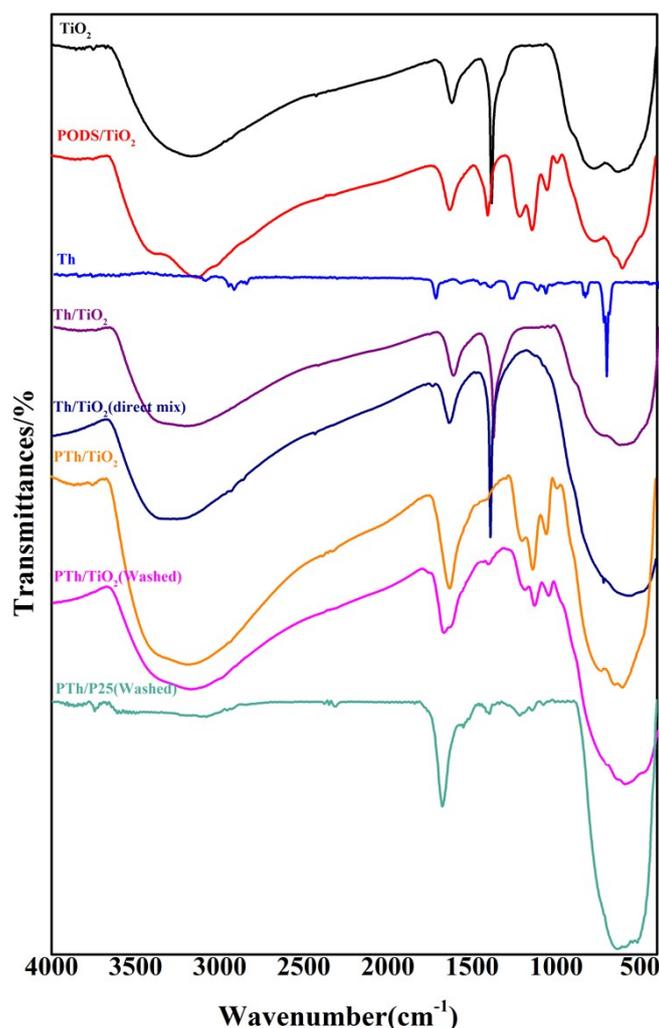
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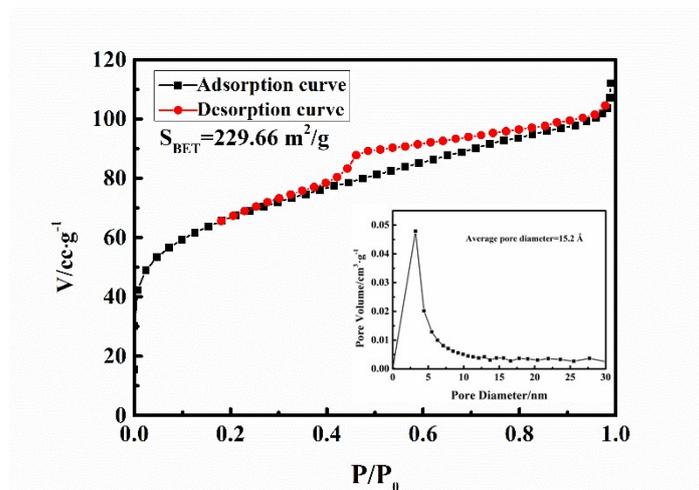


**Scheme S1.** Schematic illustration of the mechanism proposed for the synthesis of PTh/TiO<sub>2</sub> particle composite via (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> oxidative polymerization in acid aqueous medium.

