

## Article

# UIO-66/Ag/TiO<sub>2</sub> Nanocomposites as Highly Active SERS Substrates for Quantitative Detection of Hexavalent Chromium

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**Abstract:** Sensitive determination of Cr(VI) is of great importance as this is one of the most toxic heavy metal ions in the environment. In this work, a metal–organic framework (MOF) material, UIO-66 (University of Oslo, UIO), was introduced for the first time to develop a composite substrate, UIO-66/Ag/TiO<sub>2</sub>, for the sensitive SERS detection of Cr(VI) in water. The composition, morphology, crystal structure and optical property of the UIO-66/Ag/TiO<sub>2</sub> were characterized by SEM, XRD, EDX, UV-Vis and Raman spectroscopy. The control experiment revealed the introduction of UIO-66 and TiO<sub>2</sub> can improve the adsorption to Cr ions and thus greatly enhance the SERS signal of Cr(VI) on this composite substrate. The SERS signal can also be tuned by changing the dosage of TiO<sub>2</sub>. Under optimized conditions, UIO-66/Ag/TiO<sub>2</sub> was used to detect Cr(VI) in water with different concentrations, which showed high sensitivity and good stability. The SERS signals showed a linear increase as the concentration of Cr(VI) increases from  $5 \times 10^{-9}$  M to  $5 \times 10^{-6}$  M. The detection limit was 5 nM, which was lower than the safe drinking water standard of the US Environmental Protection Agency (1  $\mu$ M). Detection of Cr(VI) in the range of  $1 \times 10^{-7}$  M to  $5 \times 10^{-6}$  M in real lake water was also achieved. These results demonstrate the great potential of UIO-66/Ag/TiO<sub>2</sub> composites as SERS substrates for the trace determination of Cr(VI) in the environmental field.

**Keywords:** surface enhanced Raman scattering; metal–organic framework; composite material; enhancement substrate; Cr(VI); environment analysis; chemical sensor



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## 1. Introduction

Over the past few decades, hexavalent chromium Cr(VI) has been widely used in industries such as electroplating [1], pigment [2], printing [3], tanning [4], wood preservation [5] and steel production [6], resulting in its growth in the environment at an alarming level. According to a previous report [7], heavy metal ions are highly toxic environmental pollutants, among which Cr(VI) has been reported as a carcinogen and is one of the relatively common heavy metal ions in the environment. Due to its solubility in water and high oxidation potential, after Cr(VI) enters the body, Cr(VI) can penetrate biofilms and cause a variety of chronic and acute diseases ranging from dermatitis and edema to lung and kidney cancer [8]. As a result, the World Health Organization (WHO) has set the maximum limit for Cr(VI) contamination in groundwater at 0.17  $\mu$ M, and the Environmental Protection Agency (EPA) has set the standard for total chromium at 1  $\mu$ M [9] to promote the public health benefits of chromium in drinking water.

Detection of Cr can be achieved by traditional methods such as inductively coupled plasma mass spectrometry (ICP-MS) and atomic absorption spectrometry (AAS) [10–15]. These methods require large experiments, complex operations and time-consuming measurements, although they display high sensitivity and accuracy. Therefore, there is still an urgent need to develop an efficient and rapid method for detecting Cr(VI) in water.

Surface-enhanced Raman scattering (SERS) technology has the advantages of high sensitivity, fast detection speed, non-destructive detection and no sample pretreatment [16], and it is often used to identify harmful substances including organic dyes, pesticides and

heavy metal ions [17–19]. SERS detection of Cr can be divided into the indirect approach and the direct approach [20–24]. For the indirect approach, the SERS signal of report molecules instead of the signal from Cr(VI) is recorded. As the reporter's signal intensity is changed in the presence of Cr(VI), indirect detection of Cr(VI) is achieved [20,21]. The indirect approach often displays high sensitivity, but the ingenious design of the report molecule and surface modifier makes the preparation of the SERS probe complex. For direct detection, the SERS signal of Cr(VI) from symmetric and asymmetric stretching vibrations of the Cr-O bond was recorded for detection of Cr(VI). Compared to the indirect approach, direct detection is simple as no report molecule is needed. In addition, direct detection may be more accurate due to the fingerprint characteristics of SERS spectra from Cr(VI) itself. However, the sensitivity of this approach is poor on bare noble metal SERS substrates due to the poor affinity of Cr(VI) to noble metal surfaces. Fortunately, by rational combination with other functional materials, high adsorption to heavy metal and thus good sensing sensitivity can also be achieved. For example, Wang's research group prepared a  $\text{Fe}_3\text{O}_4@m\text{-ZrO}_2@\text{Ag}$  nanostructure [22]. Porous  $\text{ZrO}_2$  was not only conducive to the load of AgNPs, but also conducive to the adsorption of Cr(VI) due to the abundant hydroxyl groups on its surface, thus improving the SERS detection ability for Cr(VI). Wang et al. proposed a rapid quantitative Cr(VI) method based on  $\text{Mg}(\text{NO}_3)_2$ -induced polymerization of AgNPs [23], whose SERS signal was attributed to the Cr-O bond. Therefore, the SERS technique integrated with new functional materials, especially those with high affinity or adsorption to Cr(VI), is a promising way for sensitive detection of Cr(VI) in the environment.

Recently, metal-organic frameworks (MOFs) and metal oxides have shown great promise for the adsorption or sensing of Cr(VI) and other pollutants [24,25]. The large surface area, adjustable pore size and attractive chemical diversity of MOFs endow them with high affinity and adsorption to Cr(VI). For example, a  $\text{Fe}^{2+}$ -involved MOF+ technique was developed for Cr removal, showing an extraordinary adsorption capacity of 796 Cr mg/g [26]. A  $\text{Zr}^{4+}$ -MOF was synthesized for Cr removal and luminescence sensing. The porous structure and Zr-bonded hydroxides in the framework endow it with a high capture ability for Cr(VI) (149 mg/g) [27]. Interestingly, such high adsorption of MOFs to Cr(VI) has not been used for SERS detection of Cr(VI). Besides MOFs, metal oxides such as  $\text{TiO}_2$  and  $\text{ZrO}_2$  also show a high affinity to Cr(VI). The strong coordinating interaction between  $\text{ZrO}_2$  and  $\text{CrO}_4^{2-}$  or  $\text{Cr}_2\text{O}_7^{2-}$  has been used to improve the SERS signal of Cr(VI) on  $\text{ZrO}_2$ -based composite substrates [9,22]. An indirect approach for SERS detection of Cr(VI) was developed [28], where the interaction between Cr(VI) and Ti(IV) atoms with unfilled valence orbitals at the  $\text{TiO}_2$  surface endows the method a good selectivity.  $\text{TiO}_2$  combined with Au was also used to improve the SERS signal of Cr(VI) [29]. The hydroxyl group on the  $\text{TiO}_2$  is believed to play a major role in enhancing affinity to Cr(VI). Based on these reports, it is expected that a rational combination of a traditional Au- or Ag-based SERS substrate with an MOF and metal oxide may greatly improve the SERS sensing performance, which is seldom reported.

