# RESEARCH



# Label-free upconversion nanosensor for water safety monitoring of permanganate and dichromate ions

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# Abstract

Water contaminated with heavy metal ions poses serious threat to the human health and environment protection. It is imperative to develop analytical tools to detect heavy metal ions. Herein, we propose autofluorescence free SiO<sub>2</sub> modified upconversion nanosensor for label-free and fast determination of  $MnO_4^-$  and  $Cr_2O_7^{2-}$  anions. The highly efficient and multi-colour upconversion luminescence (UCL) of UCNPs@SiO<sub>2</sub> was effectively quenched by  $MnO_4^-$  and  $Cr_2O_7^{2-}$  anions with fast response time of 2 and 1 min, respectively. The UCNPs@SiO<sub>2</sub> nanosensor exhibits linear detection ranges of 0.6–2000, 2–2000  $\mu$ M with the LOD at 0.15, 0.04  $\mu$ M for  $MnO_4^-$  and  $Cr_2O_7^{2-}$  anions, respectively. The nanosensor demonstrates autofluorescence free and fast determination of  $MnO_4^-$  and  $Cr_2O_7^{2-}$  anions with satisfactory results. The UCNPs@SiO<sub>2</sub> UCL nanosensor demonstrates autofluorescence free and fast determination of  $MnO_4^-$  and  $Cr_2O_7^{2-}$  anions with high sensitivity, good specificity, low LOD, and wide linear detection range, holding great potential for food and environmental sample sensing.

**Keywords** Upconversion nanoparticles,  $MnO_4^{-}$ ,  $Cr_2O_7^{2-}$ , Förster resonance energy transfer, Inner filter effect

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# Introduction

In current fast paced industrialization, it is of paramount importance to detect hazardous chemicals including heavy metal cations and anions discharged from industrial effluents because of their serious threat to human health and environment protection [1]. Industrial wastewater that contains numerous heavy metal ions contamination could pose significant challenge to the aquatic plants, animals as well as to humans due to their potential adverse effects. Among the hazardous chemicals, permanganate ion (MnO<sub>4</sub><sup>-</sup>) is believed to be a potential carcinogenic chemical, which is frequently used as bleaching, disinfectant and redox reagents both in laboratory and industry [2, 3]. It is well-known that KMnO<sub>4</sub> is widely used in Hummers Method for converting graphene oxide into graphene, which produces hazardous chemical species such as Mn<sup>2+</sup>, MnO<sub>4</sub><sup>-</sup> and Mn<sub>2</sub>O<sub>7</sub>



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[4]. KMnO<sub>4</sub> is also used for water treatment to remove reductive, odorous, phenolic substances [5]. The trace amount of  $MnO_4^-$  can not only lead to the neurological disorder in human but also could impart disability [6]. World Health Organization (WHO) prescribed an upper consumption limit for total manganese in drinking water i.e., 0.1 mg L<sup>-1</sup> [4]. An excess of  $MnO_4^-$  is harmful and can lead to kidney and liver damage [7].

Besides  $MnO_4^-$ , the dichromate ion  $(Cr_2O_7^{2-})$  is another type of extremely hazardous material because of the toxic, carcinogenic and mutagenic nature [8]. The high-valent chromium species  $Cr_2O_7^{2-}$  anions are widely utilized as chemical intermediates [9]. The  $Cr_2O_7^{2-}$  presence in the industrial wastewater dominates since the chromium-based materials are widely used both in industry and home as a decorative and protective paint to prevent automobile and home/offices furniture from wear and tear thereby improving the shelf life of the components used in daily life [10]. A rather serious problem arises when the  $Cr_2O_7^{2-}$  anions are freely discharged into the water sources without any processing after being used in mineral processing, printing, plating, and tanning. According to the WHO, the total amount of Cr concentration in consumable water should not exceed above 0.05 mg  $L^{-1}$  [10]. Excess intake of this anion can cause haemorrhaging, asthma, kidney diseases, neurological disorders and cancer [11, 12].

The efficient detection and decontamination of MnO<sub>4</sub>and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> from water environments is thus highly desired yet challenging due to the coexistence of other heavy metals with them. The complex water environment containing different metal ions alongside MnO4- and  $Cr_2O_7^{2-}$  makes the detection and removal complicated because of the competition between luminescence and adsorption sites of the ions. It is difficult to fabricate reliable sensing platform to determinate  $MnO_4^{-}$  and  $Cr_2O_7^{2-}$ from such a complex environment considering significant high signal to noise ratio caused by other heavy metal ions [8]. Therefore, exploring effective ways to detect inorganic ions has attracted much attention. Thus, it is essential to quantify the traces of MnO<sub>4</sub><sup>-</sup> and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> onsite from drinking water, environment as well as from manufacturing industry, and ecological system. In this regard, developing novel probes with high sensitivity and selectivity to detect metal ions is of prime importance for human health. So far, a variety of analytical techniques have been employed to detect ions, like inductively coupled plasma mass spectrometry (ICP-MS) [13], atomic absorption spectroscopy (AAS) [14], liquid chromatography-tandem mass spectrometry [15], ion exchange [16], adsorption [17], and membrane separation [18]. However, these approaches are still limited, needing specialized and bulkier instruments, moreover, they are difficult to operate, expensive, and time-consuming [19].

Over the past decade, fluorescent studies have gained significant attention owing to superior sensitivity and selectivity, onsite detection, simple operation, and portability [20]. Fluorescent probes for sensing metal ions include metal organic frameworks (MOFs), carbon-based nanomaterials (graphene, nanotube, nanodots and quantum dots), and metal or metal oxide nanomaterials [21– 27] etc. These materials are not adequate for metal ions detection because of their tendency to aggregate, limited quantum yield, poor selectivity, and weak photostability.

Upconversion nanoparticles (UCNPs), which convert near-infrared (NIR) light to emission ranging UV-tovisible wavelength, have attracted enormous attention in recent past on account of the distinct characteristics. These include sharp emissions with long luminescence lifetime, resistance to photobleaching, high photostability, biocompatibility and negligible autofluorescence [28-30]. UCNPs have demonstrated successful applications across various fields, including bioapplications for bioimaging, single-particle biomarking, and therapeutics, optical sensing for temperature, pressure, pH, and molecular detection, and lighting and displays applications for nanoparticle lasing, full-colour display, information storage and anticounterfeiting [31]. In recent years, the UCNPs have been successfully applied to detect antibiotics [32, 33], heavy metal ions [34] as well as pesticides [35]. In addition, the rational core-shell structural design of UCNPs not only generates protective shells for upconversion luminescence (UCL) enhancement, but also regulation stoichiometric composition within a specified scale for fine tuning emission colours and dynamic control of upconversion process. It provides significant flexibility, enabling the synergistic development of new multifunctional biosensor with tuneable properties [36, 37]. The as-synthesized UCNPs are normally capped by hydrophobic ligands. A further requirement for surface modification enables UCNPs for obtaining aqueous dispersion and preventing aggregation. Silica shell exhibits transparency, biocompatibility, non-toxicity, chemical inert, and hydrophilicity. SiO<sub>2</sub> encapsulation results in SiO<sub>2</sub>-coated UCNPs both stable and well-dispersed in aqueous solution [38, 39]. Moreover, the silica shell can be further integrated with functional groups through silanization techniques.

In this study, a novel multi-shelled UCNPs@SiO<sub>2</sub> nanoprobe was designed and developed for detection of  $MnO_4^-$  and  $Cr_2O_7^{2^-}$  anions, via energy transfer (ET; Fig. 1). The oleate capped core-shell-shell-shell UCNPs (denoted as OA-UCNPs) were typically synthesized using a co-precipitation method. Subsequently, the UCNPs were modified with SiO<sub>2</sub> layer (denoted as UCNPs@SiO<sub>2</sub>). In addition to the robust UV-to-visible UCL, the resulting UCNPs@SiO<sub>2</sub> were dispersed well in water, chemically stable, and biocompatible. UCNPs@SiO<sub>2</sub>



Fig. 1 Schematics of the UCNPs@SiO<sub>2</sub> based UCL sensor for  $MnO_4^-$  and  $Cr_2O_7^{2-}$  detection

showed significant reduction in UV and visible UCL after  $\rm MnO_4^-$  addition, while extensively quenched UV UCL with the presence of  $\rm Cr_2O_7^{2-}$ . The UCNPs@SiO\_ based UCL sensor effectively detected  $\rm MnO_4^-$  and  $\rm Cr_2O_7^{2-}$  in real samples of lake and tap water. The proposed UCNPs@SiO\_ UCL sensor demonstrates feasibility, sensitivity, and selectivity for the determination of  $\rm MnO_4^-$  and  $\rm Cr_2O_7^{2-}$  in environmental contaminants.

