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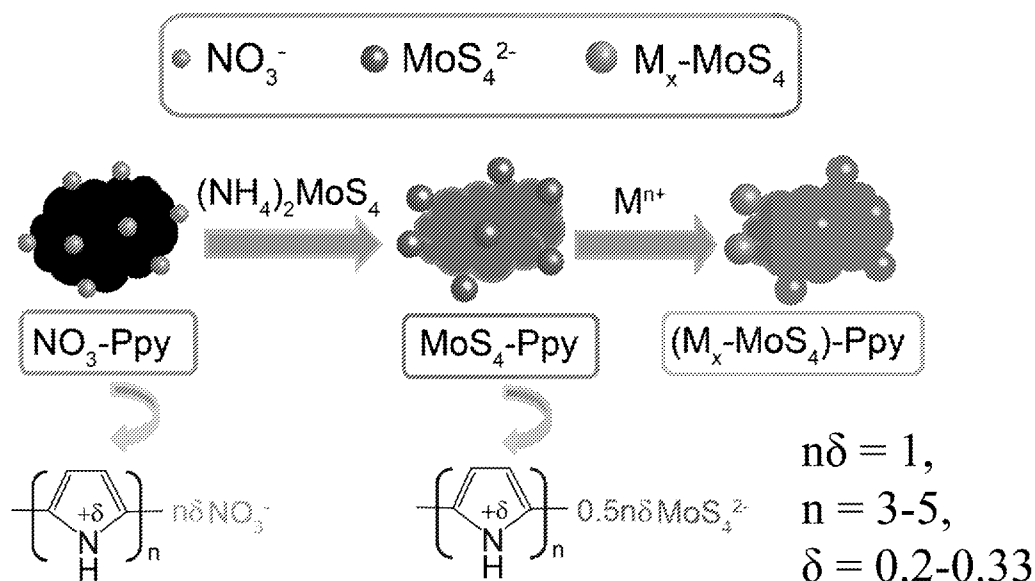
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(54) Title: THIOANION-FUNCTIONALIZED POLYPYRROLES FOR METAL ION CAPTURE

FIG. 9



(57) Abstract: Polypyrrole polymers functionalized with thioanions and methods for their use in metal capture applications are provided. Also provided are methods for making the polypyrroles using anion exchange techniques. The thioanion-functionalized polypyrroles have a conjugated, positively charged backbone of pyrrole units that is charge-balanced with associated thioanions.

THIOANION-FUNCTIONALIZED POLYPYRROLES FOR METAL ION CAPTURE**CROSS-REFERENCE TO RELATED APPLICATIONS**

[0001] The present application claims priority to U.S. provisional patent application number 62/599,316 that was filed December 15, 2017, the entire contents of which are hereby incorporated herein by reference.

REFERENCE TO GOVERNMENT RIGHTS

[0002] This invention was made with government support under DMR-1104965 awarded by the National Science Foundation. The government has certain rights in the invention.

BACKGROUND

[0003] Pollution by heavy metal ions from a wide variety of sources is a global environmental issue. Some heavy metal ions such as mercury (Hg) and lead (Pb) are extremely hazardous water pollutants because of high toxicity and carcinogenicity to living organisms, resulting in detrimental effects on the human nervous, blood circulation, immune, and reproductive systems. Silver (Ag), on the other hand, is an important industrial and precious metal, used for various applications such as electronics, catalysis, medical, and sensing materials. It exists in several raw ores such as manganese-silver ore, some natural gold-bearing ores, and complex sulfidic copper mines. Silver also exists in micro-amounts in chalcopyrite (CuFeS_2) and galena (PbS), which are widespread ores. Although a one-step process has been developed for the extraction of high-grade silver mineral resources, recovery from low-grade silver ores is of considerable interest because of rapid depletion of high-grade ones and rising demands for silver. (*See, Jiang, T., et al., Hydrometallurgy* **2003**, *69* (1-3), 177-186.)