In this study, we developed a new MOF-based SERS substrate composed of  $\text{UIO-66/Ag/TiO}_2$ , which was the first time that MOF material was applied to the SERS detection of Cr(VI).  $\text{UIO-66}$ , with a large surface area and high adsorption to Cr(VI), was used as support. AgNPs with high electromagnetic enhancement ability for SERS signaling were loaded onto  $\text{UIO-66}$  to form  $\text{UIO-66/Ag}$ . Finally,  $\text{TiO}_2$  colloids were assembled onto  $\text{UIO-66/Ag}$  to form  $\text{UIO-66/Ag/TiO}_2$ . Due to the synergy of these components, the composite substrate  $\text{UIO-66/Ag/TiO}_2$  shows significant adsorption to Cr(VI), and consequently, highly sensitive SERS detection of Cr(VI) was achieved. Such a composite substrate was successfully used for quantitative and trace detection of Cr(VI) in aqueous solutions and actual samples, which shows great promise for environment analysis.

## 2. Materials and Methods

### 2.1. Chemicals and Materials

Zirconium chloride ( $\text{ZrCl}_4$ , AR), 1,4-dicarboxybenzene (BDC, AR), polyvinylpyrrolidone (PVP K30), silver nitrate ( $\text{AgNO}_3$ , AR), sodium chloride ( $\text{NaCl}$ , AR), sodium nitrate ( $\text{NaNO}_3$ , AR), sodium carbonate ( $\text{Na}_2\text{CO}_3$ , AR), sodium sulfate anhydrous ( $\text{Na}_2\text{SO}_4$ , AR), potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ , AR), N, N-dimethylformamide (DMF), methanol, acetic acid and tetrabutyl titanate (TBT, 98%) were purchased from Aladdin chemical reagent company (Shanghai, China). Deionized water purified by a Millipore system was used as a solvent throughout the experiment.

### 2.2. Apparatus and Measurements

The material microstructure was imaged using a scanning electron microscope (SEM, S-3400, Hitachi, Tokyo, Japan); the absorption capacity of the material for Cr(VI) was assessed with an ultraviolet–visible spectrometer (UV-3900, Hitachi, Tokyo, Japan). The SERS signal was recorded with a 633 nm He-Ne laser (LABRAM-HR, Horiba, Palaiseau, France), the structure of the material was measured with an X-ray diffractometer (XRD, MINIFLEX 600, Rigaku, Akishima, Japan) and the composition of the material was characterized by X-ray photoelectron spectrometry (XPS, Escalab, Shimadzu, Kyoto, Japan).

### 2.3. Preparation of UIO-66/Ag

UIO-66/Ag was made according to a published report [30]. Briefly, 104.9 mg of zirconium(IV) chloride, 81.5 mg of terephthalic acid and 12 mL of acetic acid were added to 100 mL of dimethylformamide (DMF) solution. The mixed solution was transferred to an autoclave and heated in an oven at 120 °C for 24 h. The reaction product was centrifuged at  $10,000 \times g$  rpm for 5 min and washed with a methanol–DMF mixture. The precipitate was then dried in a vacuum oven to obtain a white UIO-66 powder. Then, 20 mg of UIO-66 and 40 mg of silver nitrate were dispersed in 20 mL of DMF. The mixture solution was then transferred to an autoclave and reacted at 160 °C for 3 h. The cooled solution was centrifuged at  $10,000 \times g$  rpm for 5 min and washed three times with methanolic DMF solution. The obtained material was then dried in an oven.

### 2.4. Preparation of $\text{TiO}_2$

First, 12.5 mL of a solution of tetrabutyl titanate (98%) was added to 4 mL of isopropanol. The mixture was shaken until a homogeneous solution appeared. Then, the mixture was added dropwise to a solution containing 150 mL of deionized water and 2 mL of  $\text{HNO}_3$  under vigorous stirring at 70–80 °C until a clear colloid was obtained [29].

### 2.5. Preparation of UIO-66/Ag/ $\text{TiO}_2$

Twenty milligrams of UIO-66/Ag powder was ultrasonically dispersed in 5 mL of 200 mg of PVP methanol solution and stirred at room temperature for 12 h. The solution at the end of the reaction was centrifuged at  $10,000 \times g$  rpm for 5 min and washed three times with methanol solution. Then the obtained material was dried in an oven. After centrifugal drying, 10 mg of sample was taken with 10 mL of  $\text{TiO}_2$  colloid and stirred for 12 h. The final sample was obtained by centrifugal drying.

### 2.6. Raman Spectroscopic Analysis

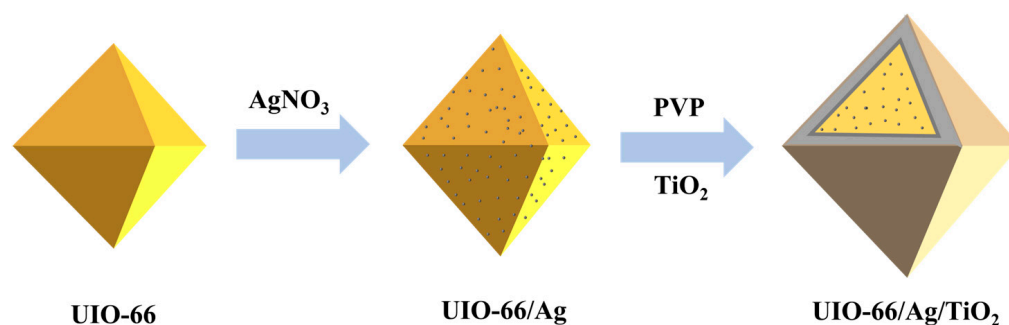
Potassium dichromate solutions were used for SERS sensitivity assessment. Potassium dichromate solutions with different concentrations from  $5 \times 10^{-6}$  to  $5 \times 10^{-9}$  M were tested. Confocal Raman spectroscopy was used for all SERS experiments. A  $50\times$  objective lens was used, and the laser excitation wavelength was 633 nm. The laser power was  $\sim 0.2$  mW. The integration time was 10 s. First, 1 mg of UIO-66/Ag/ $\text{TiO}_2$  was ultrasonically dispersed in 1 mL of deionized water. Then, 200  $\mu\text{L}$  of the UIO-66/Ag/ $\text{TiO}_2$  suspension was added to 1 mL of different concentrations of Cr(VI) aqueous solution, and the mixed solution was shaken at room temperature for 1 h to ensure complete adsorption. Then, the