## Materials and methods Materials

All the raw materials and solvents were, obtained directly from the suppliers, utilized in current study without any further purification step. The high purity ( $\geq 99.9\%$ ) raw materials i.e., Y(CH<sub>3</sub>CO<sub>2</sub>)<sub>3</sub>·xH<sub>2</sub>O, Gd(CH<sub>3</sub>CO<sub>2</sub>)<sub>3</sub>·xH<sub>2</sub>O,  $Eu(CH_3CO_2)_3 \cdot xH_2O_7$  $Yb(CH_3CO_2)_3 \cdot 4H_2O_7$ Tm(CH<sub>3</sub>CO<sub>2</sub>)<sub>3</sub>·xH<sub>2</sub>O, Lu(CH<sub>3</sub>CO<sub>2</sub>)<sub>3</sub>·xH<sub>2</sub>O along with the  $\ge 98\%$  pure NaOH and NH<sub>4</sub>F were supplied by Sigma-Aldrich. The solvents oleic acid (90%) and 1-octadecence (90%) used in current study were supplied by Sigma-Aldrich. While the tetraethyl orthosilicate (TEOS,  $\geq$  99%), ammonium hydroxide (NH<sub>3</sub>·H<sub>2</sub>O, AR, 25-28%), cyclohexane (99.7%), methanol (AR), and N, N-dimethylformamide (DMF, AR,  $\geq$  99.99%) were supplied by Macklin, China. Ethanol (99.7%) and acetone  $(\geq 99.7\%)$  were procured from Guangdong Guanghua Technology, China and Guangzhou brand, China, respectively. Igepal CO-520 (Polyoxyethylene (5) nonylphenyl ether,  $(C_2H_4O)_n \cdot C_{15}H_{24}O$ ,  $n \sim 5$ ) was supplied by Aladdin, China. The aqueous metal anions solution was prepared from their respective salts (analytic or molecular biology grade) such as NaCl, KBr,  $CH_3COONa$ , NaHCO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, NaNO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, NaH<sub>2</sub>PO<sub>4</sub>·2H<sub>2</sub>O, Na<sub>2</sub>HPO<sub>4</sub>, Na<sub>3</sub>PO<sub>4</sub>, and KSCN. Ultrapure water was produced via Milli-Q purification system installed at university. Lake water and tap water were collected from the university town campus of Guangdong University of Technology (GDUT). The membrane with 0.22 µm pore size was supplied by the Jinteng Co., Ltd., Tianjin, China. The disposable sterile syringe was purchased from Jiangsu Kangyou medical equipment Co., Ltd, China.

# Instruments

X-ray diffractometer (XRD, Malvern Panalytical DY735, UK) with a Cu K $\alpha$  irradiation ( $\lambda = 1.5406$  Å) and 2 $\theta$  range of 10-90° with a scanning rate of 5° min<sup>-1</sup> was used to study crystal structure of the prepared powders. To evaluate the nanoparticle morphology and size, transmission electron microscopy (TEM, Hitachi HT7700, Japan; 100 kV) was used. For nanoparticle elemental mapping analysis, a high-resolution TEM (HRTEM, FEI TALOS F200S, Czech Republic; 200 kV) was operated under the scanning transmission electron microscopy (STEM) mode coupled with energy-dispersive X-ray spectroscopy (EDS). Fourier transform infrared (FT-IR) transmittance spectra in the 400-4000 cm<sup>-1</sup> range with a resolution of 1 cm<sup>-1</sup> were measured on a Nicolet 6700 spectrometer (Thermo-Fisher Scientific, USA). Ultraviolet-visible (UV-Vis) absorption spectra and the zeta potentials of the liquid samples were recorded through the Lambda 950 spectrophotometer (PerkinElmer, USA) and the Zeta potential analyzer (Malvern, UK), respectively.

The UCL spectra of liquid samples were measured on a USB 2000+spectrometer (Ocean Optics, USA) using an external fibre-coupled 980 nm diode laser (BWT Beijing Ltd., China). To measure the single particle UCL lifetime, 980 nm NIR laser (Laser 1, B & A Technology Co., Ltd.) coupled Edinburgh FLS980 spectrophotometer was used with 2.9 mW laser power, 971 Hz pulsed frequency and 650 nm spot diameter. The sample droplets were descended onto the glass slides for measuring the nanoparticle UCL lifetime.

#### Synthesis of UCNPs

Co-precipitation method was used to prepare the NaYF<sub>4</sub>:0.2Eu core nanoparticles as reported in [40]with some modifications. Briefly, 2 mL water solution of  $Y(CH_3CO_2)_3$  (0.2 M) and  $Eu(CH_3CO_2)_3$  (0.2 M) was added to a 50 mL round bottom flask containing oleic acid:1-octadecence (4:6 mL) solvents. Subsequently, the mixture was heated for 30 min at 160 °C until the lanthanide-oleate complex formation and then allowed to cool down to room temperature. The methanol solution containing NaOH (1 mmol) and NH<sub>4</sub>F (1.54 mmol) was then added to the resultant mixture and heated again for 30 min at 50  $^{\circ}$ C under constant stirring. Thereafter, the reaction temperature of the mixture was raised to 110  $^{\circ}$ C for methanol evaporation. The resultant mixture was then heated at 300  $^{\circ}$ C for 1 h under an inert (argon) environment. Finally, the resultant NaYF<sub>4</sub>:0.2Eu core nanoparticles were allowed to cool naturally and washed several times in different solvents (ethanol, methanol and cyclohexane). The NaYF<sub>4</sub>:0.2Eu core nanoparticles redispersed in 4 mL cyclohexane were stored at 4  $^{\circ}$ C in a refrigerator for further use.

To synthesize NaYF<sub>4</sub>:0.2Eu@NaYbF<sub>4</sub>:0.39Gd/0.01Tm NaYF4:0.2Eu@NaYbF4:0.39Gd/0.01Tm@ (core-shell), NaYbF<sub>4</sub> (core-shell-shell), and NaYF<sub>4</sub>:0.2Eu@  $NaYbF_4{:}0.39Gd/0.01Tm@NaYbF_4@NaLuF_4 \quad (core-shell$ shell-shell) nanoparticles, similar procedures were employed, with the exception of precursor solution preparation that Y(CH<sub>3</sub>CO<sub>2</sub>)<sub>3</sub> and Eu(CH<sub>3</sub>CO<sub>2</sub>)<sub>3</sub> was replaced with Yb(CH<sub>3</sub>CO<sub>2</sub>)<sub>3</sub>, Gd(CH<sub>3</sub>CO<sub>2</sub>)<sub>3</sub> and Tm(CH<sub>3</sub>CO<sub>2</sub>)<sub>3</sub> for core-shell,  $Yb(CH_3CO_2)_3$  for core-shell-shell, and Lu(CH<sub>3</sub>CO<sub>2</sub>)<sub>3</sub> for core-shell-shell nanoparticles. The detail preparation procedures are supplied in the supplementary information.

#### Silica coating of UCNPs

By using a reverse microemulsion method, the  $SiO_2$  shell was coated onto the as-synthesized oleate capped coreshell-shell-shell UCNPs (OA-UCNPs) [41, 42]. Typically, 1.4 mL of OA-UCNPs in cyclohexane, was mixed with 8.6 mL of cyclohexane, and 0.4 g of CO-520 surfactant and stirred for 10 min. To form a water-in-oil microemulsion, 1.6 g of CO-520 surfactant and 80 µL of NH<sub>3</sub>·H<sub>2</sub>O were then added and sonicated for 30 min. Then, the mixture was constantly stirred for 48 h at room temperature after the addition of TEOS (40  $\mu$ L). Post stirring for 48 h, the acetone was used to precipitate the SiO<sub>2</sub> coated UCNPs (UCNPs@SiO<sub>2</sub>). The final product was washed twice with ethanol/water (v: v = 1:1) via centrifugation for 20 min at 9500 rpm speed. The UCNPs@SiO<sub>2</sub> was finally dispersed in water (7 mL, 10.0 mg/mL) and kept in a refrigerator for further use.

