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Comparative chemical sensor for detection of chromium (VI) in aqueous solution

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A process for purifying aqueous solutions containing heavy and toxic metals such as chromium (Cr) has been investigated. One of the extremely harmful pollutants in rivers and seawater is the heavy metal ions due to their direct impacts on human, animals and plants are hexavalent Cr (VI). Consequently, highly sensitive sensor to detect Cr is essential. Surface plasmon resonance (SPR) technique has attracted huge research interest in detecting heavy metals specifically. In this study, three types of prism-based SPR sensor, gold (Au)/silver (Ag), Au/polyaniline (PANI) and Au/titanium dioxide (TiO_2) nanostructured films, are investigated as potential sensing material to detect the presence of Cr (VI) ions in water. The base Au layer with thickness of 48.3 nm is deposited on a glass slide for all sensors. For Au/Ag, Au/PANI nanofibers and Au/TiO_2 sensor films, the Cr (VI) concentration is varied from 1 ppm to 15 ppm with sensitivity of 0.270 $°ppm^{-1}$, 0.082 $°ppm^{-1}$ and 0.039 $°ppm^{-1}$, respectively. Based on these results, the Au/PANI nanofibers are the most sensitive to Cr (VI) among the tested sensing materials.

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1. Introduction

All metals frequently used in industry and classified as toxic substances in the aquatic environment such as copper (Cu), lead (Pb), cadmium (Cd), zinc (Zn), chromium (Cr) and arsenic (As) which have relatively high atomic weight and density more than 4 g/cm^3 can be defined as heavy metals[1]. Heavy metals can be produced in the environment in various activities mainly from burning, ore mining, agricultural activities and municipal waste[2]. One of the extremely harmful pollutant in rivers and sea water is the heavy metal ions due to their direct impacts on human, animals and plants. In effect, due to the production growth rate of many industrial applications such as petrochemicals, steel manufacturing, and textiles, etc, this leads to increase inorganic pollutants rapidly in recent years. Particularly, one of the high and efficient ways to detect and remove toxic organic and inorganic combinations is using nanoscale based methods such as surface plasmon resonance (SPR). Cr appears in several oxidation formulas, and the major ones are Cr (III) and Cr (VI)[3]. Cr (VI) exists as oxyanions in water, both $Cr_2O_7^{2-}$ and $HCrO_4^-$ particularly between 0 and ~6 pH values, while CrO_4^{2-} appears at ~4.5 pH value, reaching its extreme value at pH≥8, and remains even with higher pH. Alternatively, another five formulas of Cr (III) found in water according to pH value are Cr^{3+}, $CrOH^{2+}$, $Cr(OH)_2^+$, $Cr(OH)_3^0$ and $Cr(OH)_4^-$[4]. The richest Cr formulas can be noticed in effluents are Cr (III) and Cr (VI) ions. The two Cr ions are toxic, while Cr (VI) can be considered the most hazardous and risky because it possesses higher aquatic solubility, such as irritation at the contact site, the nasal mucosa, also the skin may be caused by a relatively high dose of the Cr even if exposed for a short period. World Health Organization, European Union, also many countries governments have established the maximum level of Cr contamination in potable water at 0.050 mg/L[5].

Some portable devices that developed for Cr ion detection had high cost and complicated sample preparation procedure such as and inductive coupled plasma-mass spectrometry (ICP-MS), graphite furnace atomic absorption (GFAA), atomic fluorescence spectroscopy (AFS), anodic stripping voltammetry (ASV), and inductively coupled plasma-atomic emission spectrometry (ICP-AES)[6]. These techniques' based methods are costly and need intricate sample pre-treatments. The other intriguing method is predicated on a potent instrument known as bulky, time-consuming SPR spectroscopy. The simplest and more efficient methods utilized in retrieving data are from the optical properties of nanomaterials also biomaterials, for characterization of a solid/liquid interface in situ and real-time, low cost, noninvasive and label free nature, which makes it a good

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sensor.