mixed solutions were centrifuged at  $5000\times g$  rpm for 10 min and washed several times with ultrapure water. Finally, the precipitate was dispersed in 0.5 mL of ultrapure water for SERS analysis.

### 3. Results

#### 3.1. Fabrication and Characterization of UIO-66/Ag/TiO<sub>2</sub> Nanocomposites

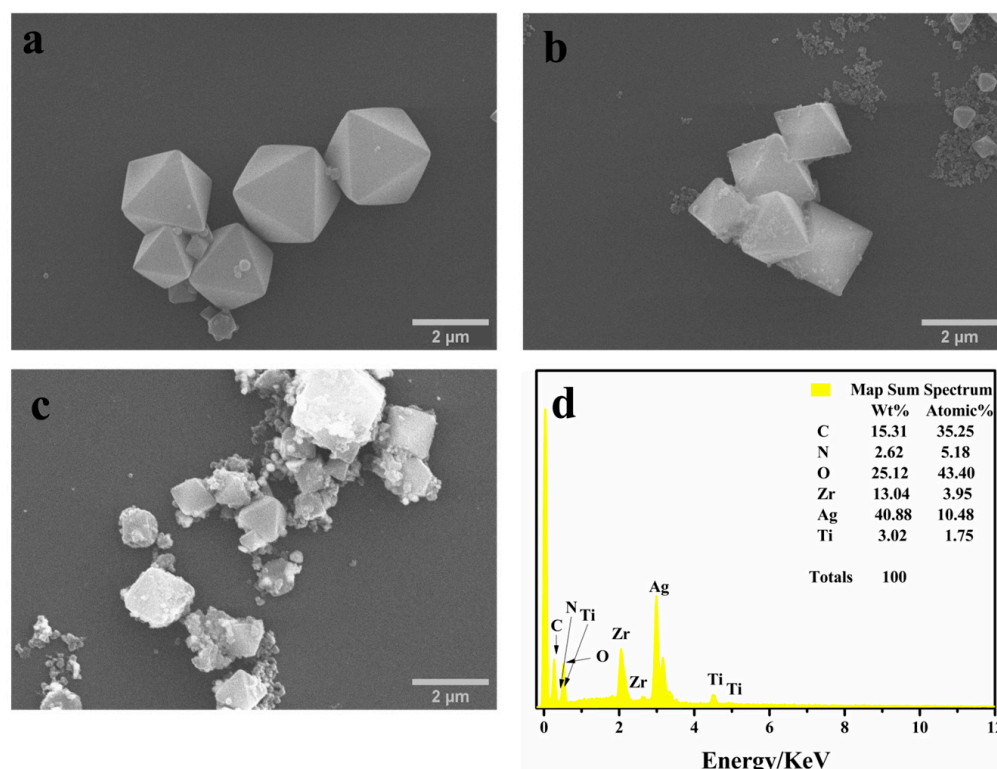
The formation of UIO-66/Ag/TiO<sub>2</sub> nanocomposites involved several steps. As shown in Scheme 1, UIO-66 nanoparticles (average size in the range of 1.5–2.5  $\mu\text{m}$ ) were synthesized by the solvothermal method, and it could be seen that the synthesized UIO-66 surface was well crystallized. Then, UIO-66/Ag composite nanoparticles were synthesized by the solvothermal method; a layer of AgNPs loaded on the surface of UIO-66 can be clearly seen in Figure 1a–c. AgNPs were prepared by reducing silver nitrate with DMF as the reducing agent to avoid damage to the UIO-66 framework. Compared with the AgNPs synthesized alone, the agglomeration of AgNPs loaded on UIO-66 was significantly reduced, which may be related to the porous structure of UIO-66 and the large specific surface area for adsorption of AgNPs. The AgNPs were embedded in the pores of UIO-66, which reduced the mobility of AgNPs and allowed the AgNPs to be uniformly dispersed on the surface of UIO-66. Finally, TiO<sub>2</sub> colloids were self-assembled onto UIO-66/Ag to form the final product UIO-66/Ag/TiO<sub>2</sub>. As can be seen in Figure 1d, the presence of both Ti and Ag elements shows the successful synthesis of UIO-66/Ag/TiO<sub>2</sub>. Moreover, a large amount of Ag elements can be seen according to the elemental content in Figure 1d, which proves that a large amount of AgNPs are loaded on the MOF surface to form a stable and uniform hot spot.



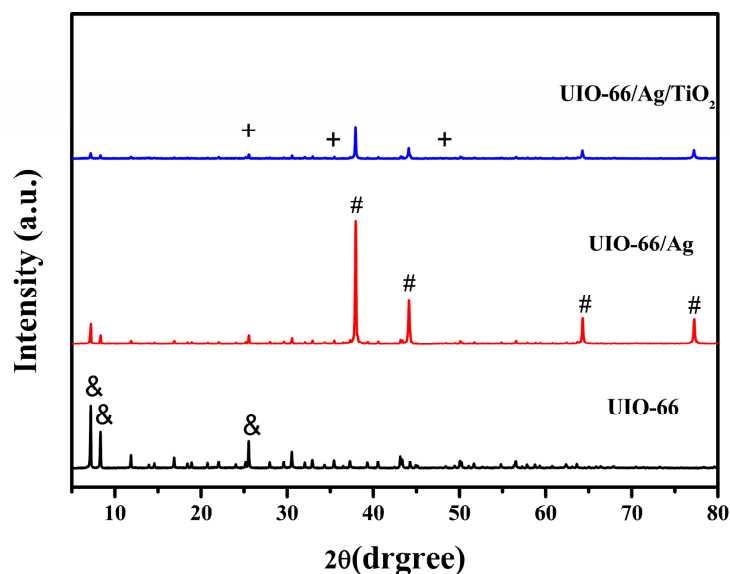
**Scheme 1.** Schematic illustration of the fabrication process of UIO-66/Ag/TiO<sub>2</sub>.

