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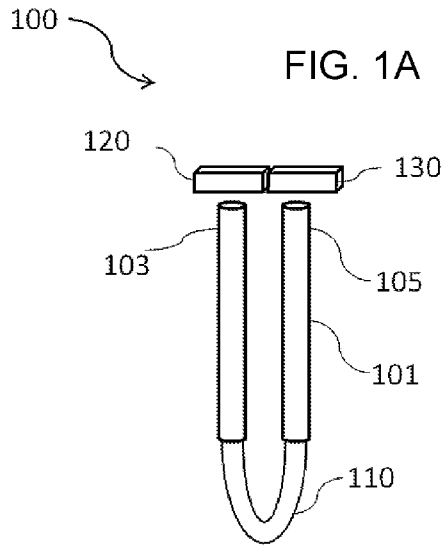

FIG. 1A

(57) Abstract: The invention discloses a reproducible and scalable process for a stable zeolite imidazole (ZIF-67) coating over a U-bent fiber optic sensor (U-FOS) for Cr^{+6} ion detection in aqueous samples. The ZIF-67 is formed in-situ over the U-FOS out of cobaltous nitrate hexahydrate and 2-methyl imidazole. ZIF-67 selectively entraps Cr^{6+} ions and the high evanescent wave absorbance (EWA) sensitivity of the U-FOS allows specific detection of Cr^{6+} ions by means of their intrinsic optical absorption around 395 nm. The developed sensor demonstrates high selectivity for chromium ion detection with respect to other potential interfering heavy metal ions present in water. The other advantages of the invention includes a wide dynamic range and useful detection limits. The sensor probes are stable when stored under normal ambient conditions without any significant loss in the sensitivity.

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OPTICAL SENSOR FOR HEXAVALENT CHROMIUM

CROSS-REFERENCES TO RELATED APPLICATION

[0001] This application claims priority to Indian patent application No. 202141023371 entitled OPTICAL SENSOR FOR HEXAVALENT CHROMIUM filed on May 25, 2021.

FIELD OF THE INVENTION

[0002] The disclosure generally relates to sensors and in particular to sensors for heavy metal ions.

DESCRIPTION OF THE RELATED ART

[0003] Chromium is a widely used heavy metal, because of which hexavalent chromium ions are hazardous pollutants frequently found in natural resources such as water. The permissible limits for Cr^{6+} ions in water is 50 parts per billion (ppb) as per WHO. Hence, monitoring of Cr^{6+} contamination in water resources is very important.

[0004] Conventional techniques for Cr^{6+} detection and quantification by means of the standard methods using atomic absorption spectrometry or mass spectrometry are limited by requirement of expensive infrastructure and skilled personnel. Field deployable rapid detection systems would help in faster measurements, without the need to send the samples to central laboratories, improving the reach and timely remedial steps.

[0005] Recently, several sensing techniques for Cr^{6+} ion detection have been reported. However, most of them are limited by their field deployability, ease of operation or selectivity/sensitivity. The Chinese patent discloses a method for removing hexavalent chromium in water by using modified diatomite-loaded nanoscale zero-valent iron. The US patent application US20170038303A1 describes a selective colorimetric detection sensor and a method for detecting hexavalent chromium ions using size-controlled label-free gold nanoparticles.

[0006] The invention proposes a novel composite device configuration that overcomes some of the drawbacks of the existing devices.

SUMMARY OF THE INVENTION

[0007] The invention discloses a method of fabricating a silica optical probe for Cr^{6+} detection. The method includes fabricating a U-bent silica optic fiber probe having a first end, a second end and a U-bent region. An outer surface of the U-bent region is activated to generate hydroxyl groups on the surface. A metal organic framework (MOF) comprising zeolite imidazole (ZIF-67) is grown on the outer surface by dipping the outer surface in a solution consisting of cobaltous nitrate hexahydrate and 2-methyl imidazole. In various embodiments post-thermal treatment is provided to the coated probe.

[0008] In various embodiments the ZIF-67 is synthesized in an aqueous medium at room temperature conditions. In various embodiments the coating of ZIF-67 on silica optical fiber comprises an in-situ deposition method. In various embodiments activating the outer surface includes cleaning the U-bent optical fiber, by heating and sonicating the U-bent region in acetone or treating the U-bent region in HCl and methanol at a ratio of 1:1 for a predetermined time of 15 minutes.

[0009] In various embodiments the absorbance of ZIF-67 is at least 0.25 OD at 605 nm. In various embodiments the optimum condition for ZIF-67 includes coating the U-bent region with growth solution made of 0.515 M cobaltous nitrate and 8.45 M 2-methyl imidazole and incubating the U-bent probe region for at least 3 minutes. In various embodiments the post-thermal treatment includes heating the coated probe at a temperature in the range 70°C-75°C for 15 minutes. The invention in various embodiments includes an optical probe for detecting Cr^{6+}. The probe includes an U-bent silica optic fiber probe having a first end, a second end and a U-bent region and a metal organic framework (MOF) comprising zeolite imidazole (ZIF-67) coated on an outer surface of the U-bent region. In various embodiments the optical fiber the optical fiber is a multimode fiber with its core diameter at least 50 μm.

[0010] In various embodiments the selectivity of Cr^{6+} ions is 400 times or more over other potentially interfering heavy metals. In various embodiments the ZIF-67 coated U-bent fiber optic sensor are stable at room temperature with less than 5% loss of

sensitivity at least for a month. In various embodiments the detection range of Cr^{6+} ions in the optical probe is in the range 5 – 100,000 ppb.

[0011] This and other aspects are described herein.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] The invention has other advantages and features, which will be more readily apparent from the following detailed description of the invention and the appended claims, when taken in conjunction with the accompanying drawings, in which:

[0013] FIG. 1A illustrates a schematic of the sensor probe for highly selective chromium (VI) sensing.

[0014] FIG. 1B shows the ZIF-67 probe coating for Cr^{6+} sensing.

[0015] FIG. 2 illustrates the method of producing optical probe for detecting Cr^{6+} ions.

[0016] FIG. 3A illustrates the UV-Vis absorption spectrum of ZIF-67 growth solution.

[0017] FIG. 3B shows the absorbance response showing deposition of ZIF-67 on a hydroxylated and a bare probe.

[0018] FIG. 3C illustrates the optical absorption spectra recorded from the U-bent FOS during the in-situ deposition of ZIF-67 over the fiber core surface at an interval of 100 s.

[0019] FIG. 3D depicts the temporal response of ZIF-67 deposition at 605 nm.

[0020] FIG. 3E illustrates the UV-Vis absorption spectrum of 100 ppm of Cr^{6+} in $K_2Cr_2O_7$ in cuvette.

[0021] FIG. 4 illustrates the characteristic chromium absorbance spectral response from bare (control) and ZIF-67 coated silica optical probes subjected to different concentrations of Cr^{6+}solutions.

[0022] FIG. 5A shows the SEM images of ZIF-67.

[0023] FIG. 5B illustrates the SEM images of ZIF-67/Cr.

[0024] FIG. 6A illustrates the SEM-EDAX (10 kV) spectrum for elemental composition of ZIF-67 coated fiber.

[0025] FIG. 6B shows the SEM-EDAX (10 kV) spectrum for elemental composition of ZIF-67 coated fiber after chromium treatment.

[0026] FIG. 7 illustrates the absorbance spectra obtained from the sensor probes with $A_{605\ nm}$ at 0.1, 0.2, 0.5 and 1.0.

[0027] FIG. 8A depicts the spectral response of fibers coated at $A_{605\ nm}$ equal to 0.1 and exposed to 1, 10 and 50 ppm Cr^{6+} solutions.

[0028] FIG. 8B depicts the spectral response of fibers coated at $A_{605\ nm}$ equal to 0.2and exposed to 1, 10 and 50 ppm Cr^{6+} solutions.

[0029] FIG. 8C depicts the spectral response of fibers coated at $A_{605\ nm}$ equal to 0.5 and exposed to 1, 10 and 50 ppm Cr^{6+} solutions.

[0030] FIG. 8D depicts the spectral response of fibers coated at $A_{605\ nm}$ equal to 1 and exposed to 1, 10 and 50 ppm Cr^{6+} solutions.

[0031] FIG. 9A illustrates the absorbance spectral response due to Cr^{6+} binding from the ZIF-67 coated U-FOS probes, having $A_{605\ nm}$ values of 0.1, 0.2, 0.5 and 1.0 optical density (O.D) units, subjected to 50 ppm of Cr^{6+} solutions.

[0032] FIG. 9B illustrates the comparison of the sensitivity of these ZIF-67 coated U-FOS probes subjected to 1, 10 and 50 ppm of Cr^{6+} concentrations, in terms of their absorbance response at 395 nm (n= 3).

[0033] FIG. 10A illustrates the absorption spectra from ZIF-67 coated U-FOS probes subjected to 50 ppm of Fe^{3+}.

[0034] FIG. 10B shows the absorption spectra from ZIF-67 coated U-FOS probes subjected to 50 ppm of Mn^{2+} respectively.

[0035] FIG. 10C shows the comparison of absorbance response at 395 nm from the sensor probes subjected to potential interfering heavy metal ions at 50 ppm concentration with that of Cr^{6+} at 1 ppm (n = 3).

[0036] FIG. 11A illustrates the temporal absorbance response for sensor probes exposed to different concentrations of Cr^{6+} with concentrations ranging from (a) 0 (b) 1 (c) 2.5 (d) 5 (e) 10 (f) 50 (g) 100 (h) 250 (i) 500) ppb; (j) 1 (k) 5 (l) 10 (m) 25 (n) 50 and (o) 100) ppm.