The fundamental mechanism of SPR relies on the optical properties of its metal layer and a prism for optical excitation of the surface plasmon through attenuated total reflection as revealed by SALIM et al[7] and QIN et al[8]. Higher sensitivity of the SPR sensing system is obtained from the Kretschmann setup, which lets refractive detection indices that are as low as 5×10^{-7} RIU, and matches to a 1 pg/mm^2 of material surface coverage. However, it is difficult to detect acquired signals for low impurity concentrations using SPR, since the angle variation is significantly small. Thus, the metal layer has to be enhanced using an active layer in order to overcome this issue[9]. A few articles reported the investigation or execution of detecting heavily polluted waters for SPR sensors. It could be observed that the silver-based SPR sensor obtains greater sensitivity to heavy metals[10]. According to TAO et al[11], the sensor was successfully employed in detecting the mercury ion [Hg (II)] in drinking water. Silver is an appropriate choice of metal for SPR sensors' performance due to its large permittivity which controls absorption and reflection of light in the metal. Most of the SPR studies on heavy metal detection have concentrated on the development of optical sensors for different metal ions like cadmium [Cd (II)], copper [Cu (II)], lead [Pb (II)], and mercury [Hg (II)], while extremely few have focused on Cr (V) ion[12]. One of the well-known polymers, which was utilized and studied in the literature due to numerous advantages such as low cost, chemical stability, high conductivity and biocompatibility, is polyaniline, also it has strong nitrogen atoms affinity, which enables it to interact with many metal ions using the large number of amine and imine functional groups. A polyaniline (PANI) nanomaterial has attracted much attention for the adsorption of heavy metals.

RAJAKUMAR et al[13] reported Mn_2O_3 after coating it with polyaniline to detect Pb (II), Cd (II), and Ni (II) ions. In another study, the uptake of Cr (VI) by a nanocomposites on ZnO/PANI was examined[14]. In another work, MnO_2-coated polyaniline nanofibers were investigated for the removal of Cr (VI) with a 250—300 nm average length. Also in the study reported by SAHU et al[15], a thorium oxide nanoparticle core-coated polyaniline nanocomposite was applied to remove Cr (VI).

One of the widely used technologies to decrease pollution and purification of wastewater metal oxides by environmental remediation is detection-based technologies. Examples of suitable adsorbents are titanium oxide $(TiO)_2$, taking into consideration the active sites' number effect on the adsorbent material surface which increase the selectivity for adsorbing different ions of heavy metal[16] due to its unique electrical and optical property. Incorporation of TiO_2 at nanoscale size has been found to significantly enhance the heavy metals' adsorption due to its large surface area.

However, until now, only few studies have been reported on the investigation of Cr in aqueous solution adopting the SPR technique. In this study, a very concerning environmental pollutant, Cr (VI) ion, was detected using an SPR-based sensor that used a nanostructured thin film.

2. Materials and methods

2.1 Preparation of sensing layers

Synthesis of Ag was initiated with the addition of 80 μL ammonia (25 wt%) into a 10 mL silver nitrate solution (20 mM). The mixture was vigorously stirred until a clear solution was observed, indicating the formation of complexes silver nitrate in ammonia ($Ag(NH_3)_2OH$).

Emeradine-based PANI nanofibers were synthesized by chemical polymerization on the basis of the technique in Ref.[17]. The PANI was re-doped with camphor sulfonic acid (CSA) and then diluted in chloroform to yield a 3.75 mg/mL CSA-doped PANI solution. The solution was sonicated for an hour after being stirred for an hour at room temperature using a magnetic stirrer. TiO_2 nanoparticles preparation was conducted using the process of chemical precipitation[18].

2.2 Ions standard solution

The testing solution of Cr (VI) must be prepared beforehand. The procedure of preparing Cr (VI) is described as follows. Prepare 1 000 mg·mL^{-1} Cr (VI) by dissolving 2.82 g of potassium dichromate ($K_2Cr_2O_7$) (sigma Aldrich) as reported in Ref.[19]. Other concentrations, 1 ppm, 5 ppm 10 ppm, and 15 ppm, were prepared using systematic dilution. They were prepared on the day it will be utilized. All chemicals used were analytical grade reagents and not enough purified. All solutions prepared used deionized water with 18.1 μS·cm^{-1} conductivity, from a source using a Millipore purification system.

All the spectroscopic tool parts that used in filling and extracting the sample cells were cleaned by acetone.

The pH value of Cr (VI) ion solutions was evaluated and measured using a PH meter (pB-10 Sartorius).

2.3 Surface plasmon resonance setup

The refractive index of the prism is n=1.778 5 with 22×22 mm^2 area of glass cover slips, which were provided by fisher scientific. All parts including glass cover slips, slide surfaces and any fingerprints or dirt were cleaned using acetone. For the deposition of Au layer on the glass slip, a sputter coater was utilized. Fig.1 shows the SPR setup used in this work.