[0004] Polypyrrole (Ppy) is a prototypical low cost conductive polymer, and its derivatives have been studied intensely in various fields such as sensors, electrodes, and batteries. Ppy can be easily synthesized by the oxidative polymerization of pyrrole using mild oxidants, and the resulting polymer chains carry positive charges which are neutralized by counter anions (usually nitrate, chloride, perchlorate, and sulfate) which are incorporated into the growing conjugated polymer chain. Recently, a series of Ppy-based materials have been obtained by functionalizing with dodecyl sulfate or octadecyl sulfate, which were utilized as

adsorbents for removing deoxyribonucleic acid (DNA) and proteins. (See, Saudi, B., *et al.*, *Synthetic Met.* 1997, 87 (2), 97-103; and Zhang, X., *et al.*, *Sep. Purif. Technol.* 2006, 52 (1), 161-169.) Ppy composites can also be prepared simply by coating Ppy on the surface of solid substrates such as glass, cloth, paper as powders, fibers, wood, and sawdust (SD). Ppy composites have been reported for metal ion removal from aqueous solutions. (See, Mahmud, H. N. M. E., *et al.*, *RSC Adv.* 2016, 6 (18), 14778-14791.) For example, Ppy/SD was reported to be an efficient sorbent for Cr(VI), relying on the anion exchange property of Ppy. (See, Ansari, R., *et al.*, *React. Funct. Polym.* 2007, 67(4), 367-374.) The magnetic nanocomposite of Ppy/Fe₃O₄ was demonstrated to be an adsorbent with an enhanced capacity for Cr(VI) capture. (See, Bhaumik, M., *et al.*, *Hazard. Mater.* 2011, 190 (1-3), 381-390.)

SUMMARY

[0005] Polypyrrole polymers functionalized with thioanions, such as molybdenum tetrasulfide, and methods for their use in metal capture applications are provided.

[0006] A thioanion-functionalized polypyrrole comprises: a conjugated, positively charged backbone of pyrrole units; and charge-balancing thioanions associated with the conjugated, positively charged backbone of pyrrole units.

[0007] A molybdenum tetrasulfide-functionalized polypyrrole comprises: a conjugated, positively charged backbone of pyrrole units; and charge-balancing MoS₄²⁻ anions associated with the conjugated, positively charged backbone of pyrrole units.

[0008] An embodiment of a method of removing metal ions from a sample comprising the metal ions, comprises: exposing a thioanion-functionalized polypyrrole to the sample, wherein metal ions are adsorbed by the thioanion-functionalized polypyrrole; and removing the thioanion-functionalized polypyrrole and the absorbed metal ions from the sample.

[0009] Other principal features and advantages of the invention will become apparent to those skilled in the art upon review of the following drawings, the detailed description, and the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] Illustrative embodiments of the invention will hereafter be described with reference to the accompanying drawings, wherein like numerals denote like elements.

[0011] **FIG. 1A – 1E.** (FIG. 1A) IR and (FIG. 1B) Raman spectra of (trace a) NO₃-Ppy precursor and (trace b) MoS₄-Ppy, X-ray photoelectron spectra (XPS) with the deconvolution of corresponding XPS peaks of (FIG. 1C) Mo 3d and (FIG. 1D) S 2p in MoS₄-Ppy, (FIG. 1E) Scanning electron microscope (SEM) image of MoS₄-Ppy.

[0012] **FIG. 2A – 2D.** Adsorption kinetics curves for Mⁿ⁺ (Mⁿ⁺ = Ag⁺, Pb²⁺, Hg²⁺) by MoS₄-Ppy: (FIG. 2A) Concentration change following contact time, (FIG. 2B) Removal rate as a function of contact time, (FIG. 2C) Sorption capacity (q_t) with contact time, (FIG. 2D) Pseudo-second-order kinetic plots for the sorption.

[0013] **FIG. 3A and 3B.** Sorption isotherms for sorption of Ag⁺ by MoS₄-Ppy under strong acid (SA) condition. Langmuir equilibrium isotherms were derived from equilibrium concentration (C_e , ppm), plotted against the adsorption capacity (FIG. 3A) q (mg/g) and (FIG. 3B) C_e/q_e (g/L).