In Figure 2, the characteristic XRD peaks of UIO-66 (black line) are located at  $7.3^\circ$  and  $8.4^\circ$ ; these peaks are consistent with those reported in the literature [31]. For UIO-66/Ag, new peaks at  $38.20^\circ$ ,  $44.40^\circ$ ,  $64.60^\circ$  and  $77.40^\circ$  attributed to the (111), (200), (220) and (311) crystal silver planes appear [30]. In addition, all diffraction peaks are very sharp, which indicates that the UIO-66/AgNPs composites have high crystallinity. For the final composite, characteristic peaks at  $25.3^\circ$ ,  $37.8^\circ$  and  $48^\circ$  corresponding to (101), (004) and (200) crystal planes of TiO<sub>2</sub> can be observed [32], implying the successful formation of UIO-66/Ag/TiO<sub>2</sub>.

Figure 3 shows the main elements of the material, namely C, O, Zr, Ag and Ti. The C1s spectrum is divided into three peaks of 284.4, 285.8 and 288.2 eV, which are attributed to C-C, C-O and C=C groups on UIO-66 [33]. The O1s spectrum is divided into two peaks of 529.6 and 531.4 eV, which are attributed to Ti-O in TiO<sub>2</sub> and C-O/C=O groups [34]. Zr3d was divided into two peaks of 182.1 and 184.5 eV, which were attributed to Zr3d<sub>5/2</sub> and Zr3d<sub>3/2</sub> of the Zr in UIO-66 [35]. Ag3d was divided into two peaks of 368.0 and 374.1 eV, with a difference of about 6 eV between the two peaks, confirming that AgNPs are present in the zero valence state and further confirming the loading of AgNPs on UIO-66 [36]. Ti2p was divided into two peaks: Ti2p<sub>3/2</sub> and Ti2p<sub>1/2</sub> at 458.4 and 464.1 eV [37]. The successful synthesis of UIO-66/Ag/TiO<sub>2</sub> was confirmed by the above SEM, EDX, XRD and XPS results.



**Figure 1.** SEM images of (a) UIO-66, (b) UIO-66/Ag and (c) UIO-66/Ag/TiO<sub>2</sub>; (d) EDX images of UIO-66/Ag/TiO<sub>2</sub>.



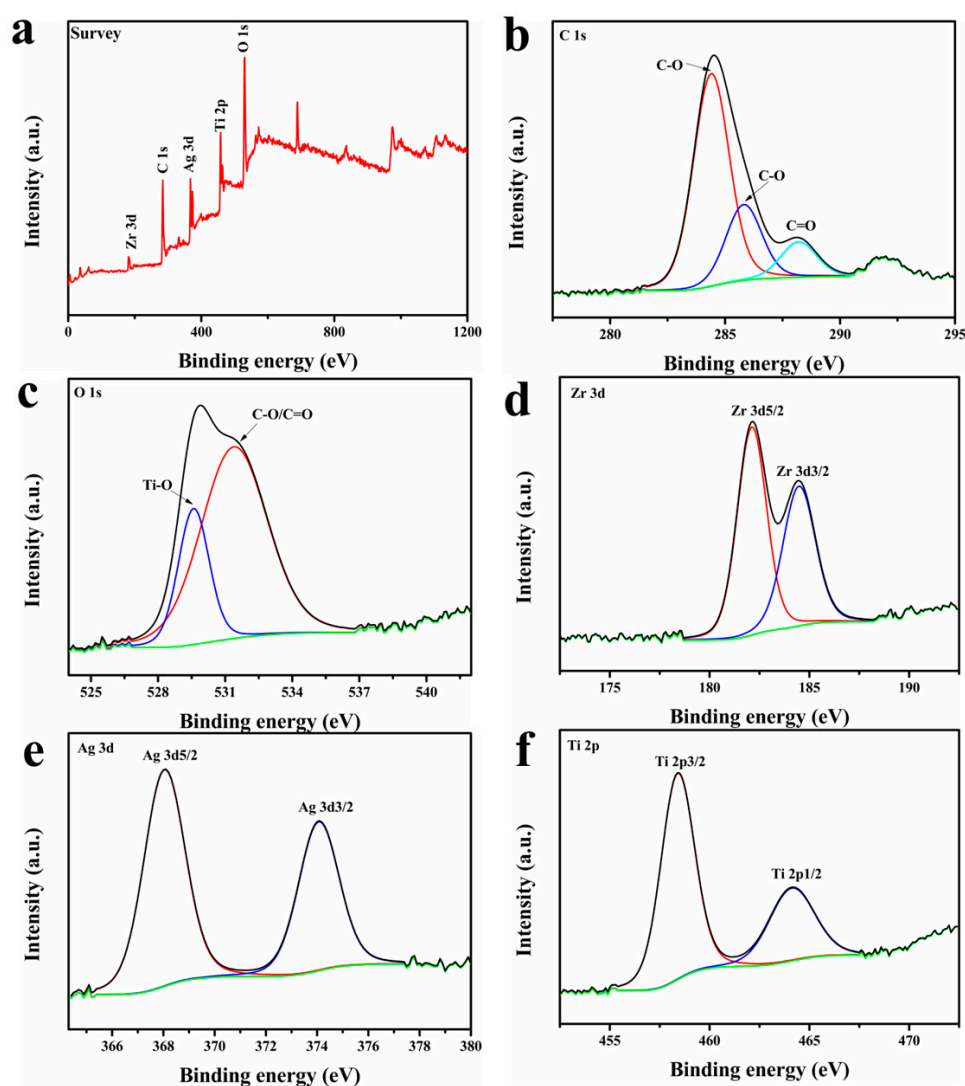
**Figure 2.** XRD pattern of different materials. Note that peaks marked with symbols "&", "#" and "+" represent the peaks from UIO-66, AgNPs and TiO<sub>2</sub>, respectively.