[0037] FIG. 11B illustrates the temporal absorbance curves obtained from the sensor probes subjected to Cr^{6+} ions in tap water at 0, 5, 10, 50, 100, 250, 500, 1000, 5000 and 10000 ppb, from (a) to (j) respectively.

[0038] FIG. 11C illustrates the linear response obtained from log concentrations of 1 ppb to 100 ppm.

[0039] FIG. 11D illustrates the linear dose response (with R^2=0.99, $n \geq 3$) derived from log concentrations of 5 ppb to 10000 ppb acquired from sensor probes exposed to Cr^{6+} ions spiked in tap water and DI water for 10 minutes.

[0040] FIG. 12 illustrates evaluating the shelf life of the sensor probes with different concentrations over a period of 4 weeks.

[0041] FIG.13 illustrates the evaluation of the stability of the ZIF-67 coated U-FOS probes stored under the ambient conditions over four weeks in terms of percentage deviation from the sensitivity of the freshly prepared sensor probes.

[0042] Referring to the drawings, like numbers indicate like parts throughout the views.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0043] While the invention has been disclosed with reference to certain embodiments, it will be understood by those skilled in the art that various changes may be made and equivalents may be substituted without departing from the scope of the invention. In addition, many modifications may be made to adapt to a particular situation or material to the teachings of the invention without departing from its scope.

[0044] Throughout the specification and claims, the following terms take the meanings explicitly associated herein unless the context clearly dictates otherwise. The meaning of "a", "an", and "the" include plural references. The meaning of "in" includes "in" and "on." Referring to the drawings, like numbers indicate like parts throughout the views. Additionally, a reference to the singular includes a reference to the plural unless otherwise stated or inconsistent with the disclosure herein.

[0045] The embodiments presented herein disclose ZIF-67 coated U bent fibre optic sensor (U-FOS) for highly selective chromium (VI) sensing, with many advantages as set forth here. The invention discloses a reproducible and scalable process for a stable ZIF-67 coating over the U-FOS. ZIF-67 selectively entrap Cr^{6+} ions and the high EWA sensitivity of the U-FOS allows specific detection of Cr^{6+} ions by means of their intrinsic optical absorption around 395 nm. The developed sensor demonstrates high selectivity for chromium ion detection with respect to other potential interfering heavy metal ions present in water such as Mn^{7+}, Fe^{3+}, Co^{2+}, Cl^{-}, Cu^{2+}, Pb^{2+}, Hg^{2+}, Mg^{2+}, Ca^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+}, Li^{+}.

[0046] In various embodiments an optical probe **100** for detecting Cr^{6+} is disclosed. The optical probe **100** as shown in FIG. 1A has a U-bent silica optic fiber probe **101** that has a first end **103**, a second end **105**, a U-bent region **110** and a metal organic framework (MOF) **110** coated on an outer surface of the U-bent region **107**. In various embodiments the MOF is zeolite imidazole frameworks (ZIF-67) **111**. In various embodiments the zeolite imidazole (ZIF-67) is formed out of cobaltous nitrate hexahydrate and 2-methyl imidazole. In various embodiments the ZIF-67 is synthesized

in an aqueous medium at room temperature conditions. The coating of ZIF-67 on silica optical fiber is done by an in-situ deposition method.

[0047] In various embodiments activating the outer surface includes cleaning the U-bent optical fiber, by heating or sonicating the U-bent region in acetone or treating the U-bent region in HCl and methanol at a ratio of 1:1 for a predetermined time of 15 minutes. The absorbance of ZIF-67 is at least 0.25 OD at 605 nm. In various embodiments the optimum condition for ZIF-67 includes coating the U-bent region with growth solution made of 0.515 M cobaltous nitrate and 8.45 M 2-methyl imidazole and incubating the U-bent probe region for at least 3 minutes.

[0048] In various embodiments the optical probe has a light source **120** placed at the first end **103** and a photodetector **130** placed at the second end **105** for optical set-up. In some embodiments the light source is a miniaturized LED or a violet LED based light source. In one embodiment the selectivity of Cr^{6+} ions is 400 times or more over other ionic species. In another embodiment the sensitivity detection range of Cr^{6+} ions is in the range 5 – 100,000 ppb.

[0049] In various embodiments the optical probe is configured to work as a FOS. The sensor works on the principle of highly selective adsorption of Cr6+ ions to the stable ZIF-67 film and simultaneous quantification by means of their characteristic spectral absorbance at 395 nm. In various embodiments the U-bent fiber optic sensor (FOS) has highly sensitive evanescent wave absorbance (EWA).

[0050] The invention in various embodiments is a method of fabricating an optical probe for Cr^{+6} detection. The method as shown in FIG. 2 includes in step **201** fabricating a U-bent optic fiber probe having a first end, a second end and a U-bent region. In various embodiments, fabricating the U-bent optic fiber probe includes decladding an optic fibre at a middle portion by removing a buffer and polymer clad layer followed by acetone wiping. In various embodiments the fibers are then bent into U-shape with a predetermined bend diameter and the distal ends are further cleaved using fiber cleaver to get smooth and flat ends for efficient optical coupling.

[0051] In step **202** an outer surface of the U-bent region is activated to generate hydroxyl groups on the surface. In various embodiments, cleaning the U-bent region includes heating the U-bent region, sonicating the U-bent region in acetone and activating the U-bent surface by treating the U-bent region with HCl and methanol in the ratio 1:1 for 15 minutes to generate hydroxyl (-OH) groups on the sensor probe surface. In step **203** a MOF having zeolite imidazole (ZIF-67) is grown on the outer surface of the U-bent portion of the probe by dipping the outer surface in a solution consisting of cobaltous nitrate hexahydrate and 2-methyl imidazole. In various embodiments in step **204** the coated probe is provided with post-thermal treatment to obtain the U-bent optic fiber probe of silica with adherent ZIF-67 coating in step **205**. In various embodiments the post-thermal treatment includes placing the coated probe in a hot air oven at a temperature in the range 70°C-75°C for 15 minutes.

[0052] The zeolite imidazole framework (ZIF-67) coated U-bent silica fiber optic absorbance sensor is applied for selective detection of chromium ions in water. The advantages of the invention includes a wide dynamic range and useful detection limits. The sensor probes are stable when stored under normal ambient conditions without any significant loss in the sensitivity. The sensor performance was at par with that of the standard techniques for heavy metal ion quantification such as ICP-MS.

[0053] While the invention has been disclosed with reference to certain embodiments, it will be understood by those skilled in the art that various changes may be made and equivalents may be substituted without departing from the scope of the invention in the foregoing and as delineated in the examples to follow. In addition, many modifications may be made to adapt to a particular situation or material the teachings of the invention without departing from its scope as delineated in the appended claims.

[0054] EXAMPLES

[0055] Example. 1: Method of fabricating the zeolite imidazole framework (ZIF-67) coated U-bent silica fiber optic sensor.

[0056] Materials: Step-index multimode silica optical fibers with 200 μm core diameter and 0.39 numerical aperture (FT200UMT, Thorlabs Inc. USA) was used for all experiments. All the chemicals including cobalt nitrate hexahydrate, 2-methyl imidazole, potassium dichromate, potassium permanganate, potassium chloride, zinc nitrate hexahydrate, lithium chloride, ferrous chloride, lead nitrate, cadmium chloride, copper chloride, nickel sulphate, magnesium sulphate, calcium chloride, mercuric sulphate, methanol, hydrochloric acid, and acetone used in the study were of analytical grade and were used as received. Milli-Q deionized water (DI) was used for all experiments.

[0057] Fabrication of U-bent fiber optic sensor probes: Optical fibers of 25 cm length were decladded over 2 cm at the middle by removing the buffer and polymer clad layer using a mechanical stripper and a candle flame followed by acetone wiping, respectively. The fibers were bent into U-shape with a bend diameter of ~0.7 mm using a CO2 laser based automated bending system built-in-house. The distal ends were cleaved using fiber cleaver to get smooth and flat ends for efficient optical coupling.

[0058] Optical setup: The U-bent fiber optic sensor probes were connected to a halogen light source and a fiber optic spectrometer (HL2000 and USB4000-XR1-ES respectively, Ocean Optics Inc., USA) with the help of bare fiber terminator (BFT1) adapters and multimode SMA905 connectors (Thorlabs Inc., USA). The absorbance spectra were obtained with an integration time of 20 ms and an average of 50 spectra using Spectrasuite® software.

[0059] To realize a ZIF-67 based fiber optic Cr^{6+} sensor, a miniaturized LED and photodetector based optical set-up was used. Here, one of the fiber probe ends was coupled to a violet LED based light source (VLED-SMA, 60 mW, ChemBioSens Pvt. Ltd. India) with a peak emission at 380 nm and driven by a constant current source, while the other end was connected to a compact fiber optic photodiode (S150C, Thorlabs

Inc., USA). The photodiode response was recorded with the help of a USB power meter console (PM-100) and the optical power meter utility (version 5.9) software. MOF adsorbed to hydroxyl-rich U-bent probes alone as revealed by the photographic images and the EWA spectra that matches with that of ZIF-67 solution as shown in FIG. 4.