The absorption spectrum of polythiophene would be expected to closely resemble the monomer, and one should be very careful to distinguish the spectral. For better understanding the functional groups, we carried out the FTIR investigation, and the IR spectrum of Ti alkoxide precipitate before any thiophene or oxidizer is added ( $\text{TiO}_2$ ), the precipitate after exposure to  $\text{S}_2\text{O}_8^{2-}$  (peroxydisulfate), but without thiophene (PODS/ $\text{TiO}_2$ ), thiophene monomer (Th), PTh/commercially available  $\text{TiO}_2$  (PTh/P25), thiophene monomer blended with Ti alkoxide precipitate (Th/ $\text{TiO}_2$ ) were obtained and listed in Fig.S1. It needs to be pointed out that the sample of the Th/ $\text{TiO}_2$  used in IR spectrum investigation was acquired by the process as follows: 0.8 mL of  $\text{HNO}_3$  was added in 400 ml of deionized water at 60 °C to prepare the acid solution, and 20 ml of titanium (IV) isopropoxide was added in the solution. After being stirred for 60 min, the solution was cooled to room temperature. Then 3.6 mL of thiophene (0.05 mol) was added to the mixture and stirred for 60 min. Finally, the obtained powder was filtrated and dried at 50 °C for 24 h. While the sample of the Th/ $\text{TiO}_2$  (direct mix) used in IR spectrum investigation was acquired via mixing the thiophene monomer and the as-prepared  $\text{TiO}_2$ . FT-IR spectra of  $\text{TiO}_2$ , PODS/ $\text{TiO}_2$ , Th, Th/ $\text{TiO}_2$ , Th/ $\text{TiO}_2$  (directly mix), PTh/ $\text{TiO}_2$ , PTh/ $\text{TiO}_2$  (washed) and PTh/P25 composite were illustrated in Fig.S1.



**Fig.S1.** FT-IR spectra of  $\text{TiO}_2$ , PODS/ $\text{TiO}_2$ , Th, Th/ $\text{TiO}_2$ , Th/ $\text{TiO}_2$  (directly mix), PTh/ $\text{TiO}_2$ , PTh/ $\text{TiO}_2$  (washed) and PTh/P25 composite.



**Fig.S2.** Nitrogen gas adsorption-desorption isotherms and pore size distribution (insets) of the PTh/TiO<sub>2</sub> composite (Builder SSA-4200; temperature, 77K).

**Information about Langmuir, Freundlich, Dubinin-Radushkevich and Temkin models:**

The Langmuir model was proposed by Langmuir in 1918, and it's mainly based on the assumption as follows: (a) it's an adsorption process of monomolecular layer; (b) each adsorption site fixes only one molecule, and all the adsorption sites are equivalent; (c) there is no reaction among the adsorbed molecules<sup>1, 2</sup>. The Langmuir model can be presented as the following equation:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}, \quad (S1)$$

and its liner form can be represented as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{1}{q_m} C_e, \quad (S2)$$

where  $q_e$  (mg/g) is the adsorption capacity;  $q_m$  (mg/g) is the maximum adsorption capacity;  $C_e$  (mg/L) is the equilibrium concentration of adsorbate;  $K_L$  (L/mg) is an Langmuir constant.

The Freundlich model is an empirical equation based on the consideration of existence of heterogeneous surfaces and various kinds of adsorption sites, making it to be more appropriate to describe practical adsorption process<sup>3</sup>. The Freundlich model can be expressed as the following equation:

$$q_e = K_F C_e^{1/n}, \quad (S3)$$

and its liner form can be represented as follows:

$$\lg q_e = \lg K_F + \frac{1}{n} \lg c_e, \quad (S4)$$

where  $K_F$  ( $L^{1/n} \cdot mg^{1/n-1} \cdot g^{-1}$ ) and  $n$  are the Freundlich constants related to the adsorption capacity and intensity, respectively.

The Dubinin-Radushkevich Model doesn't assume a homogeneous surface or a constant biosorption potential as the Langmuir model<sup>4</sup>. It can be described as followed:

$$q_e = q_m e^{-K_D \varepsilon^2}, \quad (S5)$$

or

$$\ln q_e = \ln q_m - K_D \varepsilon^2, \quad (S6)$$

where  $\varepsilon$  ( $J \cdot mol^{-1}$ ) is the Polanyi potential, and it can be obtained from the equation as follows:

$$\varepsilon = 8.314T \ln\left(1 + \frac{1}{C_e}\right). \quad (\text{S7})$$

$K_D$  (kJ/mol) is constant related to the free energy ( $E$ ) for adsorption. The free adsorption energy ( $E$ ) is an important factor whose values determine the adsorption type, and it can be gained from the followed equation<sup>5</sup>:

$$E = \frac{1}{\sqrt{2K_D}}. \quad (\text{S8})$$

If  $E < 8$  kJ/mol, it may be a physical adsorption process. If  $E > 16$  kJ/mol, chemisorption process may be involved. If  $8 \text{ kJ/mol} < E < 16 \text{ KJ/mol}$ , the adsorption process may relate to ion exchange<sup>6,7</sup>.