### 3.2. SERS Performance

According to the electromagnetic mechanism (EM) and chemical mechanism (CM) of SERS, a strong SERS signal will be produced when probe molecules are directly adsorbed on or very close to the surface of the enhancement substrate. So, enhancing the adsorption of the substrate to target molecules is important for a strong SERS signal. Here, an MOF and TiO<sub>2</sub> were both used to enhance the adsorption to Cr(VI). As Figure 4 shows, pristine potassium dichromate solution displays an absorption peak at 352 nm [38]. After incuba-



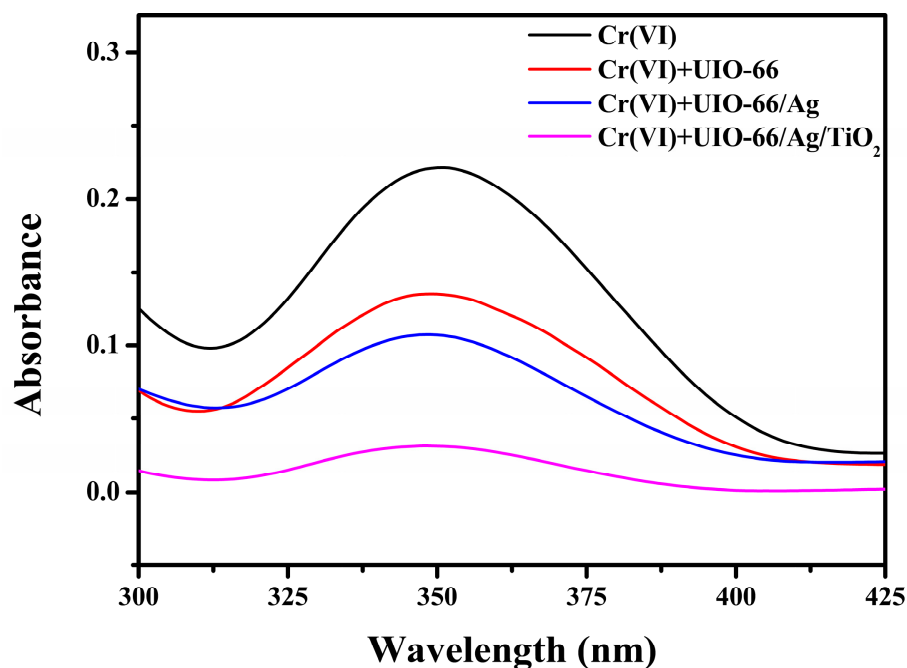
tion with UIO-66, the UV absorption peak of Cr(VI) decreases significantly (red curve), confirming that MOF materials with large specific surface area have strong adsorption capacity. The UV absorption peak of Cr(VI) further decreases slightly when UIO-66/Ag is used for incubation with the Cr(VI) solution (blue curve). This result confirms that bare noble metal only displays a low affinity to Cr(VI). The UV absorption peak of Cr(VI) further significantly decreases when UIO-66/Ag/TiO<sub>2</sub> is used for incubation with Cr(VI), indicating TiO<sub>2</sub> can obviously improve the ability of adsorption to Cr(VI). The enhanced adsorption can be ascribed to the plentiful hydroxyl groups of TiO<sub>2</sub> colloids, as detailed in previous reports [28,29]. The results in Figure 4 indicate bare silver nanoparticles show poor adsorption to Cr(VI), while introducing an MOF and TiO<sub>2</sub> can significantly improve the adsorption to Cr(VI) owing to the large specific area of the MOF and abundant hydroxyl groups of TiO<sub>2</sub> for Cr(VI) binding. The high adsorption observed on UIO-66/Ag/TiO<sub>2</sub> is beneficial for obtaining a strong SERS signal for sensitive detection of Cr(VI).



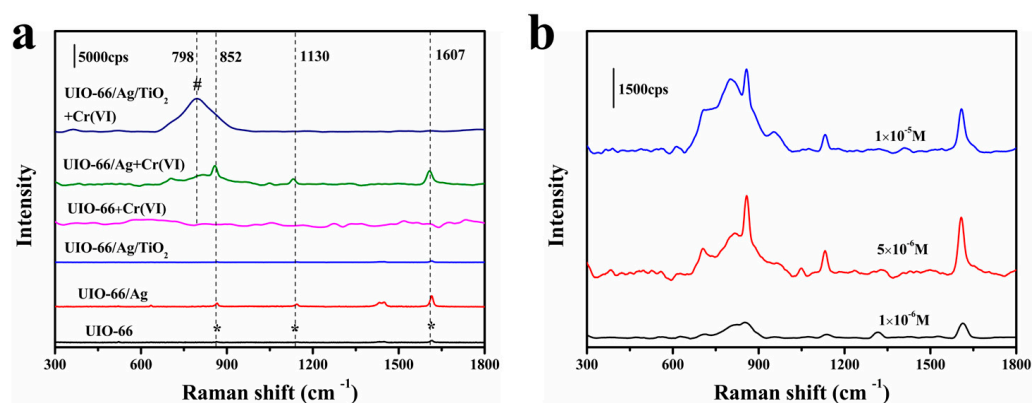
**Figure 3.** High-resolution XPS spectra of (a) the survey scan, (b) C 1s, (c) O 1s, (d) Zr 3d, (e) Ag 3d and (f) Ti 2p from UIO-66/Ag/TiO<sub>2</sub>.

Here, we compare the original Raman signals of the above materials and their direct SERS response in the presence of Cr(VI). Figure 5 shows the original Raman characteristic peaks of UIO-66 (black curve), UIO-66/Ag (red curve) and UIO-66/Ag/TiO<sub>2</sub> (blue curve). The peaks at 852 cm<sup>−1</sup>, 1130 cm<sup>−1</sup> and 1607 cm<sup>−1</sup> are ascribed to the out-of-plane bending vibration of C-H on the aniline ring, C-C-C bending vibration and C=C stretching of the