[0060] ZIF-67 deposition on U-bent fiber optic probes: The as-prepared U-bent fiber probes were further subjected to the blue region of the Butane flame without affecting its bent regime. The U-bent region was also carefully wiped and then sonicated in acetone for 15 minutes. Consequently, the fiber was treated in HCl/methanol (1:1) for 30 minutes to generate hydroxyl (-OH) groups on the sensor probe surface. The hydroxylated probes were dipped in a freshly prepared growth solution consisting of cobaltous nitrate hexahydrate (0.515 M, 75 µL) and 2-methyl imidazole (8.45 M, 75 µL) in water for an in-situ growth of MOF. Each of the probes was dip coated in 150 µL of ZIF-67 growth mixture solution for 10 minutes at room temperature followed by post-thermal treatment by placing the coated probes in a hot air oven at 70°C for 15 minutes.

[0061] Chromium ion solutions: A stock solution of 100 ppm Cr^{6+} solution was prepared by diluting 27 mg of $K_2Cr_2O_7$ made up to 100 mL with DI water. Aqueous Cr^{6+} ion solutions with concentrations between 1 ppb to 100 ppm were prepared in either DI water or municipal tap water by serial dilution. Similarly, 100 ppm stock solutions of other metal ions were prepared. The probes were dipped in a typical sample volume of 150 µL.

[0062] Surface characterization of ZIF-67 coated U-FOS: The surface morphological features of the ZIF-67 thin film on U-bent probes (with an absorbance value at 605 nm wavelength (A605 nm) equal to 0.5) have been studied using HR-SEM (Hitachi S4800, Japan) with an accelerating voltage of 5 kV. The hydroxylated probes coated with ZIF-67 were used for the study and three out of six sensor probes were then exposed to 10 ppm chromium solution. The as-prepared sensor probes with and without chromium exposure were gold sputtered for 10 s to obtain a continuous conducting surface on the U-bent surface before mounting on the sample holder. Energy dispersive

X-ray technique (EDAX) technique was used to analyse the elemental composition of MOF. The EDAX spectrum (10 kV) for elemental composition of coatings on chromium treated and non-treated probes were analysed, and average measurements taken at three different points of the probe is reported. Surface morphology and elemental composition of U-bent probes coated with ZIF-67 alone and subsequently treated with Cr^{6+} ion solution (10 ppm) were investigated. The corresponding SEM images are shown in Fig. 4. No considerable change in the morphology of ZIF-67 matrix was observed upon Cr^{6+} ion adsorption/entrapment. However, the EDAX analysis as shown in FIG. 5 shows an anticipated elemental composition of ZIF-67 matrix on the silica probe surface that includes the presence of cobalt, carbon, silicon and oxygen and the presence of chromium element for the probe subjected to Cr^{6+} ion solution.

[0063] The influence of ZIF-67 coating over the probes on the ability to detect Cr^{6+} ions is shown in FIG. 6. The ZIF-67 coated probes with $A_{605\ nm}$ value of 0.5 gave rise to a linear response with a minimal standard deviation in comparison to that of $A_{605\ nm}$ = 1.0. In addition, the probes with $A_{605\ nm}$ = 0.5 are advantageous due to lower optical extinction by the ZIF-67 layer and hence better availability of optical power for Cr^{6+} ion detection, leading to an improved signal to noise ratio (SNR). These results suggest ZIF-67 coating with $A_{605\ nm}$ = 0.5 as optimum for Cr^{6+} ion detection over the range of interest.

[0064] **Sensor Performances – Sensitivity and Selectivity Dose response:** The dose response of the ZIF-67 coated U-bent FOS sensor was obtained by subjecting them to various concentrations of chromium samples prepared in DI and tap water. The LED-photodetector set-up was used to record the intensity of the light passing through the probe as a function of time for ten minutes. The corresponding calibration curve was generated from the temporal responses.

[0065] **Selectivity:** The selectivity of the MOF based sensor probes were challenged with thirteen heavy metals (Li^{+}, Zn^{2+}, Cl^{-}, Fe^{3+}, Pb^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, Mg^{2+}, Ca^{2+}, Hg^{2+}, Mn^{7+}, Co^{2+}). The experimental set up of spectrometer and halogen light source was used, to see the spectral characteristics of these metal ions. The sensor performance was

analysed with 1 ppm of chromium ion solution with respect to 50 ppm of other metal ion solutions.

[0066] Selectivity of the ZIF-67 coated probes for Cr^{6+} ion detection was investigated by challenging the sensor with thirteen potential interfering heavy metal ions each at 50 ppm. The absorbance spectral responses obtained from each of these heavy metals (at 50 ppm) reveal a considerable interference from Mn^{7+}, Fe^{3+}, Co^{2+}, and Cu^{2+}. The spectral absorbance response was at 13%, 8%, 4%, and 3% with reference to the response obtained for Cr^{6+} at 1 ppm. While the Mn^{7+} and Fe^{3+} ions show their characteristic peak at 432 nm and 407 nm respectively, no significant absorbance at 395 nm was observed in case of other heavy metal ions. These possible interferences for Mn^{7+} and Fe^{3+} ions could be attributed to their potential adsorption to the ZIF-67 matrix mainly because of the comparable molecular weight of Mn, and Fe (55 and 56 amu respectively) with reference to that of chromium (52 amu). Except for Mn^{7+} and Fe^{3+} ions, the ZIF-67 coated probes show high selectivity towards Cr^{6+} ions.

[0067] **Environmental water collection and comparison with ICP-MS**: The polluted water samples were collected from various industrial, residential, and agricultural sites located within the city of Chennai in India. A total of five chromium contaminated sites (each site sampled thrice) were identified and the chromium ion levels were quantified using inductively coupled plasma mass spectroscopy (ICP-MS) (Perkin Elmer, NexION 300X). The samples were diluted with ultrapure water and then acidified using 2% HNO_3 to remove volatile substances. The samples were then filtered through 0.22 μm syringe filters prior to ICP-MS analysis (Argon plasma source; flow rate = 18 L/min). The calibration standards were prepared using multi-element standard solutions. The ZIF-67 coated sensor probes were subjected to 150 μL of these acidified samples. The sensor responses were recorded with LED-photodetector set-up. The recovery rate is estimated based on the calibration curves generated for these sensors.

[0068] **Shelf-life studies:** The sensor probes were prepared by offline exposure of hydroxylated fibers to 150 μL of ZIF-67 growth solution over 5 minutes, and then dried

in hot air oven for 15 minutes at 70°C. They were stored in an air-tight container (without accounting for moisture sensitivity) over a month. The sensitivity of the probes after each week was recorded with chromium ion solutions in the range of 50 to 1000 ppb.

[0069] **Results and Discussion:** Stable ZIF-67 films over U-bent fiber optic probes: Prior to realizing ZIF-67 films over an optical fiber surface by *in-situ* deposition, ZIF-67 was prepared in solution phase and its characteristic optical absorption spectra were verified as shown in FIG. 3A. To obtain ZIF-67 thin film formation over the U-bent silica optical fiber via *in-situ* crystallization approach, the probes were dipped in freshly prepared growth solution in a microcentrifuge tube. The enhanced EWA phenomenon in the U-bent fiber optic probes was exploited to monitor the physisorption of ZIF-67 to the fiber probe surface using a fiber optic spectrometer. The EWA spectra recorded from bare and HCl/MeOH treated hydroxyl-rich silica fiber probes dipped in freshly prepared ZIF-67 precursor solution. Interestingly, MOF adsorbed to hydroxyl-rich U-bent probes alone as revealed by the photographic images and the EWA spectra that matches with that of ZIF-67 solution as shown in FIG. 3B and FIG. 3C. In contrast to the absorption spectral characteristic of ZIF-67 in solution phase with a peak wavelength at 589 nm that corresponds to the characteristic absorption of cobalt ions caused by d-d band transitions, a red-shifted peak at 605 nm was consistently obtained in all the experiments. The red-shift in the characteristic peak could be attributed to the change in chromogenecity of the cobalt ions in ZIF-67 due to their interaction with silica surface.

[0070] Real-time monitoring of the formation of MOF film over the sensor surface at 605 nm wavelength shows a quick binding of MOF to the probe surface within 10 min as illustrated in FIG. 3D. An abrupt rise in the absorbance within 30 s followed by only a moderate increase over the next 5 min was evident pointing to the complete surface coverage of ZIF-67 film growth. To investigate the stability of the ZIF-67 film, the probe was immediately washed with DI water while recording the optical response from the probe. A significant drop in the absorbance response was observed as shown in FIG. 3D.

This indicates almost a complete desorption of ZIF-67 from the silica surface due to poor adhesion.

[0071] In order to improve the adhesion of ZIF-67 to the probe surface, the probes were simply withdrawn from the MOF growth solution after 10 minutes of incubation and subjected to a thermal treatment by placing them in a hot air oven at 70°C for 15 minutes. Subsequently, the MOF coated probes with and without thermal treatment were evaluated for adhesion by dipping them in DI water. No desorption was observed while monitoring their absorbance spectral and temporal characteristics unlike the probes without the thermal treatment. This technique has significantly helped in achieving consistent production of working probes. Thus, the hydroxylated U-bent fiber optic sensor probes coated with ZIF-67 and further subjected to a post-thermal treatment were identified as the optimum working probes and were used for subsequent studies.