The Temkin model considers the interaction between the adsorbates during adsorption, and it can be presented as the follows:

$$q_e = \frac{RT}{b} \ln A_T C_e, \quad (\text{S9})$$

or

$$q_e = B_T \ln A_T + B_T \ln C_e, \quad (\text{S10})$$

and

$$B_T = 8.314T/b, \quad (\text{S11})$$

where  $A_T$  (L/mg) and  $B_T$  (mg/g) are the Temkin constants which relates to the binding energy between adsorbents and adsorbates and adsorption heat<sup>5</sup>.

***Information about the pseudo-first-order and pseudo-second-order models:***

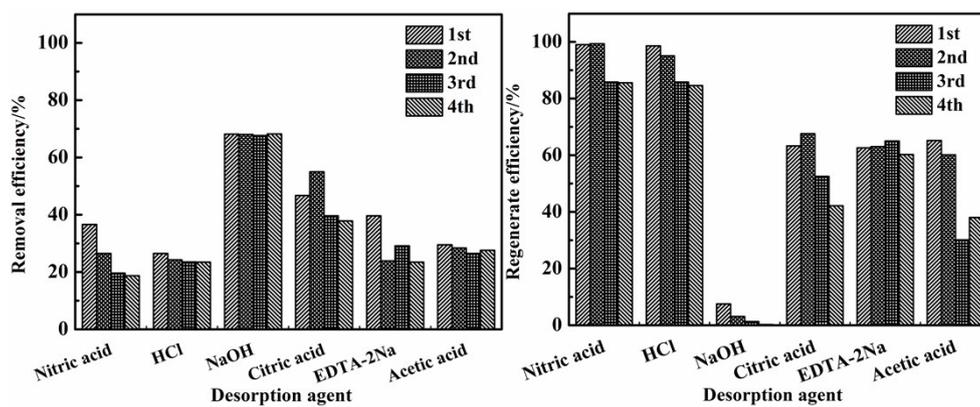
The pseudo-first-order and pseudo-second-order models equations can be arranged into the linear form are given as:

$$\text{(The pseudo-first-order model) } \ln(q_e - q_t) = \ln q_e - k_1 t, \quad (\text{S12})$$

$$\text{(The pseudo-second-order model) } \frac{t}{q_t} = \frac{1}{q_e^2 k_2} + \frac{1}{q_e} t, \quad (\text{S13})$$

where  $q_e$  (mg/g) and  $q_t$  (mg/g) are the adsorption amount at equilibrium state and at time  $t$  (min), respectively;  $k_1$  ( $\text{min}^{-1}$ ) and  $k_2$  ( $\text{g}/(\text{mg} \cdot \text{min})$ ) are the rate constant. Additionally,  $k_2$  can be used to estimate the initial adsorption rate  $h$  ( $\text{mg}/(\text{g} \cdot \text{h})$ ) as follows:

$$h = k_2 q_e^2 (t \rightarrow 0). \quad (\text{S14})$$



**Fig.S3.** The desorption performance of  $Pb^{2+}$  from the as-prepared PTh/ $TiO_2$  composite in various agents (initial concentration, 400 mg/L; volume, 20 mL; pH value, 6; adsorbent dosage, 2.0 g/L; contact time, 3 h; temperature, 25 °C; agitation speed, 200 r/min; recycle time, 4 ).

**Table S1.** Adsorption equilibrium parameters acquired from two models in the adsorption of  $\text{Pb}^{2+}$  onto  $\text{TiO}_2$ . (initial concentration, 20, 50, 100, 200, 300, 400 mg/L; volume, 20 mL; contact time, 24 h; temperature, 25 °C; agitation speed, 200 r/min; pH value, 6; adsorbent dose, 2.0 g/L).

|      | Langmuir model            |                           |                | Freundlich model  |      |                |
|------|---------------------------|---------------------------|----------------|---|------|----------------|
|      | $q_m$ /mg·g <sup>-1</sup> | $K_L$ /L·mg <sup>-1</sup> | R <sup>2</sup> | $K_F$ /L <sup>1/n</sup> ·mg <sup>1/n-1</sup> ·g <sup>-1</sup> | 1/n  | R <sup>2</sup> |
| 25°C | 79.36                     | 0.034                     | 0.996          | 5.73  | 0.49 | 0.947          |

## References

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