## UCL determination of anions

To achieve optimum UCL based sensing performance of UCNPs@SiO<sub>2</sub> towards  $MnO_4^-$  and  $Cr_2O_7^{2^-}$ , the optimal sensing time was investigated. The UCL spectra were measured for UCNPs@SiO<sub>2</sub> (1.0 mg/mL) in presence of  $MnO_4^-$  (20, 2000  $\mu$ M) and  $Cr_2O_7^{2^-}$  (1000  $\mu$ M) anions, respectively, mixed at different stirring times. The stirring time for  $MnO_4^-$  and  $Cr_2O_7^{2^-}$  was (2, 5, 10, 15, 20, 30, 40, 60, 180, and 360 min) and (1, 2, 4, 5, 7, 9, 11, 13, 15, 17, 19, 21, 23, 25, 27, 29, 40, 50, 60, 120, and 180 min), respectively.

By fixing the optimized time, i.e., 2 min for  $MnO_4^-$  and 1 min for  $Cr_2O_7^{2^-}$ , the  $MnO_4^-$  and  $Cr_2O_7^{2^-}$  concentration dependent UCL spectra of UCNPs@SiO<sub>2</sub> (1.0 mg/mL) were recorded where the concentrations of  $MnO_4^-$  and  $Cr_2O_7^{2^-}$  were (0.6, 0.8, 2, 5, 10, 20, 50, 80, 100, 150, 200, 500, 800, 1000, 1400, 1600 and 2000  $\mu$ M) and (2, 5, 10, 20, 100, 200, 500, 800, 1000, 1500 and 2000  $\mu$ M), respectively.

To evaluate the selectivity and anti-interference properties of UCNPs@SiO2 nanoprobes for determination of MnO<sub>4</sub><sup>-</sup>, the UCL spectra of UCNPs@SiO<sub>2</sub> (1.0 mg/ mL) containing different anions (including 800 µM of MnO<sub>4</sub><sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, SO42-, H2PO4-, HPO42-, PO43-) at the optimized stirring times (2 min) were measured. Also, the UCL spectra of UCNPs@SiO<sub>2</sub> (1.0 mg/mL) were measured when  $MnO_4^{-}$  (800  $\mu M)$  was coexisted with 800  $\mu M$  of Cl<sup>-</sup>, Br<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>,  $HPO_4^{2-}$ ,  $PO_4^{3-}$  individually or in combination with all other anions (800 µM of Cl<sup>-</sup>, Br<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, HCO<sub>3</sub><sup>-</sup>,  $CO_3^{2-}$ ,  $NO_3^{-}$ ,  $SO_4^{2-}$ ,  $H_2PO_4^{-}$ ,  $HPO_4^{2-}$ ,  $PO_4^{3-}$ ) under the aforementioned optimal conditions to check the antiinterference properties of the UCNPs@SiO2. All the UCL spectra of the UCNPs@SiO2 were carried out at room temperature.

To evaluate the selectivity and anti-interference performance of UCNPs@SiO<sub>2</sub> sensor for determining  $Cr_2O_7^{2-}$ , the UCL spectra for UCNPs@SiO<sub>2</sub> (1.0 mg/mL) containing different anions (including 2000  $\mu$ M of  $Cr_2O_7^{2-}$ , Cl<sup>-</sup>, Br<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, SCN<sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, HPO<sub>4</sub><sup>2-</sup>, and PO<sub>4</sub><sup>3-</sup>) were measured at the optimized stirring time (1 min). Furthermore, the UCL spectra of UCNPs@SiO<sub>2</sub> (1.0 mg/mL) in the presence of  $Cr_2O_7^{2-}$  (2000  $\mu$ M) coexisted with 2000  $\mu$ M of Cl<sup>-</sup>, Br<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>,

SCN<sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, HPO<sub>4</sub><sup>2-</sup>, and PO<sub>4</sub><sup>3-</sup> individually or in combination with all other anions (2000  $\mu$ M of Cl<sup>-</sup>, Br<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, SCN<sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, HPO<sub>4</sub><sup>2-</sup>, and PO<sub>4</sub><sup>3-</sup>) under the aforementioned optimal conditions. All the UCL spectra of the UCNPs@SiO<sub>2</sub> were carried out at room temperature.

#### Determination of anions in lake and tap water sample

To check the performance of the UCNPs@SiO<sub>2</sub> probes in real samples sensing application, different types of water (tap and lake) was collected and the presence of the anions was assessed. The lake water was injected using disposable sterile syringes and filtered through a 0.22 µm membrane to remove insoluble particles according to the described procedures [33]. For analysis, different concentrations of  $MnO_4^-$  (1, 5, 20, 100, 500, 1000 and 2000  $\mu$ M) or Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> (10, 50, 100, 500, 1000 and 1500 µM) were added to the 100-fold ultrapure water diluted lake water. On the other hand, the obtained non-filtered tap water was 100-fold diluted with ultrapure water and loaded with MnO<sub>4</sub><sup>-</sup> (1, 5, 20, 100, 500, 1000 and 2000  $\mu$ M) or Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> (10, 50, 100, 500, 1000, and 1500  $\mu$ M). The UCL spectra were measured for the real samples of UCNPs@SiO<sub>2</sub> (1.0 mg/mL) with anions using 980 nm laser excitation.

## **Results and discussion** Characterization of UCNPs

We developed the NaYF<sub>4</sub>:Eu@NaYbF<sub>4</sub>:Gd/Tm@NaYbF<sub>4</sub>@ NaLuF<sub>4</sub> core-shell-shell UCNPs for UCL covering the UV, blue, and red emission. The 980 nm NIR excitation extracted by Yb<sup>3+</sup> ions was upconverted for Tm<sup>3+</sup> UV and blue emission, which was transferred through the Gd sublattice [40]. Interfacial energy transfer from  $Gd^{3+}$ (inner shell) to  $Eu^{3+}$  (core), is responsible for the red UCL [43, 44]. An extra NaYb $F_4$  sensitizer layer is designed to obtain the UCL with great enhancement [45], as demonstrated in previous publication of our group [35]. The inert outermost NaLuF<sub>4</sub> shell is to protect the upconversion process [32]. Recently, Chen group [46] developed NaYF<sub>4</sub>:Yb, Er UCNPs with surface attaching DNAzymes labelled with BHQ1 dye for detection of Cu<sup>2+</sup> ions at the single-nanoparticle-level with LOD of 220 pM. Ding et al. [47] developed poly acrylic acid functionalized NaYF<sub>4</sub>:Yb, Er/2,2-bipyridine system for ciprofloxacin sensing in the 0.05-1000 ng/mL range and 0.13 ng/mL LOD. However, the proposed core-shell-shell UCNPs present several significant benefits, such as relatively small particle size for nanosensor application, robust strong multicolor UCL covering the UV-Vis region, significantly enhanced UCL due to the extra NaYbF<sub>4</sub> sensitizer layer combined with the inert protection shell  $(NaLuF_4)$  as outmost layer.

NaYF<sub>4</sub>:Eu core nanoparticles were prepared for successive growth of the layers of NaYbF<sub>4</sub>:Gd/Tm, NaYbF<sub>4</sub>,

and NaLuF<sub>4</sub> using coprecipitation method [40]. Fig. S1a-c shows representative TEM images of the core (NaYF<sub>4</sub>:Eu), core-shell (NaYF4:Eu@NaYbF4:Gd/Tm) and core-shellshell  $(NaYF_4:Eu@NaYbF_4:Gd/Tm@NaYbF_4)$  nanoparticles, respectively. The nanoparticles are well-dispersed, uniform in size, and have a regular spherical shape. The particle size distribution histograms are shown in the Fig. S1d-f, which shows the particle diameter of 17.0 nm, 27.0 nm, and 32.9 nm, respectively. The TEM image of the core-shell-shell NaYF4:Eu@NaYbF4:Gd/Tm@ NaYbF<sub>4</sub>@NaLuF<sub>4</sub> UCNPs presented in Fig. 2a, shows that the UCNPs are monodispersed, uniform in size, and have a regular spherical shape. The particle size distribution histogram is shown in the Fig. S2, with an average diameter of 39.5 nm. The TEM image of the UCNPs displayed in Fig. 2(b-h) along with corresponding elemental mapping, indicating that the  $(Y^{3+}, Eu^{3+})$ ,  $(Gd^{3+}, Tm^{3+})$  and Lu<sup>3+</sup> are present in the core, inner shell, and outermost shell, respectively, which is consistent with the designed composition. The EDS result shown in Fig. 2i is in line with the elemental mapping and the designed UCNPs composition. Through HRTEM of a single core-shellshell-shell nanoparticle, see Fig. 2j, the lattice fringes are found to exhibit *d*-spacing of 0.520 nm that corresponds to the (100) plane arises from  $NaYF_4$  hexagonal structure. To further investigate the structure of the as-synthesized UCNPs, the XRD patterns of the UCNPs (Fig. 2k), core, core-shell, core-shell-shell nanoparticles (Fig. S3), reveal main characteristic peaks at 17.2° (100), 30.0° (110), 30.89° (101), 43.55° (201) and 53.79° (211) of a NaYF<sub>4</sub> hexagonal structure (JCPDS No. 16-0334), which are consistent with the lattice *d*-spacing result indicated in Fig. 2j.