[0072] ZIF-67 based Cr^{6+} ion sensing - Proof-of-concept studies: Prior to the proof-of-the-concept studies, the UV-visible absorption spectrum of Cr^{6+} ions was obtained from an aqueous solution of K2Cr2O7 (100 ppm). The characteristic absorption spectrum of Cr^{6+} ions shows a peak at 372 nm as shown in FIG. 3E. To establish the detection of Cr^{6+} ions using ZIF-67 coated U-bent probes, the EWA spectral studies were performed for three different concentrations of Cr^{6+} ions in the range of 1 to 50 ppm. Bare U-bent probes were used as control for these experiments (DI water was taken as reference). FIG. 4 shows the EWA spectral response with a characteristic absorbance peak at 395 nm due to Cr^{6+} adsorption that increases with the Cr^{6+} ion concentrations, in contrast to a null response from the bare probes. This result demonstrates the potential of MOF coated U-bent fiber optic sensor probes for chromium ion detection. The red-shift in the characteristic absorbance peak from 372 nm to 395 nm could be attributed to the chromogenecity of Cr^{6+} ions, when there occurs an ion exchange between surface hydroxyl groups of ZIF-67 and Cr^{6+} ion.

[0073] A pertinent observation from the absorbance spectral response was the significant baseline shift during the binding of ZIF-67 as shown in FIG. 3A and

subsequently Cr^{6+} ions as shown in FIG. 4, in addition to their characteristic absorbance. Similar observations were made in our previous work on the U-bent probes coated with graphene oxide film. By the virtue of probe geometry, the U-bent probes are known for their high sensitivity to refractive index (RI) changes at the core surface, as a result of optical losses due to the refraction of the light from the bent fiber core. Here, an effective increase in the RI is anticipated upon the formation of ZIF-67 matrix on the U-bent probe surface (with reference to DI water) due to the metallo-organic nature of the polymer film. A similar change is expected with the subsequent process of Cr^{6+} ion adsorption/entrapment to ZIF-67. (Note: the refractive index of ZIF-67 growth solution and chromium solution (100 ppm) were found to be 1.62 and 1.74 RI units, respectively.) Thus, the baseline shift in the absorbance can be attributed to the refractive losses caused by the ZIF-67 film and Cr^{6+} ion adsorption. While further studies are necessary to quantify the RI of the films for a detailed understanding, since the aim of the study is to realize a chromium ion detection using ZIF-67, the subsequent studies mainly focus on the realization of a highly sensitive chromium ion sensor.

[0074] Consequently, surface morphology and elemental composition of U-bent probes coated with ZIF-67 alone and subsequently treated with Cr^{6+} ion solution (10 ppm) were investigated. The corresponding SEM images are shown in FIG. 5A and FIG. 5B. No considerable change in the morphology of ZIF-67 matrix was observed upon Cr^{6+} ion adsorption/entrapment. However, the EDAX analysis shows an anticipated elemental composition of ZIF-67 matrix on the silica probe surface that includes the presence of cobalt, carbon, silicon and oxygen and the presence of chromium element for the probe subjected to Cr^{6+} ion solution as illustrated in FIG. 6A and FIG. 6B.

[0075] Optimization of ZIF-67 coating for Cr^{6+} sensing: ZIF-67 coating over the fiber probe was optimized to realize a Cr^{6+} sensor with high sensitivity. The peak absorbance of the ZIF-67 at 605 nm wavelength ($A_{605\ nm}$) was taken as reference to modulate the ZIF-67 coating over the probe surface. The fiber optic probes with $A_{605\ nm}$ values equal to 0.1, 0.2, 0.5 and 1.0 were obtained by either controlling the incubation

time (for 0.1, 0.2 and 0.5) or tripling the volume of the growth solution (500 µL, for 1.0). Spectral characteristics of these ZIF-67 coated sensor probes is shown in FIG. 7. Subsequently, these sensor probes were exposed to 1, 10 and 50 ppm of Cr^{6+} solutions and the respective absorbance spectral response was recorded for 10 minutes as illustrated in FIG. 8A-8D. FIG. 9A shows representative spectra obtained from these probes subjected to 50 ppm Cr^{6+} solution. An improved characteristic absorption due to Cr^{6+} binding was observed with an increase in ZIF-67 coating till $A_{605\ nm}$ equal to 0.5.

[0076] FIG. 9B illustrates the influence of ZIF-67 coating over the probes on the ability to detect Cr^{6+} ions. The sensor probes coated with ZIF-67 with $A_{605\ nm}$ equal to 0.1 and 0.2 show a poor sensitivity in comparison to that of $A_{605\ nm}$ equal to 0.5 and 1.0. The ZIF-67 coated probes with $A_{605\ nm}$ value of 0.5 gave rise to a linear response with a minimal standard deviation in comparison to that of A605 nm = 1.0. In addition, the probes with A605 nm = 0.5 are advantageous due to lower optical extinction by the ZIF-67 layer and hence better availability of optical power for Cr^{6+} ion detection, leading to an improved signal to noise ratio (SNR). These results suggest ZIF-67 coating with A605 nm = 0.5 as optimum for Cr^{6+} ion detection over the range of interest. To fabricate a large number of probes consistently with A605 nm = 0.5 without the need for an online monitoring, an effective ZIF-67 coating protocol was realized to carry out offline deposition. The sensor probes dipped in 150 µL of ZIF-67 growth solution were found to achieve a quick saturated deposition, with the A605 nm values reaching 0.5 over 5 minutes. All the subsequently studies were carried out using the ZIF-67 coated probes obtained by following this protocol.

[0077] Selectivity of ZIF-67 coated U-bent probes for Cr^{6+} detection: Selectivity of the ZIF-67 coated probes for Cr^{6+} ion detection was investigated by challenging the sensor with thirteen potential interfering heavy metal ions each at 50 ppm as illustrated in FIG. 6. The absorbance spectral responses obtained from each of these heavy metals (at 50 ppm) reveal a considerable interference from Mn^{7+}, Fe^{3+}, Co^{2+}, and Cu^{2+} (Fig. S7). The spectral absorbance response was at 13%, 8%, 4%, and 3% with reference to

the response obtained for Cr^{6+} at 1 ppm. While the Mn^{7+} and Fe^{3+} ions show their characteristic peak at 432 nm and 407 nm respectively as illustrated in FIG. 10A, FIG. 10B, no significant absorbance at 395 nm was observed in case of other heavy metal ions. These possible interferences for Mn^{7+} and Fe^{3+} ions could be attributed to their potential adsorption to the ZIF-67 matrix mainly because of the comparable molecular weight of Mn, and Fe (55 and 56 amu respectively) with reference to that of chromium (52 amu). Except for Mn^{7+} and Fe^{3+} ions, the ZIF-67 coated probes show high selectivity towards Cr^{6+} ions as illustrated in FIG. 10C.

[0078] Realization of ZIF-67 coated fiber optic Cr^{6+} sensor: With an aim to realize a hand-held device for chromium sensing using the ZIF-67 coated optical fiber, the set up was improvised by replacing Halogen lamp/ fiber optic spectrometer with a pair of narrow band LED (peak at 380 nm) and photodetector. A LED-PD based set-up is known also to improve the sensitivity and analyte detection limits of the sensor. All the subsequent studies in this paper were carried out using LED-PD set-up.

[0079] The sensor response to the Cr^{6+} ion solutions prepared in DI water and municipal tap water was evaluated. The temporal response of the sensor over 10 minutes dipped in Cr^{6+} ion solutions prepared in DI water (1 ppb to 100 ppm) and municipal tap water (5 ppb to 10 ppm) are presented in FIG. 11A and FIG. 11B, respectively. The saturated sensor response was observed within 5 minutes for the Cr^{6+} concentration below 0.5 ppm. FIG. 11C shows the sensor dose response curves for log concentrations of Cr^{6+} in tap water and DI water derived from the absorbance values obtained at the end of 10 minutes. The sensor response in DI water was found to be linear over the range 1 – 5 ppb and 5 ppb – 100 ppm with a sensitivity of 0.011 A_{395nm} /log (ppb) (R^2=0.98) and 0.152 A_{395nm} /log (ppb) (R^2=0.99) respectively as shown in FIG. 11D. Based on the experimental data, the sensor response for 1 ppb was distinguishable from that of the DI water (blank signal response) (SD=0.003, n≥5). With a confidence level of 95%, the limit of detection (LoD) estimated as thrice the standard deviation of the sensor response in DI and tap water upon the slope of dose response curve ($3\sigma/S$) is found to be 1 ppb

and 1.5 ppb, respectively. The recoveries for spiked tap water sensitivity falls within the acceptable range of 92%. The lower sensitivity for the spiked tap water could be attributed to the interference from dissolved ions and change in pH. The sensor performance is compared with the other chromium ion sensing techniques reported in literature as listed in Table. 1.

