## **Supplementary Information**

## Ultrasensitive $Na^+$ exchanging performance of free-standing $Fe_3O_4@Na_2Ti_3O_7$ nanosheets indicated by fluorescein<sup>†</sup>

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**Table S1**. Experimental conditions, chemical compositions, and morphologies for various samples involved in the studies

starting Materials	reaction T (°C)	reaction t (h)	Chemical Compositions	Fe : Ti : Na (molar ratio, ICP)	morphology
$TiO_2 (0.07 g) + Fe (0.015 \sim 0.02 g) +NaOH (10 g) + H_2O (25 mL)$	160	48	$Fe_3O_4 + Na_2Ti_3O_7$	1:3.2:2.1	Nanosheets
$TiO_2 (0.07 g) + NaOH (10 g) + H_2O$ (25 mL)	160	48	Na <sub>2</sub> Ti <sub>3</sub> O <sub>7</sub>		Nanotubes
$\begin{array}{c} {\rm TiO_2} \ (0.07 \ g) + {\rm NaOH} \ (10 \ g) + {\rm H_2O} \\ (25 \ mL) \end{array}$	180	48	Na <sub>2</sub> Ti <sub>3</sub> O <sub>7</sub>		Nanobelts
Fe (0.015~0.02 g) + NaOH (10 g) + $H_2O$ (25 mL)	160	48	Fe <sub>3</sub> O <sub>4</sub>		Irregular particles



Figure S1. XRD pattern of the TiO<sub>2</sub> used in the synthesis, where A and R denote anatase and rutile,

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respectively.



**Figure S2.** This figure shows the interactions of  $Fe_3O_4@Na_2Ti_3O_7$  nanosheets with FITC (top) and FDC (bottom). a, d) UV-vis absorption spectra of solution **1** (black line) and **3** (green line). Insets: Structural formula of FITC and FDC. b, e) Normalized PL spectra of solution **1** (black line) and **3** (green line). Excitation wavelength: 450 nm. c, f) Photographs of the initial solution (**1**), the solution after adding  $Fe_3O_4@Na_2Ti_3O_7$  nanosheets (**2**), and the solution after separating the nanosheets (**3**). The significant enhancement of absorbance and fluorescence in these FL derivates share a same mechanism as the description in FL.



**Figure S3.** Ions exchange between interlayer  $Na^+$  in various  $Na_2Ti_3O_7$  nanostructures and heavy metal ions  $M^{2+}$ . A: M = Cd; B: M = Cu; C: M = Pb. In all cases, Fe<sub>3</sub>O<sub>4</sub>@Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> nanosheets showed the highest releasing level of Na<sup>+</sup> and adsorption level of  $M^{2+}$ .

The ion exchange experiments were conducted as follows: firstly, 25 mL of aqueous solution of  $M^{2+}$  (M=Cd, Cu, or Pb) with a concentration of 1.0 mmol/L were prepared. Then, 10 mg of Fe<sub>3</sub>O<sub>4</sub>@Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> nanosheets or Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> nanotubes or Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> nanoribbons was dispersed in the respective solutions and stirred for 24 h for sufficient exchange between interlayer Na<sup>+</sup> in titanates nanostructures and  $M^{2+}$  in the solution. After that, solids were separated from the solution by centrifugation at a rate of 2000 rpm and washed four times with deionized water. Both the solids and the supernatants containing Na<sup>+</sup> released by titanates were collected. Na<sup>+</sup> in the supernatants was directly analyzed by ICP-AES. To determine the amounts of M<sup>2+</sup> fixed by various titanate nanostructures, the collected solids were dissolved by concentrated HNO<sub>3</sub>. The resulting solutions were then analyzed by ICP-AES.

	$\mathrm{Cd}^{2+}(\mathrm{mg})$	Cu <sup>2+</sup> (mg)	$Pb^{2+}(mg)$
Fe <sub>3</sub> O <sub>4</sub> @Na <sub>2</sub> Ti <sub>3</sub> O <sub>7</sub> nanosheets	26.2	30.4	40.5
Na <sub>2</sub> Ti <sub>3</sub> O <sub>7</sub> nanotubes	14.7	20.2	30.6
$Na_2Ti_3O_7$ nanoribbons	21.3	25.4	23.8

**Table S2**. The adsorption ability of per gram titanate nanostructures towards  $Cd^{2+}$ ,  $Cu^{2+}$ , and  $Pb^{2+}$ 



**Figure S4**. a, b) SEM images and c) XRD pattern of  $Fe_3O_4@Na_2Ti_3O_7$  nanosheets after interactions with FL four times. The nanosheets still maintained their morphology and structure well, suggesting that they were quite stable.