The UCL spectra of the NaYF4:Eu@NaYbF4:Gd/Tm@ NaYbF<sub>4</sub>@NaLuF<sub>4</sub> UCNPs carried out at room temperature under 980 nm excitation can be seen in Fig. 2l. The prominent UCL in the UV to visible region centered at 345, 361, 450, 477 and 646 nm, are readily assigned to the Tm<sup>3+</sup> transitions of  ${}^{1}I_{6} \rightarrow {}^{3}F_{4}$ ,  ${}^{1}D_{2} \rightarrow {}^{3}H_{6}$ ,  ${}^{1}D_{2} \rightarrow {}^{3}F_{4}$ ,  ${}^{1}G_{4}$  $\rightarrow$   ${}^{3}\text{H}_{6}$ ,  ${}^{1}\text{G}_{4} \rightarrow {}^{3}\text{F}_{4}$ , respectively [40, 48]. The prominent Eu<sup>3+</sup> peaks were observed at 510 ( ${}^{5}D_{2} \rightarrow {}^{7}F_{3}$ ), 525 ( ${}^{5}D_{1} \rightarrow$  ${}^{7}F_{1}$ ), 535 ( ${}^{5}D_{1} \rightarrow {}^{7}F_{2}$ ), 555 ( ${}^{5}D_{1} \rightarrow {}^{7}F_{3}$ ), 590 ( ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ ), 615 ( ${}^5D_0 \rightarrow {}^7F_2$ ) and 695 nm ( ${}^5D_0 \rightarrow {}^7F_4$ ) [49]. The UCL peak related to the  ${}^{6}P_{7/2} \rightarrow {}^{8}S_{7/2}$  transition of Gd<sup>3+</sup> was detected at 312 nm [50]. The UCL intensity was similar for NaYF<sub>4</sub>:Eu@NaYbF<sub>4</sub>:Gd/Tm core-shell nanoparticles in comparison with NaYF<sub>4</sub>:Eu@NaYbF<sub>4</sub>:Gd/Tm@NaYbF<sub>4</sub> core-shell-shell nanoparticles with outmost NaYbF<sub>4</sub> sensitization layer, while ~ 100 folds stronger for NaYF<sub>4</sub>:Eu@ NaYbF<sub>4</sub>:Gd/Tm@NaLuF<sub>4</sub> core-shell-shell nanoparticles with outmost NaLuF<sub>4</sub> protection layer than NaYF<sub>4</sub>:Eu@ NaYbF<sub>4</sub>:Gd/Tm core-shell nanoparticles, indicating the inert NaLuF<sub>4</sub> layer capable of eliminating the non-radiative energy losses related surface defects and quenching [51]. Inserting of NaYbF $_4$  sensitization layer between



**Fig. 2** TEM image of the (**a**) core-shell-shell NaYF<sub>4</sub>:0.2Eu@NaYbF<sub>4</sub>:0.39Gd/0.01Tm@NaYbF<sub>4</sub>@NaLuF<sub>4</sub> UCNPs, (**b**) randomly chosen core-shell-shell-shell UCNPs for elemental analysis, (**c**–**h**) elemental mapping and (**i**) EDS spectrum of the core-shell-shell-shell UCNPs; (**j**) HRTEM image of individual core-shell-shell-shell nanoparticles (*d*-spacing = 0.520 nm); (**k**) XRD pattern of the core-shell-shell-shell UCNPs; (**j**) UCL spectra of NaYF<sub>4</sub>:Eu@NaYbF<sub>4</sub>:Gd/Tm@ NaYbF<sub>4</sub>@NaLuF<sub>4</sub> in comparison with NaYF<sub>4</sub>:Eu@NaYbF<sub>4</sub>:Gd/Tm, NaYF<sub>4</sub>:Eu@NaYbF<sub>4</sub>:Gd/Tm@NaYbF<sub>4</sub>:Gd/Tm@NaYbF<sub>4</sub>:Eu@NaYbF<sub>4</sub>:Gd/Tm@ NaYF<sub>4</sub>:Eu@NaYbF<sub>4</sub>:Gd/Tm@ NaYF<sub>4</sub>:Eu@NaYbF<sub>4</sub>:Gd/Tm@ NaYF<sub>4</sub>:Eu@NaYbF<sub>4</sub>:Gd/Tm@ NaYF<sub>4</sub>:Eu@NaYbF<sub>4</sub>:Gd/Tm@ NaYF<sub>4</sub>:Eu@NaYbF<sub>4</sub>:Gd/Tm@ NaYF<sub>4</sub>:Eu@NaYbF<sub>4</sub>:Gd/Tm@ NaYF<sub>4</sub>:Eu@NaYbF<sub>4</sub>:Gd/Tm@ NaYF<sub>4</sub>:Eu@NaYbF<sub>4</sub>:Gd/Tm@ NaYF<sub>4</sub>:Eu@NaYbF<sub>4</sub>:Gd/Tm@ NaYF<sub>4</sub>:Eu@ NaYF<sub>4</sub>:Eu@ NaYbF<sub>4</sub>:Gd/Tm@ NaYbF<sub>4</sub>:Gd/Tm@ NaYF<sub>4</sub>:Eu@ NaYbF<sub>4</sub>:Gd/Tm@ NaYF<sub>4</sub>:Eu@ NaYbF<sub>4</sub>:Eu@ NaYbF<sub>4</sub>:Eu@ NaYbF<sub>4</sub>:Eu@ NaYbF<sub>4</sub>:Gd/Tm@ NaYF<sub>4</sub>:Eu@ NaYbF<sub>4</sub>:Gd/Tm@ NaYF<sub>4</sub>:Eu@ NaYbF<sub>4</sub>:Gd/Tm@ NaYF<sub>4</sub>:Eu@ NaYbF<sub>4</sub>:Eu@ NaYbF<sub>4</sub>:E

NaYbF<sub>4</sub>:Gd/Tm and NaLuF<sub>4</sub> shells can significantly enhance the UCL intensity ~ 1500-fold, as also illustrated in the inset of Fig. 2l showing the NaYF<sub>4</sub>:Eu@NaYbF<sub>4</sub>:Gd/Tm@NaYbF<sub>4</sub>@NaLuF<sub>4</sub> core-shell-shell-shell UCNPs with significantly enhanced UCL than NaYF<sub>4</sub>:Eu@NaYbF<sub>4</sub>:Gd/Tm@NaLuF<sub>4</sub> core-shell-shell nanoparticles under irradiation with a 980 nm laser.

#### Surface SiO<sub>2</sub> modification of UCNPs

The obtained core-shell-shell OA-UCNPs are hydrophobic in nature. On the other hand, silica shell could provide good hydrophilicity to UCNPs. Therefore, we introduced SiO<sub>2</sub> layer on to the UCNPs surface, to facilitate the transformation of hydrophobic OA-UCNPs to hydrophilic UCNPs@SiO<sub>2</sub>. Furthermore, the SiO<sub>2</sub> layer protects the UCNPs from the adverse environmental conditions [52]. Figure 3a, represents a typical TEM image of the UCNPs@SiO<sub>2</sub>. The UCNPs@SiO<sub>2</sub> are monodispersed with regular spherical shape with the particle size about 44.6 nm (Fig. S4). The SiO<sub>2</sub> shell exhibits integration and uniformity, with the shell thickness approximately 2.6 nm. The FT-IR spectrum of OA-UCNPs, as shown in Fig. 3b, exhibits several absorption peaks at (2926, 2853 cm<sup>-1</sup>) and (1562, 1463 cm<sup>-1</sup>) that could be attributed to the characteristic asymmetric and symmetric stretching vibrations of CH<sub>2</sub> and carboxylic (-COO) groups, respectively [48, 53], suggesting the presence of OA capping ligand on the UCNPs surface. In contrast, after encapsulation of UCNPs with SiO<sub>2</sub>, the characteristic absorption at 2926, 2853, 1562, and 1463 cm<sup>-1</sup> was significantly reduced, indicating successful removal of OA from UCNPs surface. UCNPs@SiO2 exhibit prominent absorption band at 3433 cm<sup>-1</sup> due to the O-H stretching frequency from silanol group (Si-OH). In addition, the other absorption bands due to the Si-O-Si (1074 and 795 cm<sup>-1</sup>), Si-OH (963 cm<sup>-1</sup>), and Si-O