Table 1: Optical Sensing Techniques Reported for Cr^{6+} ion

Sensing method	**Sensing medium/device**	**Sensing material**	**LOD (ppb)**	**Linear range (ppb)**
Luminescence	Paper strip	Cd-MOF	320	-
	Solution	MOR-2	4	5-50
	Paper strip/smartphone camera	GSH*-AuNC	6	-
	Solution	$CaF_2:Eu^{3+}$	148	-
	Solution	Zn(II)-MOF	96	-
Fluorescence	Solution	BUT-28 MOF	36	-
	Solution	Zn(3-ALPy)(TMA)#	140	-
	Solution	PANI/Ag(AMPSA)/GO QDs NC&	6	10-7500
Absorbance	Paper based/optical scanner	BSA-AuNP/STCP@	20	37-3700
	Paper based/smartphone camera	TDA/AuNP^	0.5	0.7-1600
	Laser-PD/POC	C-AgNP	26	10-700
	Solution	AA/AgNP~	4	6-136
	Solution	DF/Au	0.32	0.32-100
	FBG	PATAC/hydrogel+	10	10-100
	Microfluidic spectroscopy	DPC	7	-
Proposed Method	**U-FOS/LED-PD**	**ZIF-67**	**1**	**5-100,000**

*GSH-Glutathione Capped gold nanoclusters; #Zn(3-ALPy)(TMA) – Zinc /3-pyridinecarboxaldehyde/trimesic acid; & PANI/Ag(AMPSA)/GO QDs NC - Polyaniline/Ag nanoparticles/ graphene oxide nanocomposite; @STCP- Silanization-titanium dioxide modified filter paper ; ^ TDA – 2,2′-thiodiacetic acid; ~AA – ascorbic acid; +PATAC - 3-arylamidopropyltrimethylammoniumchloride

[0080] U-bent FOS based Cr^{6+} sensor – Evaluation with real samples: The performance of the sensor was evaluated by challenging with real samples collected from select chromium contamination sites across Chennai, India. The Cr^{6+} concentration in the samples were calculated based on the sensor response and the calibration curve obtained for tap water. These values were compared with that obtained from the gold-standard ICP-MS technique. For the samples with Cr^{6+} ions less than 10 ppb, the estimated values were in good agreement with the ICP-MS results and its quantitative recovery was found to be within a range of 96-118% (summarized in Table. 2). Particularly for the sample 5 with a very high Cr^{6+} concentration as estimated obtained from ICP-MS, the quantitative recovery was found to be overestimated. This could be attributed to a potential interference in the sensor response caused by the presence of other impurities in the sewage samples. These results indicate the applicability of U-bent FOS for the determination of Cr^{6+} ions in water samples.

Table. 2: The ICP-MS results of the samples and the quantitative recovery

Sample No	ICP MS Concentration (ppd)	ZIF-67/FOS (ppb)	Recovery (%)
1	4.21	4.04	95.961±0.28
2	6.57	6.33	95.88±0.31
3	7	6.08	86.82±0.37
4	8.01	8.22	102.6±0.38
5	440	516	117.7±4.25

[0081] **Shelf-life studies:** The stability of the sensor stored under the ambient conditions was evaluated by quantifying the absorbance response over a period of one month at an interval of 7 days. The probes were tested with 5 different Cr^{6+} concentrations in the range of 50 ppb to 1000 ppb. The lowest concentration in this study was chosen as 50 ppb since it is the MCL (maximum contamination limit) of hexavalent chromium in water as per safety guidelines of WHO. A dose response was obtained from at least 3 sensors for each week and their sensitivity calculated using linear regression.

The sensitivity of probes from week 1 to week 4 were compared by taking the sensitivity of the freshly prepared probes as a reference as shown in FIG. 12. No considerable drop in the sensitivity was observed over the 4 weeks of storage under the ambient conditions illustrated in FIG. 13. However, a small increase (up to 4%) in the standard deviation of the sensitivity of the probes was observed with the storage. This suggests the sensor probes are stable and reliable for the given period (even with humid-free storage conditions not taken care of).

[0082] **Conclusion:** A ZIF-67 coated U-FOS for highly selective chromium (VI) sensor is successfully realized. A reproducible and scalable process for a stable ZIF-67 coating over the U-FOS was established. ZIF-67 selectively entrap Cr^{6+} ions and the high EWA sensitivity of the U-FOS allows specific detection of Cr^{6+} ions by means of their intrinsic optical absorption around 395 nm. The developed sensor demonstrates high selectivity for chromium ion detection with respect to other potential interfering heavy metal ions present in water such as Mn^{7+}, Fe^{3+}, Co^{2+}, Cl^{-}, Cu^{2+}, Pb^{2+}, Hg^{2+}, Mg^{2+}, Ca^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+}, Li^{+}. The ZIF-67 coated U-FOS Cr^{6+} sensor realized with a portable LED-photodetector set-up not only demonstrates a wide dynamic range and useful detection limits, but also manifests the potential to develop a handheld device. The sensor probes stored under normal ambient conditions were stable for at least 4 weeks without any significant loss in the sensitivity. The sensor performance was at par with that of the standard techniques for heavy metal ion quantification such as ICP-MS.

[0083] On a broader note, the study demonstrates the feasibility of U-FOS as a potential sensor platform for either colorimetry or refractive index change based detection of chemicals. This sensing strategy of utilizing a MOF as a chemical receptor over the fiber probe can suitably be adopted for detection of many other heavy metals and chemicals.

WE CLAIM:

1. A method of fabricating a silica optical probe for Cr^{6+} detection comprising:

fabricating a U-bent silica optic fiber probe (201) having a first end, a second end and a U-bent region;

activating an outer surface of the U-bent region (202) to generate hydroxyl groups on the surface;

growing a metal organic framework (MOF) (203) comprising zeolite imidazole (ZIF-67) on the outer surface by dipping the outer surface in a solution consisting of cobaltous nitrate hexahydrate and 2-methyl imidazole; and

providing post-thermal treatment (204) to the coated probe.

2. The method as claimed in claim 1, wherein the ZIF-67 is synthesized in an aqueous medium at room temperature conditions.

3. The method as claimed in claim 1, wherein the coating of ZIF-67 on silica optical fiber comprises an in-situ deposition method.

4. The method as claimed in claim 1, wherein activating the outer surface comprises cleaning the U-bent optical fiber by either heating and sonicating the U-bent region in acetone or treating the U-bent region in HCl and methanol at a ratio of 1:1 for a predetermined time of 15 minutes.

5. The method as claimed in claim 1, wherein the absorbance of ZIF-67 is at least 0.25 OD at 605 nm.

6. The method as claimed in claim 1, wherein the optimum condition for ZIF-67 comprises coating the U-bent region with growth solution made of 0.515 M cobaltous nitrate and 8.45 M 2-methyl imidazole and incubating the U-bent probe region for at least 3 minutes.

7. The method as claimed in claim 1, wherein the post-thermal treatment comprises heating the coated probe at a temperature in the range 70°C-75°C for 15 minutes.

8. An optical probe (100) for detecting Cr^{6+} comprising:
an U-bent silica optic fiber probe (101) having a first end (103), a second end (105) and a U-bent region (110); and
a metal organic framework (MOF) comprising zeolite imidazole (ZIF-67) (111) coated on an outer surface of the U-bent region (110).

9. The optical probe as claimed in claim 8, wherein the optical fiber is a multimode fiber with its core diameter at least 50 μm.

10. The optical probe as claimed in claim 8, wherein the selectivity of Cr^{6+} ions is 400 times or more over other potentially interfering heavy metals.

11. The optical probe as claimed in claim 8, wherein the ZIF-67 coated U-bent fiber optic sensor are stable at room temperature with less than 5% loss of sensitivity at least for 4 weeks.