Prior to the measurement, an initial test for gold in contacted with deionized water was carried out. The data of experiments were fitted by Matlab (matrix method). As shown in Fig.2, the gold optical properties were attained, with refractive indices of n=0.272 6±0.005, k=3.697 5±0.002 and d=49.3±0.1 nm. The optimum thickness was found to be at deposition time of 67 s as shown in Fig.3(a), while the measurement for deionized water was n=1.332 5 which is in line with the values published in previous works[1]. The atomic force microscopy (AFM) image shows that the overall surface roughness of the gold layer is depicted in Fig.3(b).

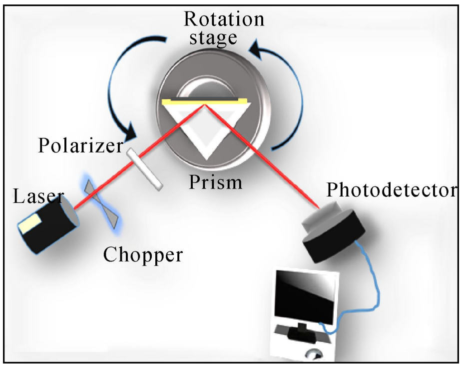

Fig.1 Experimental setup of surface plasmon resonance

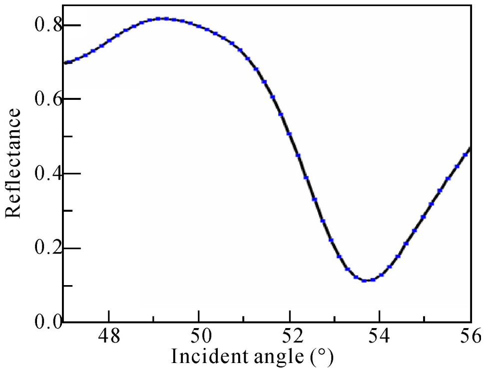

Fig.2 Theoretical and experimental (baseline) SPR curves of prism/gold/DDW reflectivity

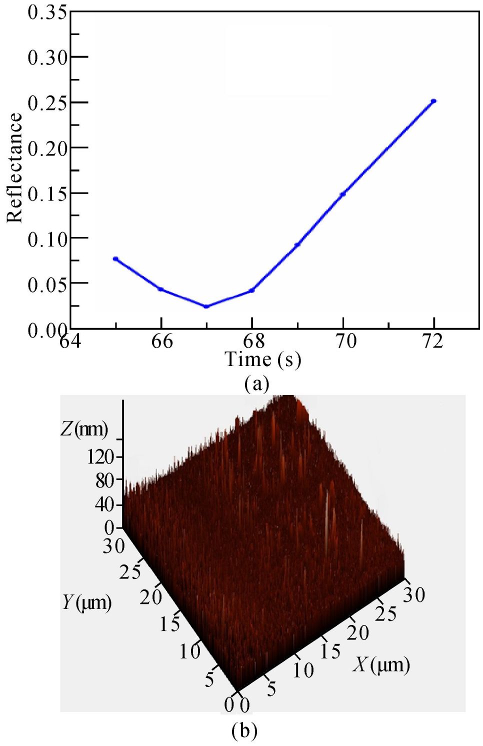

Fig.3 (a) Optimized deposition time of gold layer; (b) AFM image of the gold layer

3. Results and discussion

3.1 Sensing performance

The SPR curves with Au/Ag are shown in Fig.4. A linear increase in the resonance angle was observed as a response to the concentration increment of metal ions. This is a result from the dielectric constant changes caused by the concentration level of captured Cr (VI) ions. A reduction in the dispersion and angular bandwidth were observed on the reflectance curve, and it shows that preferred laser wavelength is the appropriated value. The resulted improvement in the sensor resolution is an induction, where subsequent modifications caused by Cr (VI) concentration are easily to capture by the photo detectors[20]. Therefore, according to the SPR response, it can be said that the sensor is sensitive to Cr (VI) ions.