**Fig. 3** (a) TEM image and (b) FT-IR transmittance spectra of UCNPs@SiO<sub>2</sub>, with later in comparison with OA-UCNPs; (c) Zeta potential of UCNPs@SiO<sub>2</sub>, and (d) UCL spectra of UCNPs@SiO<sub>2</sub> (1.0 mg/mL), UCNPs@SiO<sub>2</sub> (1.0 mg/mL) with presence of  $MnO_4^-$  (500  $\mu$ M) or  $Cr_2O_7^{2-}$  (1000  $\mu$ M) in aqueous solution under 980 nm laser excitation

(458 cm<sup>-1</sup>) were observed [32]. Figure 3c shows the result of the zeta potential analysis. The surface potentials ( $\zeta$ ) for the water-soluble negatively charged UCNPs@SiO<sub>2</sub> was found to be -12.9 mV, which agrees with previously reported result [32], confirming the SiO<sub>2</sub> surface modification. Upon addition of the analyte anions, the UCL of UCNPs@SiO<sub>2</sub> was declined significantly in presence of MnO<sub>4</sub><sup>-</sup> (Fig. 3d), while the UV UCL of Tm<sup>3+</sup> at 345, 360 nm was seriously quenched by Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> (Fig. 3d), indicating that the UCNPs@SiO<sub>2</sub> UCL is feasible for the sensing of MnO<sub>4</sub><sup>-</sup> and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> anions.

#### UCNPs@SiO<sub>2</sub> sensor optimization for the anion detection

To achieve efficient determination of anions using UCNPs@SiO<sub>2</sub> sensor, we investigated the optimal experimental conditions for the UCNPs@SiO<sub>2</sub> with the anions.

The UCNPs@SiO<sub>2</sub> were dispersed (Fig. S5a) in different solvents including water, ethanol, methanol, and DMF, respectively, and the solvent-dependent UCL was measured. The UCNPs@SiO2 exhibit the similar UCL intensity (Fig. S5b) for dispersion in water, ethanol, methanol, and DMF, respectively. On the other hand, similar as shown in Fig. 3(a) for TEM of UCNPs@SiO<sub>2</sub>, Fig. S6 shows the TEM of UCNPs@SiO<sub>2</sub> prepared in repeated batch for one week storage in water, which also exhibit a uniform morphology with SiO<sub>2</sub> layers modification on surface of UCNPs, further indicating water dispersion of UCNPs@SiO<sub>2</sub> remains stable without aggregation. Combining consideration of the  $MnO_4^-$  and  $Cr_2O_7^{2-}$ anions mostly showing presence in wastewater, the water was then chosen as the optimal solvent for sensing. The UCNPs@SiO<sub>2</sub> sensor was then incubated with  $MnO_4^{-}$  and  $Cr_2O_7^{2-}$  anions in water and the UCL was investigated to study the time-dependent UCL quenching at different stirring time. The MnO<sub>4</sub><sup>-</sup> addition at concentrations of 20 µM (Fig. S7a) and 2000 µM (Fig. S7c) significantly quenched the UCL of UCNPs@SiO2 at a 2-minute incubation time, and the corresponding timedependent relative UCL intensity with presence of 20 µM (Fig. S7b) and 2000  $\mu$ M (Fig. S7d) MnO<sub>4</sub><sup>-</sup> concentration exhibits negligible change after 2 min incubation between UCNPs@SiO2 and MnO4-. On the other hand, upon addition of Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, the UCNPs@SiO<sub>2</sub> show significantly quenched UCL (Fig. S8a) at 1 min of incubation, and progressively enhanced quenching until 7 min incubation time, then reach negligible change after 7 min incubation time, as shown in Fig. S8b for the corresponding timedependent relative UCL intensity. With increasing the incubation time between 1 to 7 min, the enhanced UCL quenching of UCNPs@SiO<sub>2</sub> upon addition of Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, may be attributed to some possible interferences, such as pH change for UCNPs@SiO<sub>2</sub> sensor, highly chemical oxidation capability for  $Cr_2O_7^{2-}$ . To eliminate the possible interferences as listed above, the incubation time was thus optimized at 1 min for UCNPs@SiO<sub>2</sub> sensor with Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>. Therefore, we chose water as the optimal solvent, and 2 and 1 min as the optimal time for incubating UCNPs@SiO<sub>2</sub> with MnO<sub>4</sub><sup>-</sup> and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> anions in water, respectively.

#### Sensing for MnO<sub>4</sub><sup>-</sup>

To assess the UCNPs@SiO<sub>2</sub> sensor sensitivity for determination of MnO<sub>4</sub><sup>-</sup> anion, the UCL of the designed UCNPs@SiO<sub>2</sub> sensor was measured under the optimal conditions in presence of various concentrations of MnO<sub>4</sub><sup>-</sup> anion. Figure 4a shows the UCL spectra of UCNPs@SiO2 in wavelength range of 300-400 nm against the different concentrations of  $MnO_4^-$  (0.6-2000  $\mu$ M) in the homogeneous assay. As the concentration of  $MnO_4^{-}$  increased (0.6–2000  $\mu$ M), the intensity of UCNPs@SiO<sub>2</sub> UCL main peaks due to the  ${}^{1}I_{6} \rightarrow {}^{3}F_{4}$ (345 nm),  ${}^{1}\text{D}_{2} \rightarrow {}^{3}\text{H}_{6}$  (361 nm),  ${}^{1}\text{D}_{2} \rightarrow {}^{3}\text{F}_{4}$  (450 nm), and  ${}^{1}G_{4} \rightarrow {}^{3}H_{6}$  (477 nm) transitions of the Tm<sup>3+</sup> ions was significantly quenched. The UCNPs@SiO<sub>2</sub> sensor exhibits promising sensing behaviour for MnO<sub>4</sub><sup>-</sup> where the UCL intensity was significantly quenched (95%) after addition of 2000  $\mu$ M of MnO<sub>4</sub><sup>-</sup> (Fig. 4a). A major UCL quenching, about 10%, was observed in presence of  $MnO_4^-$  at low concentration of 2  $\mu$ M (Fig. 4a). To explore the UCL quenching behaviour towards MnO<sub>4</sub><sup>-</sup>, a Stern-Volmer curve (Fig. 4b) was plotted using the equation,  $\frac{I_0}{I} = 1 + K_{sv} [c]$ , where  $I_0$ , and I represent the integrated intensity of strong Tm<sup>3+</sup> UCL at 345 and 360 nm for UCNPs@SiO $_2$  without and with the presence of an analyte, respectively. [c] is the concentration of the analyte in mole (as the quencher), and  $K_{sv}$  is Stern-Volmer constant  $(M^{-1})$  [54, 55]. At low  $MnO_4^-$  concentration range, a Stern-Volmer plot (Fig. 4b) shows a nonlinear behaviour while an upward trend was observed with increasing  $MnO_4^-$  concentration. The nonlinearity of the Stern-Volmer plot indicates the energy transfer among UCNPs@  $SiO_2$  and  $MnO_4^-$  or it may be related to both the static and dynamic quenching [56]. For the UCNPs@SiO<sub>2</sub> sensor towards MnO<sub>4</sub><sup>-</sup> determination, the UCL quenching efficiency (Fig. 4c), is defined as  $[(I_0-I)/I_0]$ . Figure 4c shows the efficacy of UCNPs@SiO<sub>2</sub> UCL quenching against the logarithm of MnO<sub>4</sub><sup>-</sup> concentration, which exhibits well-fitted linear relationships of y = 0.0952x + 0.0626 with correlation coefficients  $R^2$  = 0.9944 in the 0.6–80  $\mu$ M concentration range of the MnO<sub>4</sub><sup>-</sup> (Fig. 4d) and y = 0.4903 x - 0.6863 with  $R^2 = 0.9974$  for MnO<sub>4</sub><sup>-</sup> concentration ranging 80-2000 µM (Fig. 4e), respectively. As revealed in Fig. 4f, by further plotting  $c/[(I_0-I)/I_0]$  against c [57], with c referring to the concentration of  $MnO_4^{-}$ , good linear relationships were established with y = 4.2315x + 14.596 ( $R^2 = 0.9844$ ) for the MnO<sub>4</sub><sup>-</sup> concentration in range of 0.6–80  $\mu$ M (inset of Fig. 4f) and y = 0.9256x + 273.3 ( $R^2 = 0.9981$ ) for the MnO<sub>4</sub><sup>-</sup> concentration ranging 80-2000 µM (Fig. S9), indicating that UCNPs@ SiO<sub>2</sub> is qualified for determination of MnO<sub>4</sub><sup>-</sup> ion in wide 0.6–2000 µM concentration range. The limit of detection (LOD) of UCNPs@SiO<sub>2</sub> toward MnO<sub>4</sub><sup>-</sup> can be calculated using 3  $\sigma/S$  [35], where  $\sigma$  is the relative standard deviation of blank sample obtained from 5 measurements, while S represents the calibration curve slope, with a LOD of 0.15  $\mu$ M, demonstrating the high sensitivity of the synthesized  $MnO_4^{-}$  sensor i.e., UCNPs@SiO\_2. In comparison with the reported fluorescent methods for sensing of MnO<sub>4</sub><sup>-</sup> as listed in Table S1, the proposed UCNPs@SiO<sub>2</sub> sensor exhibits the excellent detection sensitivity with least LOD and wide detection range. Enabled with the NIR excited UCL for improved signal-to-noise ratio and autofluorescence free background, the proposed UCNPs@SiO<sub>2</sub> upconversion nanosensor can be potentially used for sensitive MnO<sub>4</sub><sup>-</sup> detection in aqueous samples.