12. The optical probe as claimed in claim 8, wherein the detection range of Cr^{6+} ions is 5 – 100,000 ppb.

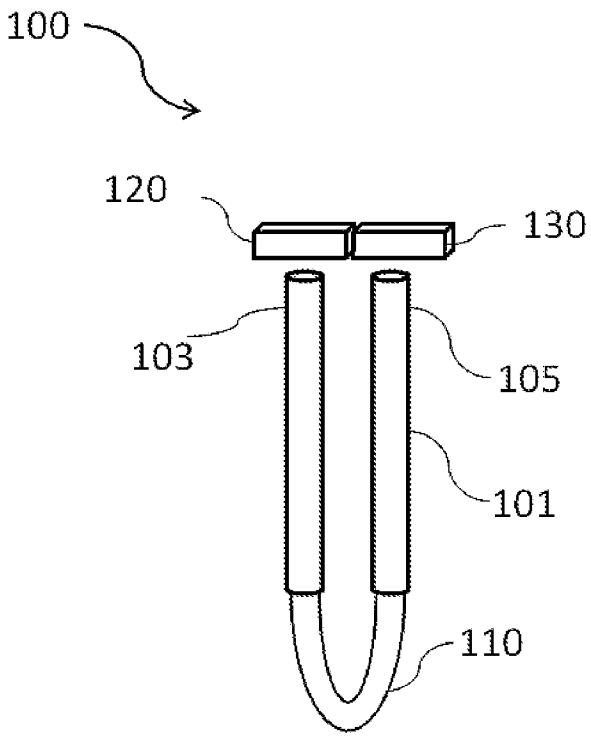


FIG. 1A

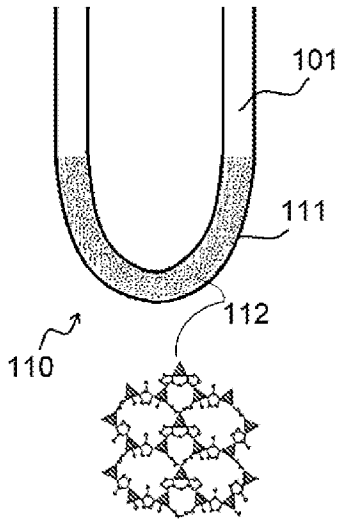


FIG. 1B

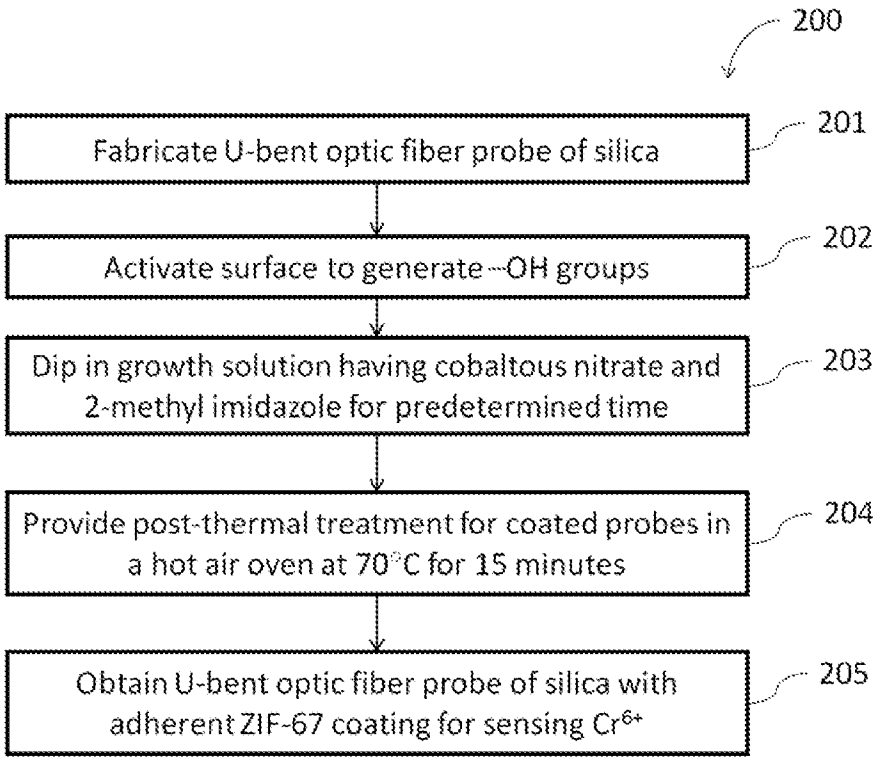


FIG. 2

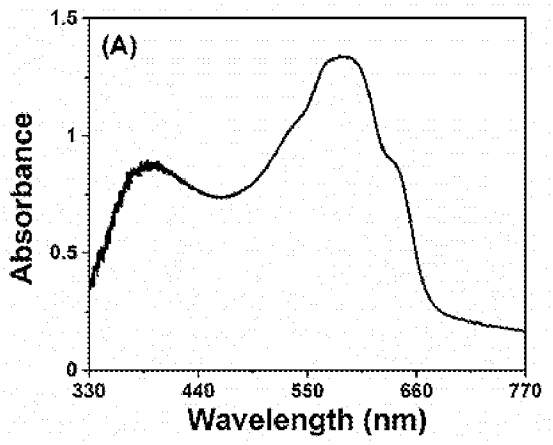


FIG. 3A

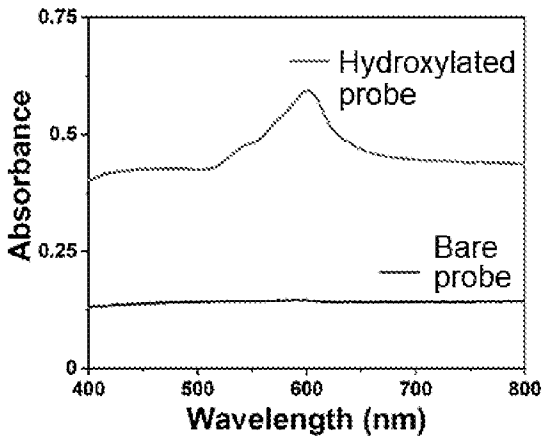


FIG. 3B

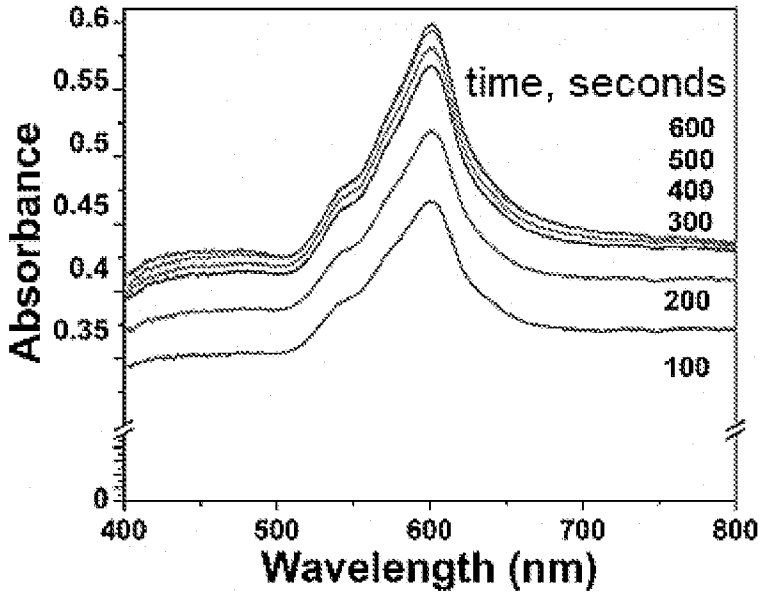


FIG. 3C

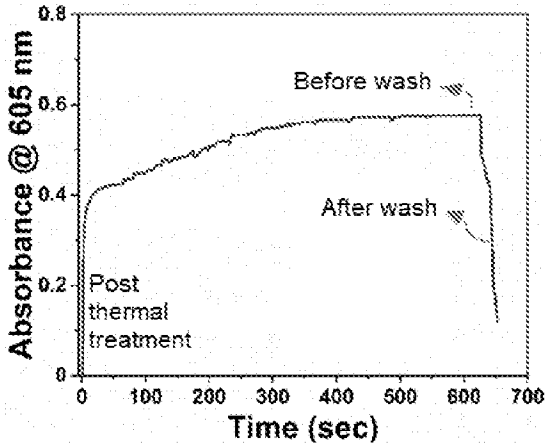


FIG. 3D