[0014] **FIG. 4A – 4D.** Adsorption kinetics curves for Ag⁺ and Hg²⁺ by MoS₄-Ppy under strong acid: (FIG. 4A) concentration change following contact time, (FIG. 4B) removal % as a function of contact time, (FIG. 4C) sorption capacity (q_t) with contact time, (FIG. 4D) pseudo-second-order kinetic plots.

[0015] **FIG. 5.** pH effect on the removal rates of Ag⁺ and Pb²⁺ by MoS₄-Ppy.

[0016] **FIG. 6A – 6D.** Selectivity towards Ag⁺ and Cu²⁺ by MoS₄-Ppy at (FIG. 6A, FIG. 6C) weak acid (pH~5) and (FIG. 6B, FIG. 6D) strong acid cases (pH~1): (FIG. 6A, FIG. 6B) bar graph of removal rates and (FIG. 6C, FIG. 6D) plots of $SF_{Ag/Cu}$ (K_d^{Ag}/K_d^{Cu}) as a function of $n(Cu^{2+})/n(Ag^+)$.

[0017] **FIG. 7A – 7C.** (FIG. 7A) The X-ray diffraction (XRD) patterns (FIG. 7A trace a) before and after MoS₄-Ppy adsorbed (FIG. 7A trace b, FIG. 7A trace c) Cu²⁺, (FIG. 7A trace d – FIG. 7A trace f) Ag⁺, (FIG. 7A trace g – FIG. 7A trace i) Pb²⁺, and (FIG. 7A trace j, FIG. 7A trace k) Hg²⁺ at various concentrations, and comparison of XRD patterns at slow scan rates of (FIG. 7B) 200 ppm Pb²⁺ adsorbed sample and (FIG. 7C) 1200 ppm Ag⁺ and standard patterns of PbMoO₄ and Ag₂S.

[0018] **FIG. 8A – 8L.** X-ray photoelectron spectra with the deconvolution of XPS peaks of samples of the MoS₄-Ppy after adsorbed (FIG. 8A, FIG. 8B, FIG. 8C) 1200 ppm Cu²⁺, (FIG. 8D, FIG. 8E, FIG. 8F) 1200 ppm Ag⁺, (FIG. 8G, FIG. 8H, FIG. 8I) 1200 ppm Pb²⁺, and (FIG. 8J, FIG. 8K, FIG. 8L) 500 ppm Hg²⁺, respectively.

[0019] **FIG. 9.** Schematic diagram showing metal ion remediation by MoS₄-Ppy.

[0020] **FIG. 10A and 10B.** Sorption isotherms for sorption of (FIG. 10A) Pb²⁺ and (FIG. 10B) Hg²⁺ by MoS₄-Ppy. Langmuir equilibrium isotherms were derived from equilibrium concentration (*C_e*, ppm), plotted against the adsorption capacity (*q*, mg/g).

[0021] **FIG. 11A and 11B.** (FIG. 11A) IR spectra of (FIG. 11A trace a) NO₃-Ppy, (FIG. 11A trace b) MoS₄-Ppy, and solid samples after MoS₄-Ppy adsorbed higher concentrations of (FIG. 11A trace c, FIG. 11A trace c') Cu²⁺, (FIG. 11A trace d, FIG. 11A trace d') Ag⁺, (FIG. 11A trace e, FIG. 11A trace e') Pb²⁺, and (FIG. 11A trace f) Hg²⁺; (FIG. 11B) IR spectra of (FIG. 11B trace a) NO₃-Ppy, (FIG. 11B trace b) MoS₄-Ppy, and solid samples after MoS₄-Ppy adsorbed 10 ppm of (FIG. 11B trace c) Co²⁺, (FIG. 11B trace d) Ni²⁺, (FIG. 11B trace e) Cu²⁺, (FIG. 11B trace f) Zn²⁺, (FIG. 11B trace g) Ag⁺, (FIG. 11B trace h) Pb²⁺, (FIG. 11B trace i) Cd²⁺, (FIG. 11B trace j) Hg²⁺, and (FIG. 11B trace k) their mixed solution. IR spectra of the Mⁿ⁺ adsorbed samples presented similar peaks with the original MoS₄-Ppy. The intensity of the 1383 cm⁻¹ band (NO₃⁻) had little change at low Mⁿ⁺ concentrations. However, with the increasing initial concentration of metal ions, the intensity of the 1383 cm⁻¹ band was remarkably enhanced, which can be interpreted that more NO₃⁻ entered for the charge balance of the polymer matrix with the increasingly adsorbed amount of the metal ions.