We investigated the selectivity of the proposed UCNPs@SiO<sub>2</sub> sensor to detect  $MnO_4^-$  by monitoring the UCL response to several anions, including Cl<sup>-</sup>, Br<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, HPO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>, and MnO<sub>4</sub><sup>-</sup>. Figure 4g and Fig. S10a display the UCNPs@SiO<sub>2</sub> UCL responses for the different anions at a fixed concentration of 800  $\mu$ M. Among these anions, only MnO<sub>4</sub><sup>-</sup> exhibited considerable quenching effect on UCL intensity of UCNPs@SiO<sub>2</sub> with quenching efficiencies of ~75%, whereas other anions showed no apparent effect on UCL response of UCNPs@SiO<sub>2</sub>. This suggests that the UCNPs@SiO<sub>2</sub> sensor exhibits high selectivity towards MnO<sub>4</sub><sup>-</sup> sensing. Moreover, the UCNPs@SiO<sub>2</sub> sensor was subjected to an



**Fig. 4** (a)  $MnO_4^-$  (0.6–2000 µM) concentration dependent UCL spectra of UCNPs@SiO<sub>2</sub> in aqueous solution, (b) plot of  $I_0/I$  against  $MnO_4^-$  concentration (Stern-Volmer), (c) the UCL quenching efficiency of UCNPs@SiO<sub>2</sub> against the logarithmic concentration of  $MnO_4^-$ , (d) the UCL quenching efficiency showing the linear relationship plot for  $MnO_4^-$  concentration in range of 0.6–80 µM, (e) linear relationship plot of UCL quenching efficiency for  $MnO_4^-$  concentration in the 80–2000 µM range, (f) relationship between  $c/[(I_0-I)/I_0]$  versus  $MnO_4^-$  concentration, inset showing the well-fitted linearity for  $MnO_4^-$  concentration in the 0.6–80 µM range, (g) UCL intensity of UCNPs@SiO<sub>2</sub> with addition of various anions (800 µM) in aqueous solutior; Anti-interference plot of UCNPs@SiO<sub>2</sub> sensor for  $MnO_4^-$  detection, (h) UCL intensity of UCNPs@SiO<sub>2</sub> in presence of the  $MnO_4^-$  (800 µM) mixed with other individual anions (800 µM); (i) UCL intensity of UCNPs@SiO<sub>2</sub> in the presence of  $MnO_4^-$  (800 µM) mixed with 800 µM other anions. (Note: integrated intensity of UCNPs@SiO<sub>2</sub> SiO<sub>2</sub> UCL at 345 and 361 nm was used.)

anti-interference experiment for the detection of  $MnO_4^$ by introducing  $MnO_4^-$  into the system concurrently with the addition of other individual or mixed anions. The UCNPs@SiO<sub>2</sub> sensor, in the presence of  $MnO_4^-$  of 800  $\mu$ M (Fig. 4h and Fig. S10b), did not show a substantial difference compared to the system together with other individual anions (800  $\mu$ M). Figure 4i and Fig. S10c, illustrate the comparable UCL quenching in intensity for UCNPs@ SiO<sub>2</sub> sensor when  $MnO_4^-$  (800  $\mu$ M) was added, both with and without different mixed anions including Cl<sup>-</sup>, Br<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, HPO<sub>4</sub><sup>2-</sup>, and PO<sub>4</sub><sup>3-</sup> at equal concentration (800  $\mu$ M). This proves that the other anions show negligible effect on the UCL of UCNPs@SiO<sub>2</sub> sensor to detect  $MnO_4^-$ . These results reveal the good selectivity of UCNPs@SiO<sub>2</sub> sensor for detecting  $MnO_4^-$ . Thus, UCNPs@SiO<sub>2</sub> could be considered as a promising candidate for detecting  $MnO_4^-$  anion in aqueous solution.

## Sensing for C<sub>2</sub>O<sub>7</sub><sup>2-</sup>

Figure 5a shows UCL spectra at the different  $\text{Cr}_2\text{O}_7^{2-}$  concentration under 980 nm laser excitation. With increase in the  $\text{Cr}_2\text{O}_7^{2-}$  concentration (2–2000  $\mu$ M), the intensity of UCNPs@SiO<sub>2</sub> was significantly quenched for the UCL at 345, and 361 nm, which are attributed to the  ${}^1\text{I}_6 \rightarrow {}^3\text{F}_4$  and  ${}^1\text{D}_2 \rightarrow {}^3\text{H}_6$  transitions of Tm<sup>3+</sup> ions. The UCNPs@SiO<sub>2</sub> sensor exhibit superior sensitivity behaviour for  $\text{Cr}_2\text{O}_7^{2-}$  through the quenching of ~74% UCL intensity



**Fig. 5** (a)  $Cr_2O_7^{2-}$  (2–2000  $\mu$ M) concentration dependent UCL spectra of UCNPs@SiO<sub>2</sub> in aqueous solution, (b) Stern-Volmer plot ( $l_0$ // versus  $Cr_2O_7^{2-}$  concentration), (c) the UCL quenching efficiency of UCNPs@SiO<sub>2</sub> against the concentration of  $Cr_2O_7^{2-}$ , the linear relationship plot of the UCL quenching efficiency for  $Cr_2O_7^{2-}$  concentration in the (d) 2–500  $\mu$ M and (e) 500–2000  $\mu$ M range, (f) plot of  $c/[(l_0-1)/l_0]$  versus concentration of  $Cr_2O_7^{2-}$ , inset showing simulated linearity correlation for  $Cr_2O_7^{2-}$  concentration in the 2–500  $\mu$ M range, (g) UCL intensity of UCNPs@SiO<sub>2</sub> with addition of various anions (2000  $\mu$ M) in aqueous solution; Anti-interference properties of the UCNPs@SiO<sub>2</sub> to detect  $Cr_2O_7^{2-}$  in aqueous solution, (h) UCL intensity of UCNPs@SiO<sub>2</sub> with the addition of  $Cr_2O_7^{2-}$  together with other individual anions (2000  $\mu$ M), and (i) UCL intensity of UCNPs@SiO<sub>2</sub> with the addition of  $Cr_2O_7^{2-}$  together with other mixed anions at a fixed 2000  $\mu$ M concentration. (Note: integrated intensity of UCNPs@SiO<sub>2</sub> UCL at 345 and 361 nm was used.)