aromatic ring from UIO-66. The Raman signal of UIO-66 was enhanced on UIO-66/Ag owing to the electromagnetic enhancement of Ag. The signal of UIO was slightly reduced on UIO-66/Ag/TiO<sub>2</sub>. This is helpful for improving the signal-to-noise ratio, although the detailed mechanism for the reduced signal of UIO is not clear at present. In the presence of Cr(VI), the characteristic peak signal of Cr(VI) was not observed on the substrate UIO-66, indicating UIO-66 was not a SERS-active substrate. For UIO-66/Ag and UIO-66/Ag/TiO<sub>2</sub>, the characteristic peak of Cr(VI) at 798 cm<sup>-1</sup> can be clearly observed. This peak comes from the stretching vibration of the Cr-O bond. For UIO-66/Ag substrate, a broad shoulder peak was observed at about 798 cm<sup>-1</sup> in addition to the enhanced signal from UIO-66 at 852 cm<sup>-1</sup>, 1130 cm<sup>-1</sup> and 1607 cm<sup>-1</sup> [39]. The signal from UIO-66 produces a large background, which makes it difficult to distinguish the signal of Cr(VI). This may lead to a low signal-to-noise ratio and is not good for trace analysis of Cr(VI). Nevertheless, as shown in Figure 5b, it can still be seen that the SERS signal intensity of the Cr-O bond of UIO-66/Ag at a Raman shift of 798 cm<sup>-1</sup> decreases as the concentration of Cr(VI) decreases. Compared with UIO-66/Ag, the SERS signal of Cr(VI) is stronger on UIO-66/Ag/TiO<sub>2</sub>, and the spectrum is clearer as no other peaks from materials are observed due to the coverage of TiO<sub>2</sub>. Thus, UIO-66/Ag/TiO<sub>2</sub> displays a higher signal-to-noise ratio for Cr(VI) sensing. Based on the above comparison of the adsorption performance and SERS performance of UIO-66, UIO-66/Ag and UIO-66/Ag/TiO<sub>2</sub>, it can be seen that the UIO-66/Ag/TiO<sub>2</sub> substrate is the best SERS substrate among them for the detection of Cr(VI). The high SERS performance of the UIO-66/Ag/TiO<sub>2</sub> can be ascribed to the synergy among different components. The plentiful pores of UIO bring high adsorption to Cr, while its large surface area provides more sites for anchoring highly SERS-active AgNPs. The uniform and dense AgNPs bring great SERS enhancement due to their extraordinary electromagnetic enhancement ability. Finally, the addition of TiO<sub>2</sub> not only improves the adsorption to Cr(VI), but also reduces the background signal, which leads to greatly enhanced performance. These results further confirm that a rational combination of Au or Ag with functional materials is beneficial for improving SERS sensing performance.

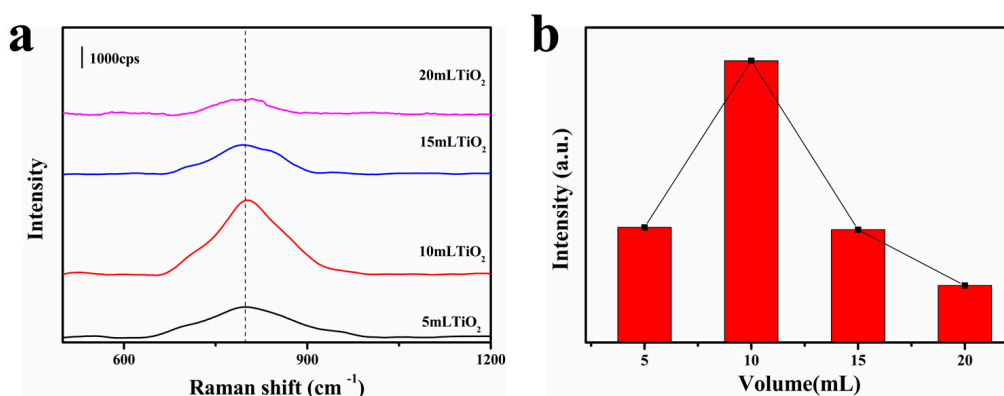


**Figure 4.** UV-vis spectra of Cr(VI) aqueous solution ( $10^{-6}$  M), after being incubated with UIO-66, UIO-66/Ag and UIO-66/Ag/TiO<sub>2</sub>.



**Figure 5.** (a) Raman spectra of UIO-66, UIO-66/Ag and UIO-66/Ag/TiO<sub>2</sub> and their SERS response in presence of Cr(VI); \* represents the Raman peak of UIO-66 and # represents the Raman peak of Cr(VI). (b) SERS spectra of different concentrations ( $1 \times 10^{-5}$ – $1 \times 10^{-6}$  M) of Cr(VI) on the UIO-66/Ag.

As TiO<sub>2</sub> is important in enhancing adsorption and improving the signal-to-noise ratio, the effect of different volumes of TiO<sub>2</sub> on the SERS response of UIO-66/Ag/TiO<sub>2</sub> was studied. Figure 6 shows that the SERS signal of Cr(VI) on UIO-66/Ag/TiO<sub>2</sub> increases as the TiO<sub>2</sub> suspension volume changes from 5 to 10 mL and then decreases when more TiO<sub>2</sub> is used for integration with UIO-66/Ag. So, 10 mL of TiO<sub>2</sub> colloids combined with UIO-66/Ag had the strongest SERS signal for Cr(VI). This is reasonable as the addition of TiO<sub>2</sub> may introduce two effects: enhancing adsorption to Cr(VI) and increasing the distance between AgNPs and surface-adsorbed Cr(VI). When the dosage of TiO<sub>2</sub> exceeded 10 mL, the TiO<sub>2</sub> film resulted in an increased distance of adsorbed Cr(VI) to the AgNPs, which significantly reduced the LSPR effect of AgNPs and thus reduced the SERS signal. UIO-66/Ag/TiO<sub>2</sub> is similar to the core-shell structure of a noble metal-MOF due to the adjustment of the thickness of the outer shell layer and thus the SERS intensity. This also proves, on the other hand, that the addition of TiO<sub>2</sub> can enhance the adsorption of Cr(VI), although it obscures part of the hot spot of AgNPs, which further enhances the SERS signal that should be reduced. Therefore, in the following work, 10 mL TiO<sub>2</sub> suspension was used as the optimized dosage to prepare the composite UIO-66/Ag/TiO<sub>2</sub> for SERS detection of Cr in various samples.