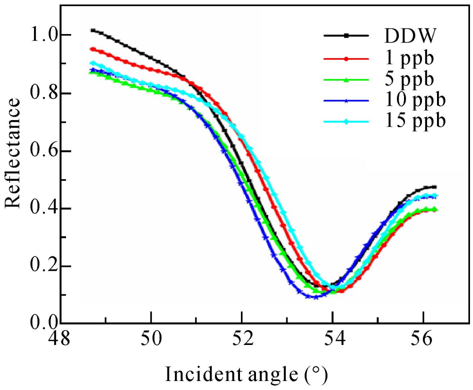

Fig.4 SPR response of Cr (VI) with Au/Ag coating

By increasing the concentration of Cr (VI) from 1 ppm to 15 ppm, the resonance angle and the angular shift ($\Delta\Theta$) also increased. The sensitivity of Au/Ag shows less response compared with other materials (PANI and TiO_2). This limitation of detection toward Cr (VI) may be one of the possible reasons behind this limitation, which is related to low stability and easy agglomeration of silver nanoparticles which decrease their adsorption toward Cr (VI) drastically and considered as major problem in their usage[21]. Hereafter, stabilizing silver nanoparticles before used as an adsorbent to detect heavy metals is essential.

The effect of Ag layer on removal of hexavalent Cr (VI) concentrations (from 1 ppm to 15 ppm) indicated that when the hexavalent Cr ions increase, the shift angle of sensing layer increases. Adsorbent and adsorption efficiency are directly correlated because AgNPs have a larger surface area and more exchangeable sites for Cr ions. The scanning electron microscopy (SEM) image in Fig.5(a) depicted that synthesized nanoparticles analysis was performed for characterizing the surface morphology and particle sizes of the Ag layer after Cr (VI) adsorption. The AFM surface roughness for sensing layer after Cr (VI) adsorption represented in Fig.5(b) revealed that particle is predominantly 70 nm. In SEM and AFM analysis, the particle size values are found to be in good agreement.

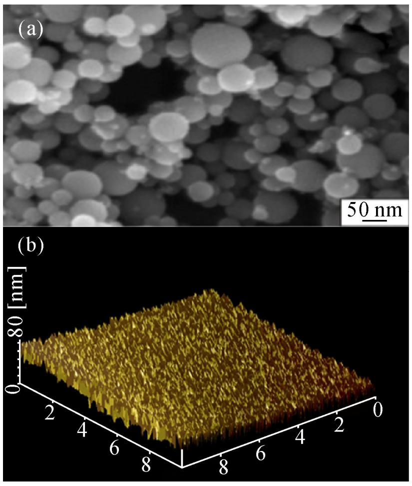

Fig.5 (a) SEM image of synthesized Ag nanoparticles and (b) 3D AFM surface roughness for the sensing layer after adsorption of Cr (VI)

The response of Au/PANI coated SPR towards pure DDW water, as well as Cr (VI) solutions at different concentrations are illustrated in Fig.6. The incidence angle of reflected light was shifted by the SPR sensors in cases of exposure to Cr (VI) concentrations from its baseline. For instance, the exposure to 1 ppm Cr (VI) shifted the baseline's incidence angle by 0.184°. Likewise, the angle changed when the sensor was subjected to 5 ppm, 10 ppm and 15 ppm concentrations of Cr (VI), respectively.

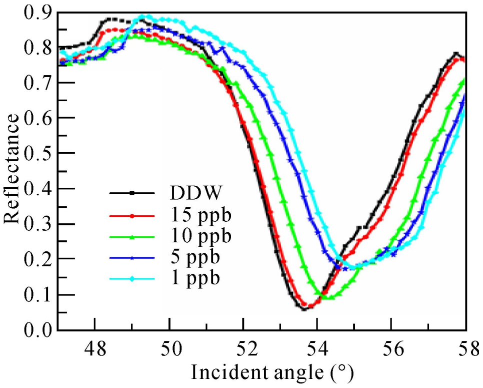

Fig.6 SPR response of Cr (VI) with Au/PANI nanofibers coating

PANI nanofibers thin film is only utilized in sensors due to the fast response time and extraordinary surface area with different structures and different morphologies[22]. The prepared nanofibers form revealed a superior thermal stability also high-order crystal structure. The sensor showed high detection for Cr (VI) concentration, which indicated that chemical reaction was involved in the adsorption process between the sensor and heavy metal ion. The reason can be explained as a rough heterogeneous and fibrillar structure surface of sensor[23].

The PANI samples are characterized by SEM and AFM. The results are displayed in Fig.7(a) and (b), respectively. Moreover, the PANI nanofibers particles were uniform and long fiber-like morphology as can observed from Fig.7(b). Lastly, it was noticed that the results obtained from particles were rougher as verified, making the particles appeared to have a layered surface structure.