when 2000  $\mu$ M of Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> anion was added (Fig. 5a). For 10  $\mu$ M of Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> concentration, the major UCL quenching (10%) was observed (Fig. 5a). To investigate the UCL quenching behaviour towards Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> determination, Fig. 5b illustrates the Stern-Volmer plot extracted from the UCL intensity shown in Fig. 5a. The Stern-Volmer plot displays an appreciable nonlinear behaviour with an upward curvature with increase in Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> concentration in range of 2-2000  $\mu$ M (Fig. 5b), revealing an energy transfer from UCNPs@SiO<sub>2</sub> to Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> or can be ascribed to both the static and dynamic quenching [56]. For the UCNPs@SiO<sub>2</sub> sensing probe toward Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> determination, the quenching efficiency for UCNPs@ SiO<sub>2</sub> UCL at 345 and 361 nm against the logarithmic concentration of Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> is shown in Fig. 5c, which shows

well-described linear relationship of  $y = 0.1474 \ x - 0.0395$ with  $R^2 = 0.9948$  for the concentration of  $\operatorname{Cr}_2 \operatorname{O_7}^{2-}$  in range of 2–500 μM (Fig. 5d) and  $y = 0.6737 \ x - 1.4801$  with  $R^2 = 0.9972$  for  $\operatorname{Cr}_2 \operatorname{O_7}^{2-}$  concentration ranging 500–2000 μM (Fig. 5e), respectively. By further plotting  $c/[(I_0 - I)/I_0]$  against c [58], with c denoting the concentration of  $\operatorname{Cr}_2 \operatorname{O_7}^{2-}$ , well-fitted linear relationships were accomplished with  $y = 2.9397 \ x + 73.66 \ (R^2 = 0.9961)$  for  $\operatorname{Cr}_2 \operatorname{O_7}^{2-}$ concentration in range of 2–500 μM (inset of Fig. 5f), and  $y = 0.8368 \ x + 1013.1 \ (R^2 = 0.9979)$  for  $\operatorname{Cr}_2 \operatorname{O_7}^{2-}$  concentration ranging 500–2000 μM (Fig. S11), indicating that UCNPs@SiO<sub>2</sub> is qualified for determination of  $\operatorname{Cr}_2 \operatorname{O_7}^{2-}$ ion in wide 2–2000 μM concentration range. The LOD of UCNPs@SiO<sub>2</sub> for  $\operatorname{Cr}_2 \operatorname{O_7}^{2-}$  ion was calculated to be 0.04 μM via the 3 σ/S formula [33], indicating the highly sensitive determination of  $\text{Cr}_2\text{O}_7^{2^-}$  by the UCNPs@SiO<sub>2</sub> sensor. The proposed UCNPs@SiO<sub>2</sub> sensor towards  $\text{Cr}_2\text{O}_7^{2^-}$  demonstrates the superior LOD and wide linear detection range than those existing fluorescent sensor materials, as shown in Table S1. With the advantages of NIR responsive UCL for negligible autofluorescence and improved signal-to-noise ratio, the UCNPs@SiO<sub>2</sub> upconversion nanosensor holds the promise for sensitive determination of  $\text{Cr}_2\text{O}_7^{2^-}$  for environmental monitoring and food safety.

To investigate the selectivity of the proposed UCNPs@  $SiO_2$  sensor for detecting  $Cr_2O_7^{2-}$ , the UCL response to different anions, including Cl<sup>-</sup>, Br<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, NO<sub>3</sub><sup>-</sup>,  $SO_4^{2-}$ ,  $SCN^-$ ,  $H_2PO_4^{-}$ ,  $HPO_4^{2-}$ ,  $PO_4^{3-}$ , and  $Cr_2O_7^{2-}$ was monitored. Figure 5g and Fig S12a, show the UCL response of the UCNPs@SiO<sub>2</sub> sensor in presence of the above anions in aqueous solution at the fixed 2000  $\mu$ M concentration. Among the above anions, only Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> exhibited considerable quenching effect on UCL intensity of UCNPs@SiO2 with quenching efficiencies of  $\sim$  74%, whereas other anions showed no apparent effect on UCL response of UCNPs@SiO2. This suggests that the UCNPs@SiO<sub>2</sub> system exhibits excellent selectivity towards Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> sensing. Furthermore, the UCNPs@ SiO<sub>2</sub> sensor was subjected to an anti-interference experiment for the detection of  $Cr_2O_7^{2-}$  by introducing  $Cr_2O_7^{2-}$ into the system concurrently with the addition of other individual or mixed anions (2000  $\mu M).$  The UCNPs@ SiO<sub>2</sub> sensor, in the presence of  $Cr_2O_7^{2-}$  (Fig. 5h and Fig. S12b), exhibited no significant difference when compared to the system together containing other individual anions (2000  $\mu$ M). Figure 5i and Fig. S12c, illustrate the similar UCL quenching in intensity for the UCNPs@SiO<sub>2</sub> sensor when  $\operatorname{Cr}_2 \operatorname{O}_7^{2-}$  was added (2000  $\mu$ M), both with and without different mixed anions such as Cl<sup>-</sup>, Br<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>,  $NO_3^-$ ,  $SO_4^{2-}$ ,  $SCN^-$ ,  $H_2PO_4^-$ ,  $HPO_4^{2-}$ , and  $PO_4^{3-}$  at equal concentration (2000 µM). These results indicate that the other anions exhibit negligible effect on the UCL response of UCNPs@SiO<sub>2</sub> to detect Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>. In summary, the excellent sensitivity and high selectivity of the UCNPs@SiO<sub>2</sub> sensor towards  $Cr_2O_7^{2-}$  make them to be potential for detecting ionic pollutants in wastewater.

#### Sensing for anions in real lake and tap water

To explore the applying feasibility of the UCNPs@SiO<sub>2</sub> sensor to determine  $MnO_4^-$  and  $Cr_2O_7^{2-}$  in food and environmental real samples, we conducted spike experiments in two different types of water (lake and tap) obtained from GDUT. Known concentration of  $MnO_4^-$  (1-2000  $\mu$ M) and  $Cr_2O_7^{2-}$  (10-1500  $\mu$ M) was added to UCNPs@SiO<sub>2</sub> and their UCL was measured. The UV UCL peaks (345 and 361 nm) were quenched upon increasing the lake water (Figs. S13a, and S14a) and tap water (Figs. S13b, and S14b) contamination with  $MnO_4^-$ ,

Table 1	Determination	and recovery	of $MnO_4^-$	in lake and	tap
water					

Samples	MnO₄ <sup>−</sup> added	MnO₄ <sup>−</sup> found	MnO₄ <sup>−</sup> recov- ery (%)	RSD (%) n=3
Lake water	1	0.96	96.3	4.5
	5	4.9	97.1	4.8
	20	21.8	109.0	3.8
	100	101.8	101.8	2.8
	500	462.4	92.5	2.4
	1000	1019.5	102.0	3.5
	2000	2161.0	108.0	3.2
Tap water	1	1.1	109.8	4.8
	5	5.5	109.3	4.1
	20	18.3	91.3	0.9
	100	114.4	114.4	1.6
	500	462.1	92.4	3.0
	1000	970.3	97.0	2.0
	2000	2095.8	104.8	2.4

**Table 2** Determination and recovery of  $Cr_2O_7^{2-}$  in lake and tap water

Samples	Cr <sub>2</sub> O <sub>7</sub> <sup>2–</sup> added	Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> found	Cr <sub>2</sub> O <sub>7</sub> <sup>2–</sup> recov- ery (%)	RSD (%)
				n=3
Lake water	10	9.1	91.0	3.3
	50	48.3	96.6	1.6
	100	97.6	97.6	5.1
	500	530.3	106.1	3.7
	1000	979.6	98.0	0.7
	1500	1469.9	98.0	1.1
Tap water	10	10.3	103.1	2.5
	50	51.6	103.3	4.7
	100	98.0	98.0	3.8
	500	539.1	107.8	3.1
	1000	996.4	99.6	1.7
	1500	1515.6	101.0	0.9

and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, respectively. The reliability of UCNPs@ SiO<sub>2</sub> as MnO<sub>4</sub><sup>-</sup> and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> anion sensor and its practical application was explored via a technique of standard addition and recovery test. Table 1 presents that the recovery rates of  $MnO_4^-$  are 92.5–109.0% and 91.3– 114.4% for lake and tap water, respectively. Table 2 displays that the recovery rates of  $Cr_2O_7^{2-}$  are 91.0–106.1% and 98.0–107.8% for lake and tap water, respectively. The relative standard deviations (RSD) for all real sample measurements are below 5.1%, indicating that the reproducibility of the UCNPs@SiO<sub>2</sub> in real sample analysis is robust and reliable. Thus, the proposed UCNPs@SiO<sub>2</sub> nanosensor shows impressive performance considering both the practical and reliable sensing aspects and holds promise for the on-site determination of MnO<sub>4</sub><sup>-</sup> and  $\operatorname{Cr_2O_7^{2-}}$  anions in real samples.