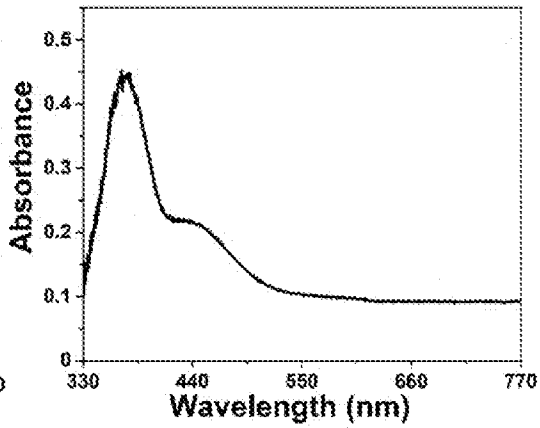


FIG. 3E

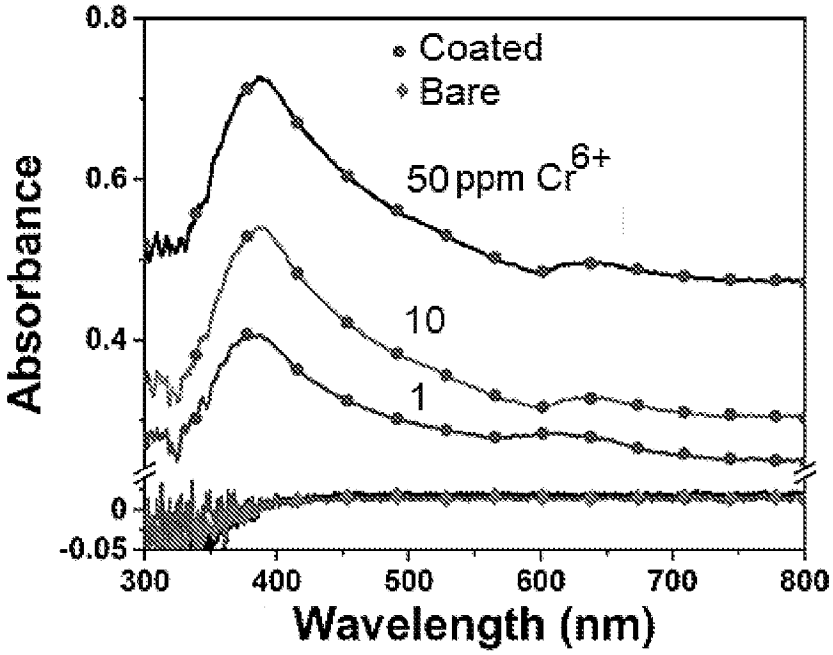


FIG. 4

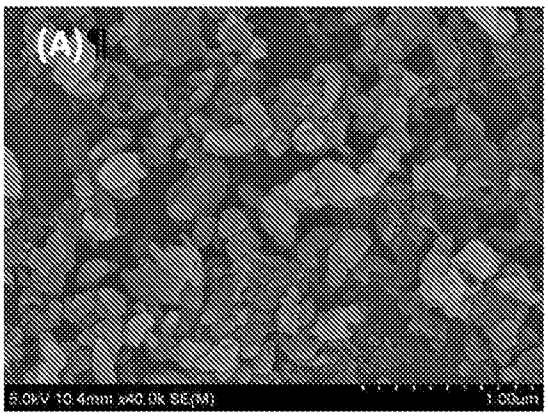


FIG. 5A

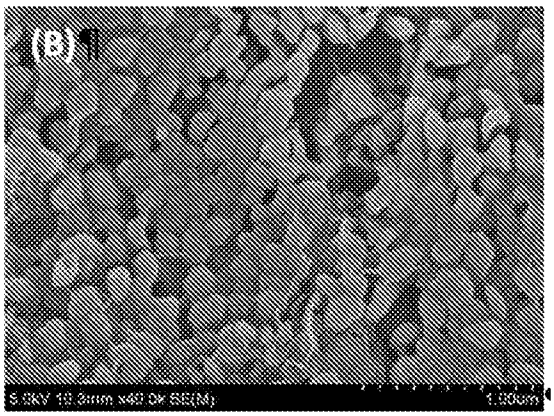


FIG. 5B

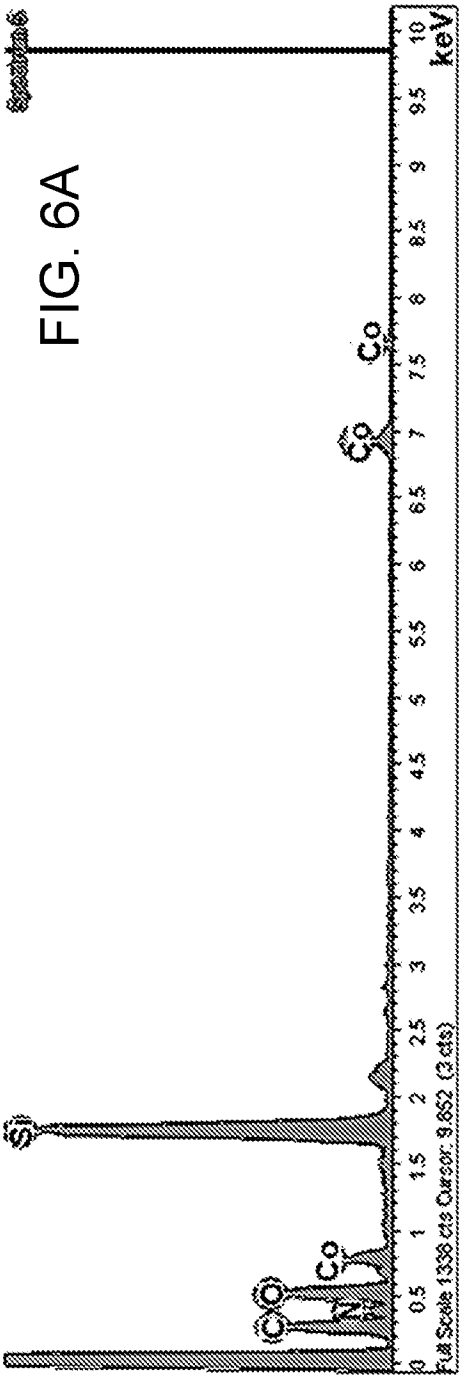
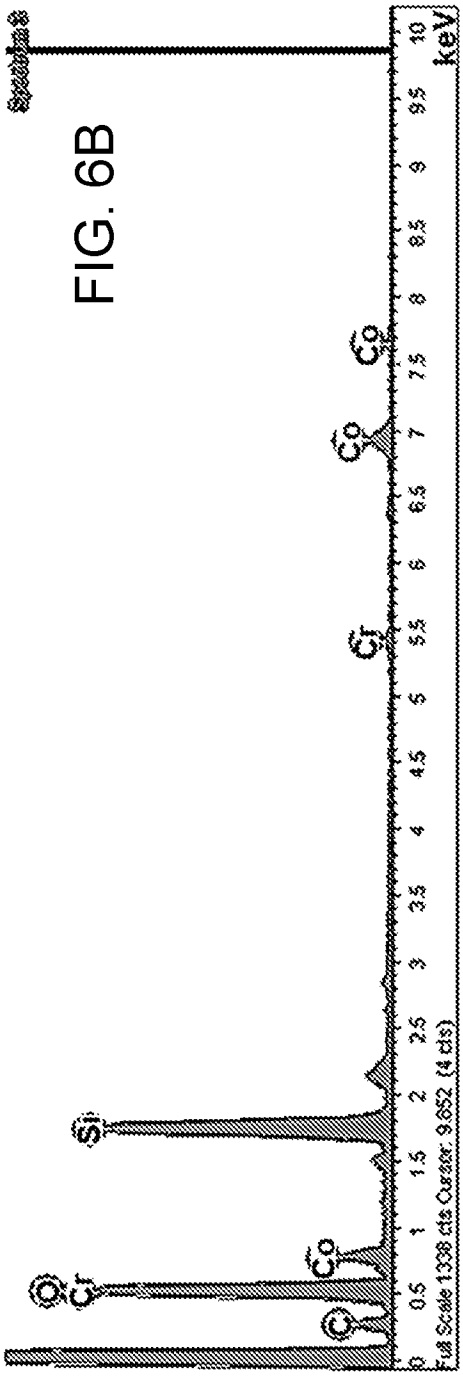

Si
Co
Co
Co
keV
Full Scale 1338 cts Cursor: 9.852 (3 cts)

FIG. 6A


Si
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Cr
Cr
keV
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FIG. 6B