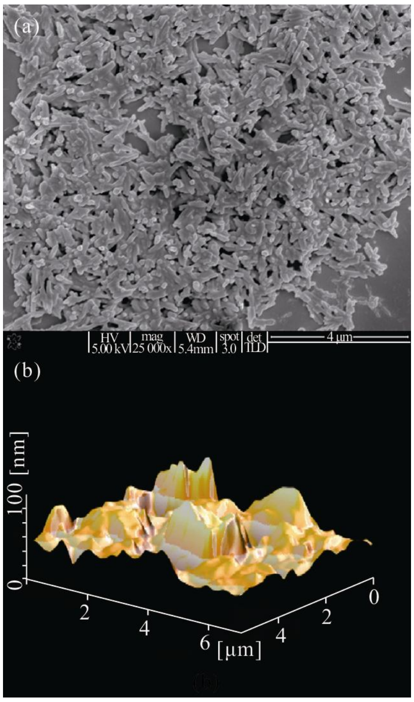

Fig.7 (a) SEM image and (b) 3D AFM image of the PANI nanofibers surface after adsorption of Cr (VI)

The fabrication of sensing layers was made for Au/TiO_2 as two previous materials. Nano TiO_2 materials have been used as adsorbent materials for this research, due to their advantages of large specific surface area and porosity. It was synthesized according to the method in Ref.[18].

The preliminary SPR experiment was also carried out for all concentrations (1 ppm, 5 ppm, 10 ppm, and 15 ppm) of Cr (VI) ion solutions in contact with gold film and the active layer to detect the Cr ion in high concentration. From the response curves of SPR shown in Fig.8, the SPR resonance angle change is obtained from the resonance angle shift of the reference. The resulting shifts of the SPR angle were monitored to detect any binding interactions with a good sensitivity of Cr (VI) ions[24]. The adsorptive process was influenced by Cr concentration variation through the dissolution of functional groups on the active sites of the adsorbent's surface. Superior level of Cr detection occurred when initial concentration was increased while the rate of adsorption increased. Furthermore, the higher the Cr concentration, the higher the boundary layer diffusion of Cr ions, which leads to extreme sorption by TiO_2[25]. As noted above, the adsorption of Cr (VI) on the surface of

TiO_2 is chemisorption.

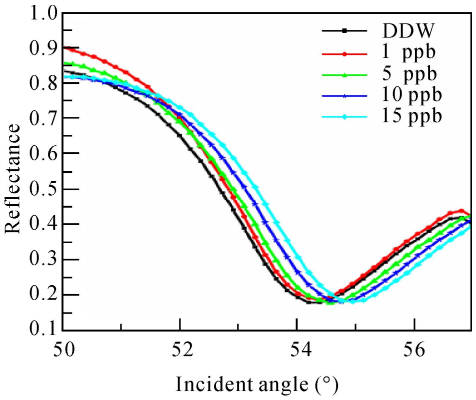

Fig.8 SPR response of Cr (VI) with Au/TiO_2 nanofibers coating

Additionally, in order to further prove the success of adsorption of toxic Cr, the surface of active layer was characterized by SEM and AFM as shown in Fig.9. The results showed that the nano TiO_2 material with a particle size of about <100 nm, which can be clearly seen from the SEM characterization with uniform spherically distribution. The AFM image after introducing Cr ion shows obviously that the adsorptions increased the roughness and made the surface more coarse.

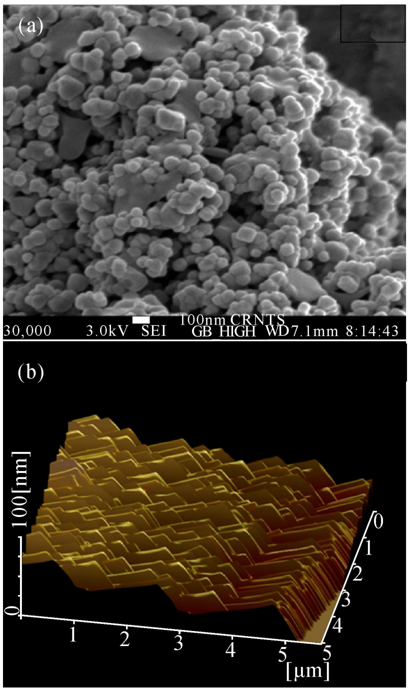

Fig.9 (a) SEM image and (b) 3D AFM image of the TiO_2 nanostructure surface after adsorption of Cr (VI)