**Fig. 6** (a) UV-Vis absorption spectra of different anions,  $MnO_4^-$  (~1 mM),  $Cr_2O_7^{2-}(\sim 0.5 \text{ mM})$ , others are 0.1 ~ 3.33 mM; (b) UV-Vis absorption spectra of the UCNPs@SiO<sub>2</sub> (1.0 mg/mL), UCNPs@SiO<sub>2</sub> with  $MnO_4^-$  (0.5 mM) and UCNPs@SiO<sub>2</sub> with  $Cr_2O_7^{2-}$  (0.5 mM), contrasted with UCL spectrum of UCNPs@SiO<sub>2</sub> (1.0 mg/mL) at 980 nm laser excitation in aqueous solution; (c) The UCL lifetime decay of UCNPs@SiO<sub>2</sub> with and without  $MnO_4^-$  addition

## Mechanism of $MnO_4^-$ and $Cr_2O_7^{2-}$ sensing

In general, the Förster resonance energy transfer (FRET) refers to a non-radiative phenomenon occurring on the basis of overlap between donor emission and the acceptor absorption, relative orientation of donor-acceptor dipoles, and the donor-acceptor distance  $\sim 1-10$  nm [59, 60]. On the other hand, the inner filter effect (IFE) is known as a radiative energy transfer process, requiring that the excitation/emission of the donor overlapped with the acceptor absorption [61]. The FRET process will affect the excited-state dynamics of the energy donor, decreasing its luminescence decay lifetime, which differentiates FRET from IFE process. UV-Vis absorption spectra were recorded for various anions and UCNPs@SiO2 before and after addition of  $MnO_4^{-}$  and  $Cr_2O_7^{2-}$ .  $MnO_4^{-}$ exhibits two prominent absorption peaks in the UV-Vis region, specifically peaking at 311 and 525 nm (Fig. 6a), which could be ascribed to  $O \rightarrow Mn$  charge transfer [62].  $Cr_2O_7^{2-}$  anion has distinct absorption observed at 355 nm (Fig. 6a), in line with the reported optical characteristics of Cr (VI) [63]. The UV absorption at 290 nm for  $Cr_2O_7^{2-}$  is attributed to the O  $\rightarrow$  Cr charge transfer [64]. As shown in Fig. 6b, the UCNPs@SiO<sub>2</sub> display negligible absorption, whereas the MnO<sub>4</sub><sup>-</sup> added UCNPs@ SiO<sub>2</sub> (UCNPs@SiO<sub>2</sub>@MnO<sub>4</sub><sup>-</sup>) and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> added one (denoted as UCNPs@SiO2@Cr2O22-) exhibit characteristic absorption peaks for MnO<sub>4</sub><sup>-</sup> and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, respectively. The UCL of UCNPs@SiO2 at 345 and 361 nm shows significant overlap with 355 nm  $\mathrm{Cr_2O_7^{2-}}$  absorption. On the other hand, the UCL of UCNPs@SiO<sub>2</sub> at 345, 361, 450, and 477 nm shows complete overlap with the 311 and 525 nm absorption bands of  $MnO_4^{-}$ .

To further understand the energy transfer processes, under 980 nm laser excitation, the UCL lifetime decay for Tm<sup>3+</sup> at 450 nm was assessed, both in the presence and absence of  $MnO_4^-$  (Fig. 6c). Considering the lifetime decay as non-monoexponential, the average decay lifetime of the UCNPs@SiO<sub>2</sub> sensor was calculated via the following Eq. [65, 66],

$$\tau_{\text{avg}} = \frac{\int_{0}^{\infty} tI(t) \,\mathrm{d}t}{\int_{0}^{\infty} I(t) \,\mathrm{d}t}$$

where I(t) is the UCL intensity at given time t after ceasing the excitation. For UCNPs@SiO2 sensor, the average lifetime ( $\tau_{avg}$ , ms) of 450 nm Tm<sup>3+</sup> UCL is found to be 0.178 ms. Upon  $MnO_4^-$  addition, a  ${}^1D_2$  UCL of the  ${
m Tm}^{3+}$  decayed faster with decreasing  $au_{
m avg}$  by 0.104 ms for UCNPs@SiO<sub>2</sub> with MnO<sub>4</sub><sup>-</sup> (50  $\mu$ M) and by 0.065 ms for UCNPs@SiO<sub>2</sub> with  $MnO_4^-$  (2000 µM). This drastic change in UCL lifetime experimentally indicates that the non-radiative FRET from UCNPs@SiO2 to MnO4took place [32, 60], which agrees with the nonlinear trend in the Stern-Volmer plot and confirms the occurrence of combined static and dynamic UCL quenching. To calculate the FRET efficiency (E) following equation [60],  $E = 1 - \frac{\tau_{\rm DA}}{\tau_{\rm D}}$ , is used, where  $\tau_{\rm DA}$  and  $\tau_{\rm D}$  are the UCNPs@SiO<sub>2</sub> (donor) lifetime with and without MnO<sub>4</sub><sup>-</sup> acceptor, respectively. The extent of efficient FRET for the UCNPs@SiO<sub>2</sub> sensor is determined to be 42% and 63% for  $MnO_4^-$  concentration of 50 and 2000  $\mu$ M, respectively. The enhancement in the FRET efficiency of the sensor with the increase in  $MnO_4^-$  content is in line with the two different linear 0.6-80 and 80-2000 µM concentration ranges for MnO<sub>4</sub><sup>-</sup> sensing, as demonstrated in Fig. 4d and e. Furthermore, the TEM results showing the diameter of core-shell NaYF<sub>4</sub>:Eu@NaYbF<sub>4</sub>:Gd/Tm nanoparticles of 27.0 nm (Fig. S1b and e) and NaYF<sub>4</sub>:Eu@  $NaYbF_4:Gd/Tm@NaYbF_4@NaLuF_4$ UCNPs@SiO<sub>2</sub> of 44.6 nm (Fig. 3a and Fig. S4), indicates the least FRET distance from Tm<sup>3+</sup> in the inner NaYbF<sub>4</sub>:Gd/Tm shell to  $MnO_4^-$  at ~ 8.8 nm, which further support the FRET process from UCNPs@SiO<sub>2</sub> to the analyte quencher (Tm<sup>3+</sup> 345, 361, 450, 477 nm UCL quenched by  $MnO_4^-$ ,  $Tm^{3+}$ 345, 361 nm UCL quenched by  $Cr_2O_7^{2-}$ ). On the other hand, the IFE process occurs with luminescence lifetime remaining unchanged by introduction of energy acceptor [67], thus IFE should also be possible for the operational energy transfer mechanism for UCNPs@SiO<sub>2</sub> sensor detecting anions (MnO<sub>4</sub><sup>-</sup> and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>). Taken all together, it is plausible that the UCNPs@SiO<sub>2</sub> upconversion nanosensor could involve both FRET and IFE mechanisms to detect MnO<sub>4</sub><sup>-</sup> and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> anions.

## Conclusions

The autofluorescence free UCNPs@SiO2 UCL nanosensor was successfully developed for label-free and fast determination of  $MnO_4^-$  and  $Cr_2O_7^{2-}$  anions. The surface SiO<sub>2</sub> modification enables UCNPs with good water solubility and biocompatibility. The highly efficient and multicolour UCL of UCNPs@SiO2 was effectively quenched by  $MnO_4^-$  and  $Cr_2O_7^{2-}$  anions with fast response time of 2 and 1 min, respectively. The UCNPs@SiO<sub>2</sub> nanosensor exhibits linear detection ranges of [0.6-80 µM and  $80-2000 \ \mu\text{M}$ ], [2-500  $\mu\text{M}$  and 500-2000  $\mu\text{M}$ ] with the LOD at 0.15  $\mu$ M and 0.04  $\mu$ M for MnO<sub>4</sub><sup>-</sup> and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> anions, respectively. The UCNPs@SiO<sub>2</sub> nanosensor with good sensing capability, demonstrated satisfactory recognition and determination of  $MnO_4^-$  and  $Cr_2O_7^{2-}$  in real lake and tap water samples. UCL lifetime decay analysis reveals the energy transfer from UCNPs@SiO<sub>2</sub> to anions through the combination of FRET and plausible IFE processes. The proposed UCNPs@SiO2 UCL nanosensor offers autofluorescence free and rapid determination of  $MnO_4^-$  and  $Cr_2O_7^{2-}$  anions with high sensitivity, good specificity, low LOD, and wide linear detection range, holding great promising for reliable environmental monitoring and food sample detection applications.

#### **Supplementary Information**

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Supplementary Material 1

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#### Author contributions

KX contributed to the preparation, characterization, sensing performance of the work, and generation of the figures. HW accomplished the conception or design of the work. WS and WC performed UCL and UCL lifetime assay. ARA, QZ, and STM contributed to participation of experiment design. Drafting the article was prepared by HW, MM and DAH. HW did the critical revision of the article and final approval of the version to be published. All authors read and approved the final manuscript.

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#### Data availability

The datasets supporting the conclusions of this article are included within the article and its additional file.

#### Declarations

**Ethics approval and consent to participate** Not applicable.

#### **Consent for publication**

Not Applicable.

#### **Competing interests**

The authors declare no competing interests.

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