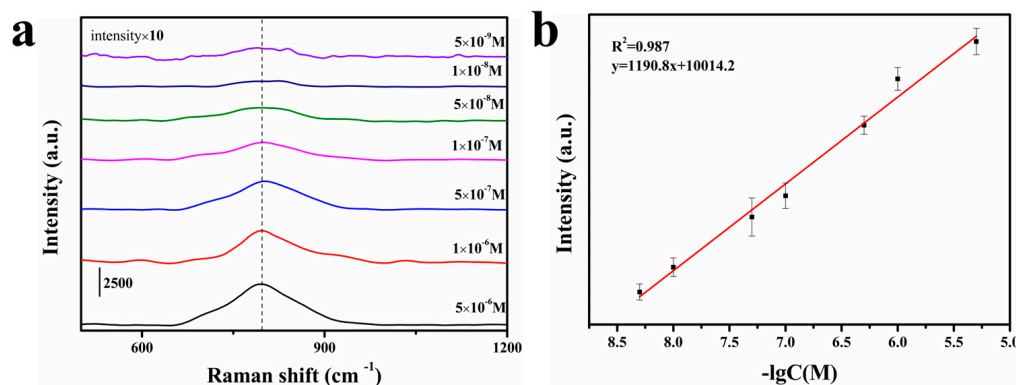


**Figure 6.** (a) SERS intensity of Cr(VI) aqueous solution ( $5 \times 10^{-6}$  M) with different volumes of TiO<sub>2</sub> colloid. (b) SERS intensity of characteristic peaks at 798 cm<sup>-1</sup>.

The optimized composite substrate UIO-66/Ag/TiO<sub>2</sub> was first used for the detection of Cr(VI) in a standard solution. As shown in Figure 7, a clear SERS characteristic peak of Cr(VI) was observed at  $5 \times 10^{-6}$  M level for UIO-66/Ag/TiO<sub>2</sub>. The SERS intensity of this peak decreased with decreasing concentration of Cr(VI). The results showed that the characteristic peak of Cr(VI) was still identifiable at the concentration of  $5 \times 10^{-9}$  M,

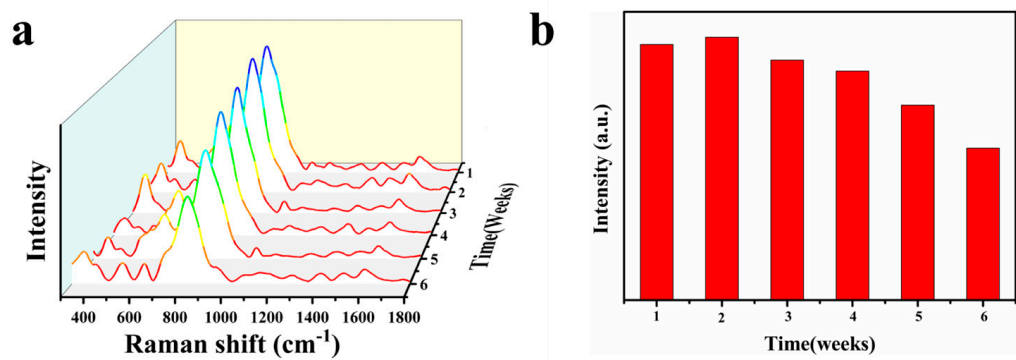


indicating that UIO-66/Ag/TiO<sub>2</sub> could detect Cr(VI) sensitively. In addition, the peak intensity (*I*) showed a good linear correlation with the logarithm of the concentration (*lgC*) in the concentration range of  $5 \times 10^{-6}$ – $5 \times 10^{-9}$  M. The regression equation was  $I = 1190.8 \lg C + 10,014.2$ ; thus, the quantitative analysis of this complex substrate was feasible. The results further demonstrate the great potential of the substrate for the quantitative detection of Cr(VI) in real samples.



**Figure 7.** (a) SERS spectra of different concentrations of Cr(VI) in aqueous solution on the UIO-66/Ag/TiO<sub>2</sub>. (b) Plot of SERS intensity at 798 cm<sup>−1</sup> versus logarithmic Cr(VI) concentration.

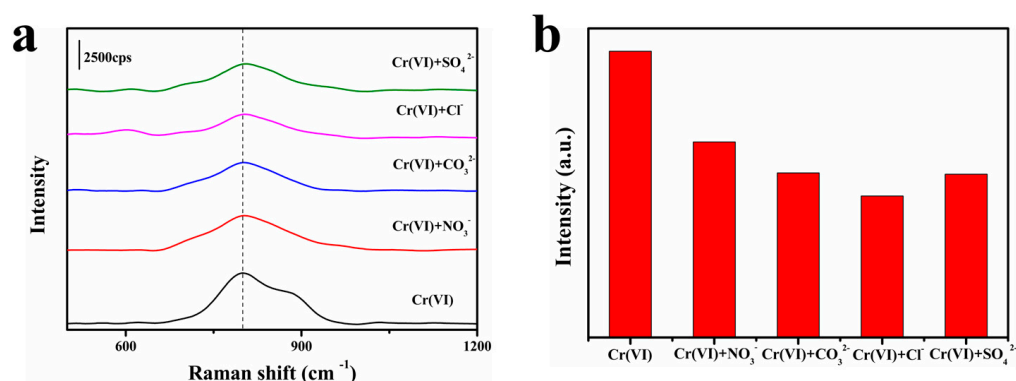
To evaluate the stability of the proposed substrate, we continuously monitored the SERS signals of Cr(VI) obtained on UIO-66/Ag/TiO<sub>2</sub> for 6 weeks to verify its practical application. The material was stored at room temperature. The variation of the characteristic peak intensity of Cr(VI) at 798 cm<sup>−1</sup> ( $5 \times 10^{-7}$  M) over 6 weeks is shown in Figure 8. The SERS signal intensity hardly changed in 4 weeks. However, the average SERS intensity of the characteristic peaks decreased by 40.5% after 6 weeks of storage. These data fully demonstrate that UIO-66/Ag/TiO<sub>2</sub> as a SERS substrate has the dual advantages of high activity and good stability due to the synergistic effect of the components. Therefore, the substrate has great potential for the sensitive detection of Cr(VI) ions in environmental samples.



**Figure 8.** (a) Average intensities of Cr(VI) aqueous solution ( $5 \times 10^{-7}$  M) peaks at 798 cm<sup>−1</sup> in 6 weeks. (b) Bar chart of peaks at 798 cm<sup>−1</sup>.