3.2 SPR sensitivity and selectivity

The sensitivity of Au/Ag active layer was tested. It has a good response. When a sensor exposed to 1 ppm, there was a slight change at SPR angle of 0.185°. However, the maximum changes at 15 ppm as 0.559° were as high with a sensitivity value of 0.270 $°\text{ppm}^{-1}$. The surface of the adsorbent Au/TiO_2 demonstrated more sense toward Cr detection compared with Au/Ag with a sensitivity of 0.039 $°\text{ppm}^{-1}$ as shown in Fig.10.

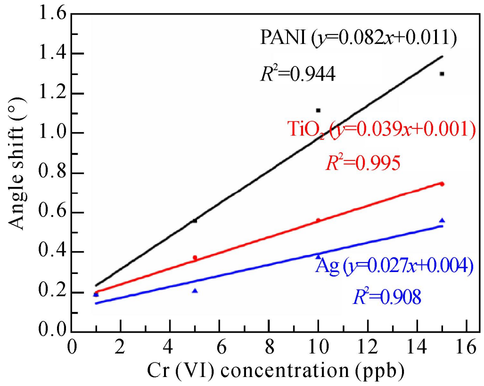

Fig.10 SPR angle shifts of Au/Ag, Au/TiO_2 and Au/PANI nanofibers for different concentrations of Cr (VI)

The Au/PANI nanofibers thin film had more sensitive response towards the exposure of Cr (VI) concentrations. The sensitivity obtained for Au/PANI thin film was 0.082 $°\text{ppm}^{-1}$. The minimum changes in SPR angle were observed at 1 ppm as 0.371 2°, while the maximum changes were observed at 15 ppm as 0.927 9° as depicted in Fig.10.

Fig.11 shows the angle shift taken after introducing each tested concentration within the range from 1 ppb to 20 ppb. Since no concentration could significantly alter the angle from the baseline at a concentration below the specified amount, it was determined that the detection limit for these sensors was 1 ppb. By testing the sensor's detection limit towards Cr (VI), the sensitivity of the sensors was further examined. The lowest concentration at which the sensor is still able to discriminate between the baseline and the sample is defined as the detection limit in this case. The SPR curve that was obtained after the addition of DI water serves as the baseline in this work. Additionally, the gradient of the trend line begins to decrease from 20 ppb and above as increasing amounts of Cr (VI) ions are injected. This was anticipated since the absorption of Cr (VI) ions at higher concentrations might have exceeded the sensing layer's maximum capacity, preventing the interaction from increasing.

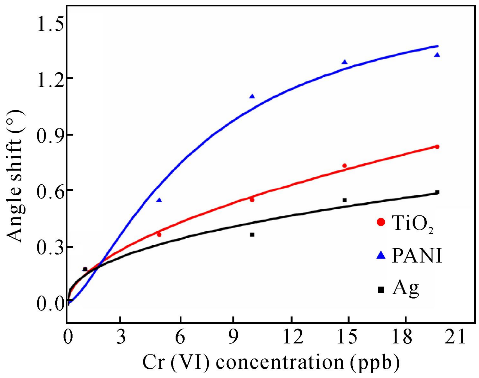

Fig.11 SPR angle shifts of different sensing layers

The optimization of active layer was examined with a different sensor and certain of Cr concentration as notable in Fig.12.

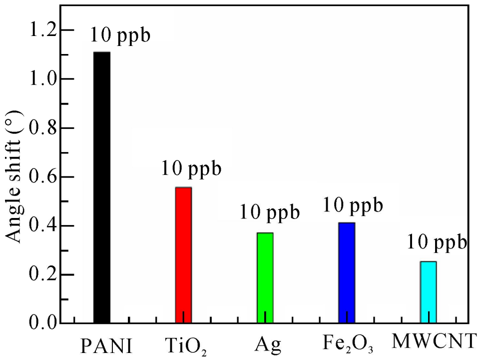

Fig.12 Response signals of different metal ions

The largest capacity absorption of PANI to detect Cr (VI) gives the maximum shift in resonance angle significantly, and thus the maximum sensitivity.

Ethics declarations

Conflicts of interest

The authors declare no conflict of interest.

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