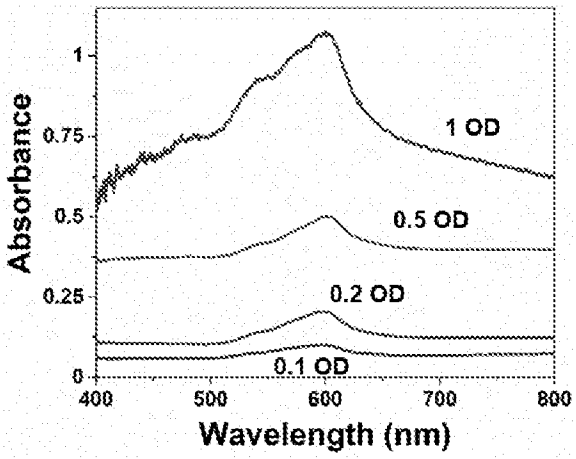

FIG. 7

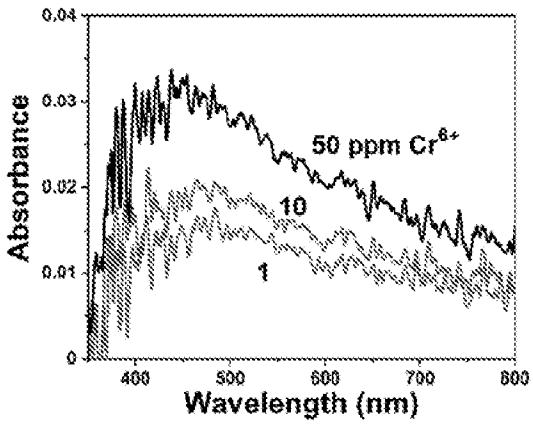

FIG. 8A

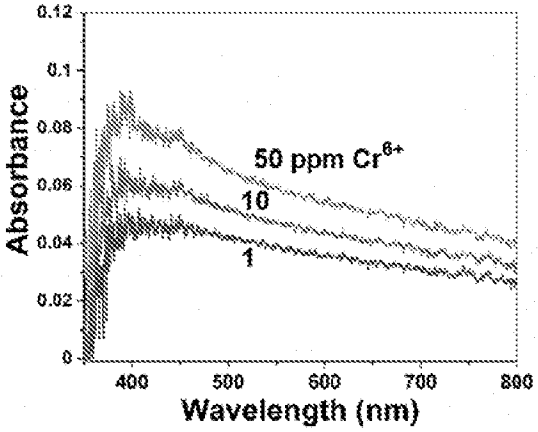

FIG. 8B

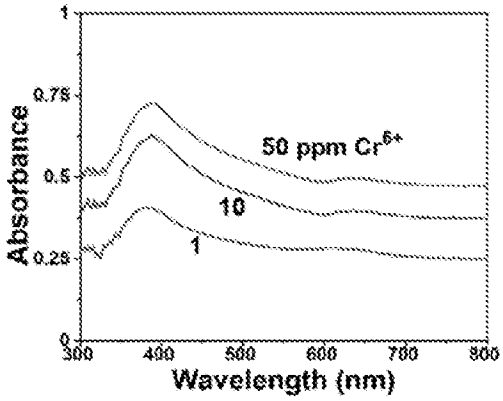

FIG. 8C

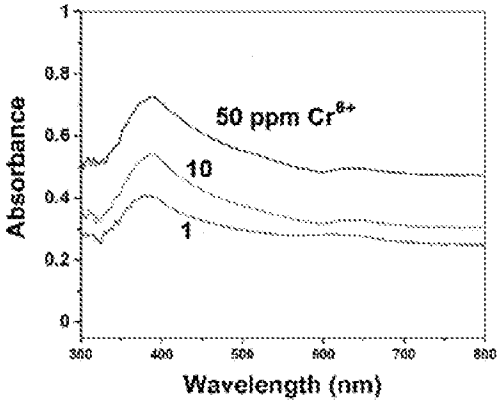

FIG. 8D

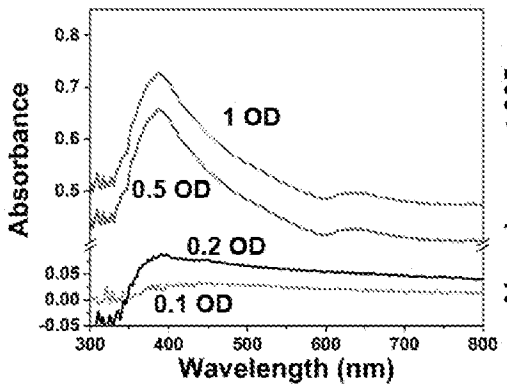

FIG. 9A

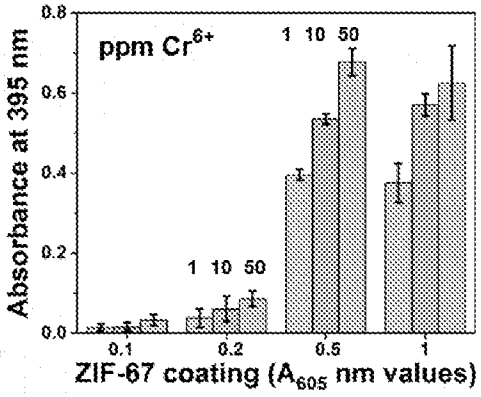

FIG. 9B

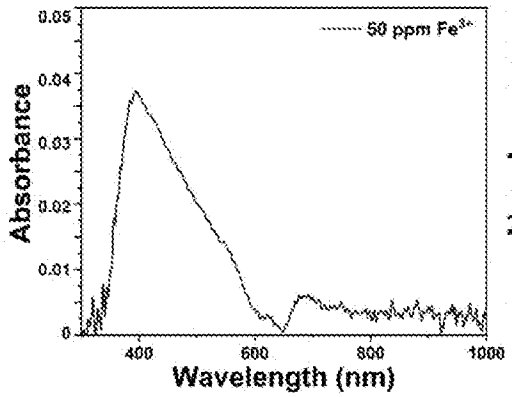

FIG. 10A

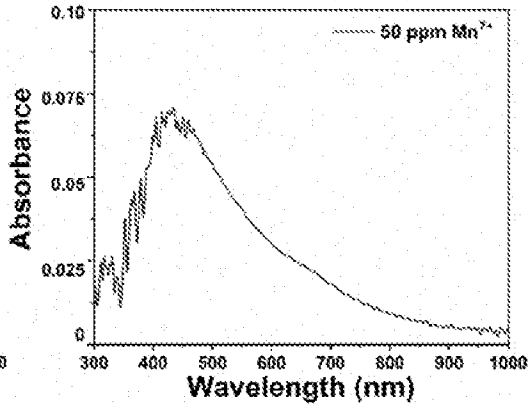

FIG. 10B

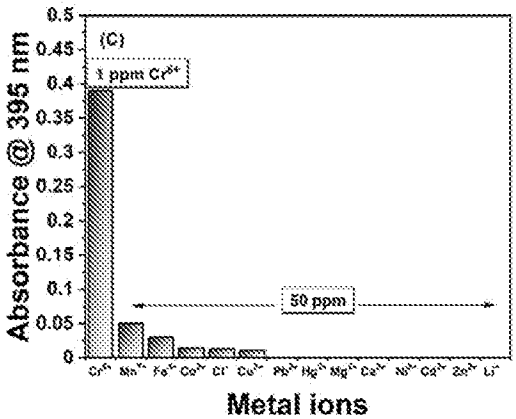

FIG. 10C

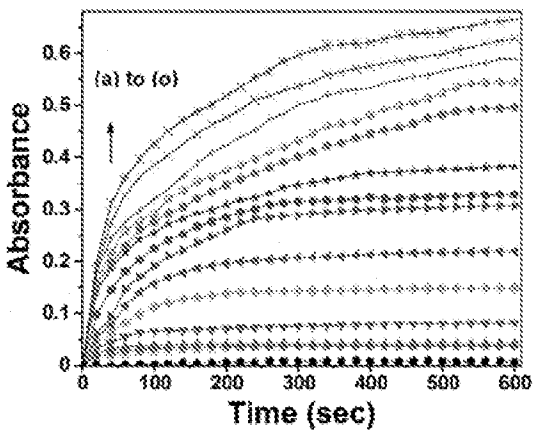

FIG. 11A

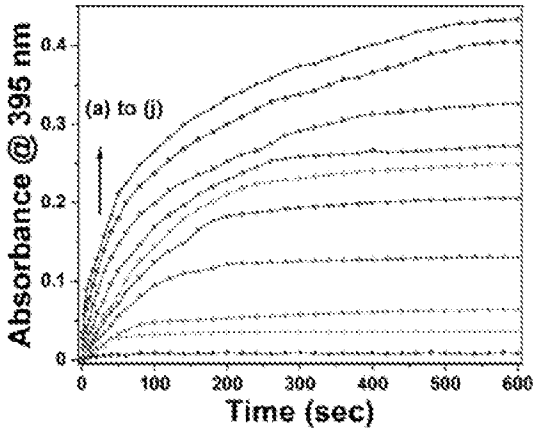

FIG. 11B

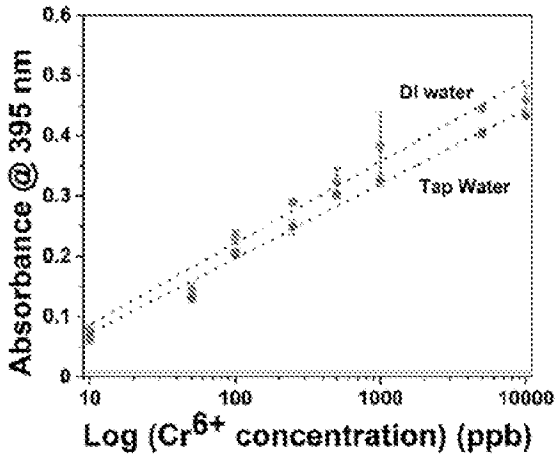

FIG. 11C

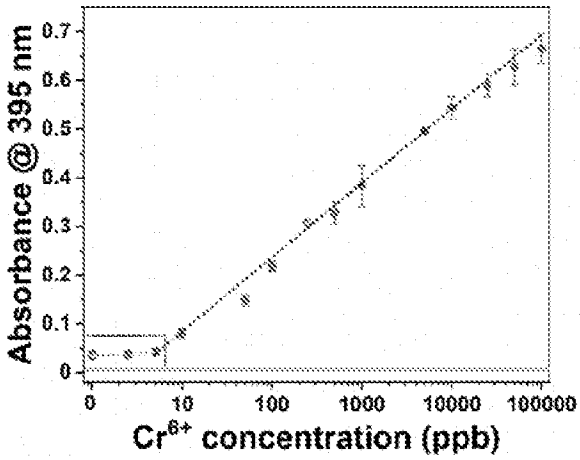

FIG. 11D

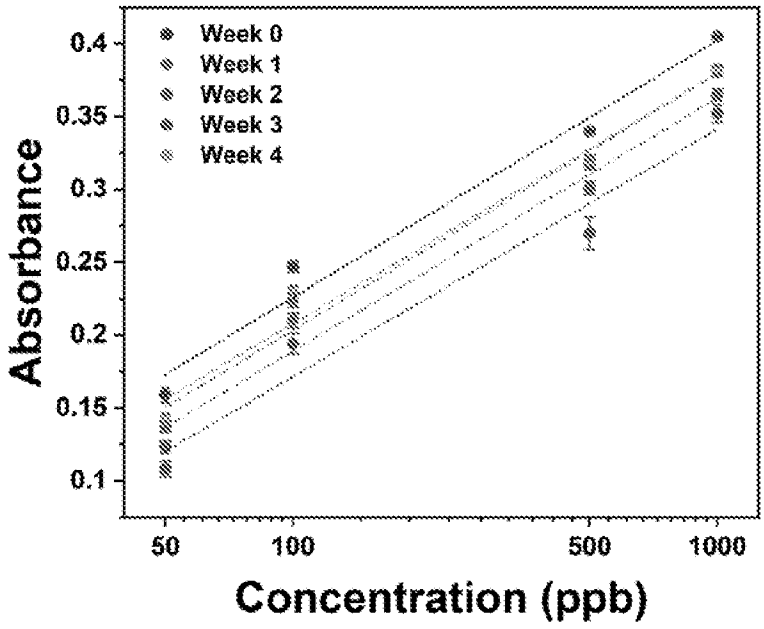
Week 0
Week 1
Week 2
Week 3
Week 4
Absorbance
0.4
0.35
0.3
0.25
0.2
0.15
0.1
50
100
500
1000
Concentration (ppb)

FIG. 12

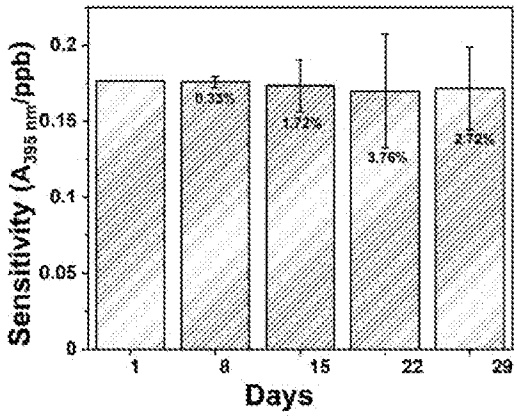
Sensitivity ($A_{395\ nm}$/ppb)
0.2
0.15
0.1
0.05
0
0.33%
1.72%
3.76%
3.72%
1
8
15
22
29
Days

FIG. 13

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IN2022/050375

A. CLASSIFICATION OF SUBJECT MATTER
C02F101/22,H01L51/42 Version=2022.01

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C01F, H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

PatSeer, IPO Internal Database

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	E. J. A. Pope; "Fiber optic chemical microsensors employing optically active silica microspheres"; Advances in Fluorescence Sensing Technology II, Volume 2388, pages 245-256; doi:10.1117/12.208484; 08 May 1995 (08/05/1995) pages 245-256	1-12
A	N. K. Sompalli et. al., "Tailor-made porous polymer and silica monolithic designs as probe anchoring templates for the solid-state naked eye sensing and preconcentration of hexavalent chromium"; Sensors & Actuators: B. Chemical 298 (2019) 126896, https://doi.org/10.1016/j.snb.2019.126896; 01 November 2019 (01/11/2019) pages 3-6	1-12

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
21-07-2022	21-07-2022
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