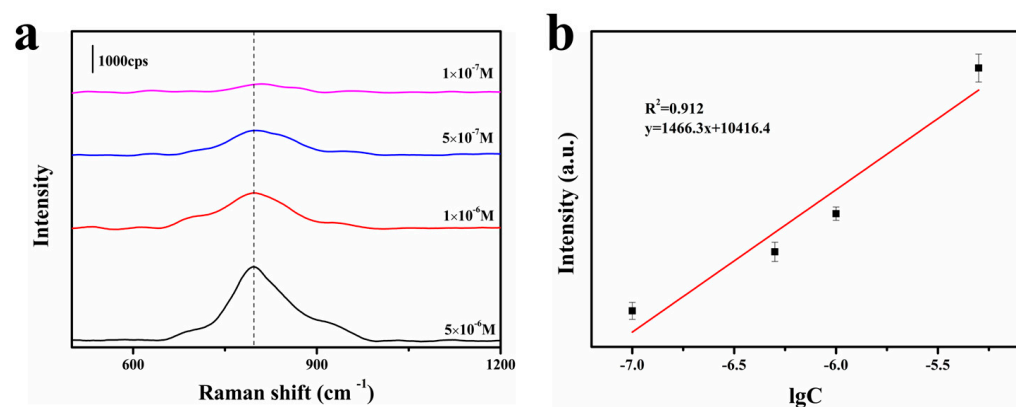
Common anions, such as CO<sub>3</sub><sup>2−</sup>, SO<sub>4</sub><sup>2−</sup>, Cl<sup>−</sup> and NO<sub>3</sub><sup>−</sup>, always coexist in real water. Thus, we performed SERS detection of Cr(VI) in the presence of CO<sub>3</sub><sup>2−</sup>, SO<sub>4</sub><sup>2−</sup>, Cl<sup>−</sup> and NO<sub>3</sub><sup>−</sup>. Compared with the SERS spectra of standard Cr(VI) solution, Figure 9 shows that SERS intensity of Cr(VI) was slightly reduced in the presence of other anions due to the competitive adsorption of coexisting ions on the active site of the UIO-66/Ag/TiO<sub>2</sub> surface. However, the peak position of Cr(VI) only shows little shifts, indicating that the presence of other anions did not interfere with the identification of Cr(VI) significantly. Therefore, UIO-66/Ag/TiO<sub>2</sub> can effectively sense Cr(VI) in complex water systems. Taken

together, these experimental results indicate that UIO-66/Ag/TiO<sub>2</sub> is well suited for the quantitative detection of Cr(VI) in aqueous solutions.



**Figure 9.** (a) SERS intensities at 798 cm<sup>-1</sup> of  $5 \times 10^{-6}$  M Cr(VI) aqueous solution in the presence of CO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup> at  $5 \times 10^{-6}$  M; (b) bar chart of peaks at 798 cm<sup>-1</sup>.

In order to verify the feasibility of the substrate for detecting the ion in real samples, a known concentration of Cr(VI) ( $5 \times 10^{-6}$ – $10^{-7}$  M) was added to the samples using local lake water as the actual sample for detection. As shown in Figure 10, the substrate maintained a good linear relationship with the Cr(VI) ion concentration ( $R^2 = 0.912$ ), but the lowest detection concentration of Cr(VI) in the actual sample was significantly higher than that in the standard solution. This result can be attributed to the competitive adsorption of Cr(VI) with other coexisting components in the lake water, blocking some hot spots that enhance the signal of Cr(VI) ions. The comparison of different nanomaterials for Cr(VI) and SERS activity is given in Table 1. The SERS activity of the prepared UIO-66/Ag/TiO<sub>2</sub> nanocomposites was slightly higher than that of the other reported substrates. It is worth mentioning that the three magnetic SERS substrates in studies 40, 32 and 20 show excellent SERS sensitivity, but the substrates need to be assembled by magnetic fields for SERS analysis and are solid-phase, which may lead to poor reproducibility of the SERS signal. In study 9, the LSPR effect of the two-layer AgNPs and the specific adsorption ability of ZrO<sub>2</sub> on Cr(VI) made the material robust for detection, but the unstable AgNPs exposed to the outer layer could not cope with the various factors in the actual sample. In study 40, the corresponding Cr(VI) concentration was obtained by impeding the binding of TiO<sub>2</sub>-ARS (Alizarin Red S) by Cr(VI) ions, which reduced the intrinsic signal of ARS. Such a detection method not only has poor detection limits but also has poor ion interference. The above results suggest that UIO-66/Ag/TiO<sub>2</sub> nanocomposites have great potential for the practical monitoring of environmental contaminants.



**Figure 10.** (a) SERS spectrum of lake water after mixing with UIO-66/Ag/TiO<sub>2</sub>. (b) Plot of logarithmic SERS intensity at 798 cm<sup>-1</sup> versus logarithmic Cr(VI) concentration.

**Table 1.** Comparison of previously reported SERS substrates for Cr(VI) detection.

Substrate	Detection Limit ( $\mu\text{M}$ )	Reference
$\text{Fe}_3\text{O}_4/\text{Ag}$	0.1	[39]
$\text{Ag}/\text{ZrO}_2/\text{Ag}$	0.5	[9]
$\text{Fe}_3\text{O}_4\text{-Au}/\text{TiO}_2$	0.05	[29]
ARS- $\text{TiO}_2$	0.6	[28]
$\text{Fe}_3\text{O}_4/\text{m-ZrO}_2/\text{Ag}$	0.05	[22]
UIO-66/Ag/ $\text{TiO}_2$	0.005	This work

#### 4. Conclusions

In this work, a new ternary composite UIO-66/Ag/ $\text{TiO}_2$  was proposed for the sensitive SERS detection of Cr(VI) in water samples. The composite combines the merits of the three components: UIO-66 can enhance the adsorption to Cr and provide a large area for AgNP loading, AgNPs produce a great electromagnetic enhancement effect amplifying the SERS signal, and  $\text{TiO}_2$  can further significantly enhance the adsorption to Cr(VI). By adjusting the volume of the  $\text{TiO}_2$  colloid, an optimized UIO-66/Ag/ $\text{TiO}_2$  with excellent SERS sensitivity was prepared for the sensitive SERS detection of Cr(VI) in water samples. The lowest detection concentration for Cr(VI) was 5 nM in a standard solution and 0.5  $\mu\text{M}$  in a real lake water sample, both of which are lower than the allowable limit of Cr(VI) in drinking water (1  $\mu\text{M}$ ) set by the U.S. EPA. In addition, the UIO-66/Ag/ $\text{TiO}_2$  nanomaterials exhibited excellent storage stability. Therefore, the prepared UIO-66/Ag/ $\text{TiO}_2$  nanomaterials have important potential applications for the effective detection of environmental contaminants.

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