[0022] **FIG. 12A and 12B.** (FIG. 12A) IR spectra (FIG. 12A trace a) before and (FIG. 12A trace b) after MoS₄-Ppy was soaked in strong acidic solution (H₂O/HNO₃, pH~1) for 24 h. (FIG. 12B) UV-Vis absorption spectra of (FIG. 12B trace a) NaNO₃ solution (50 mg was dissolved in 100 mL H₂O) for comparison, and (FIG. 12B trace b) the supernatant of strong acid-suffered sample of MoS₄-Ppy.

[0023] **FIG. 13A – 13E.** Solid sample after MoS₄-Ppy adsorbed 1500 ppm Ag⁺ under strong acid condition (pH = 0.60): (FIG. 13A) XRD patterns, (FIG. 13B) IR spectra, and X-ray photoelectron spectra with the deconvolution of corresponding XPS peaks of (FIG. 13C) Mo 3d, (FIG. 13D) S 2p, and (FIG. 13E) Ag 3d.

DETAILED DESCRIPTION

[0024] Polypyrrole polymers functionalized with thioanions and methods for their use in metal capture applications are provided. Also provided are methods for making the polypyrroles using anion exchange techniques.

[0025] Thioanion-functionalized polypyrroles polymers have a conjugated, positively charged backbone of pyrrole units that is charge-balanced with associated thioanions. Thioanions that can be used as charge-balancing anions include metal-containing anions and non-metal-containing anions, for example, molybdenum thioanions, antimony thioanions, tin thioanions, tungsten thioanions, and phosphorus thioanions. Specific examples include molybdenum tetrasulfide MoS_4^{2-} , $\text{Mo}_3\text{S}_{13}^{2-}$, SbS_3^{3-} , SbS_4^{3-} , S_x^{2-} , wherein $x = 1, 2, 3, 4, 5$, or 6 , SH^{1-} , $\text{Sb}_2\text{S}_4^{4-}$, SnS_4^{4-} , $\text{Sn}_2\text{S}_6^{4-}$, $\text{Sn}_4\text{S}_{10}^{4-}$, WS_4^{2-} and $\text{PS}_{4-x}\text{O}^{3-}$, wherein ($x = 1, 2$, or 3). The thioanions can be provided in the form of a salt (e.g. an ammonium salt, an alkali metal salt) or other soluble form of the thioanion.

[0026] In particular, the molybdenum tetrasulfide-functionalized polypyrroles polymers, which are referred to herein as $\text{MoS}_4\text{-Ppy}$, have a conjugated, positively charged backbone of pyrrole units that is charge-balanced with associated MoS_4^{2-} anions. The structure of the $\text{MoS}_4\text{-Ppy}$ is shown in FIG. 9, where $\delta (= 0.20\text{-}0.33)$ is the doping density, n is the average number of pyrrole monomers in the polypyrrole that contain one unit of positive charge (with $n\delta = 1$ and n typically in the range from 3 to 5). NO_3^- and MoS_4^{2-} are the counteranions. The thioanion-functionalized polypyrroles can be made by carrying out an anion-exchange reaction between a polypyrrole precursor that is charge balanced with NO_3^- ions or other precursor anions, such as Cl^- and ClO_4^- , as demonstrated in the Example.

[0027] In methods for metal capture, a sample containing one or more types of metal ions is exposed to the thioanion-functionalized polypyrrole, whereby the metal ions are adsorbed. The thioanion-functionalized polypyrrole, along with the adsorbed metal ions, can then be removed from the sample. The metal ions can then be removed (e.g., desorbed) from the thioanion-functionalized polypyrrole to regenerate the polypyrrole for re-use. For example, hydrochloric acid or nitric acid could be used to regenerate the polypyrrole. In acidic conditions, the polypyrrole may combine with H^+ and release the adsorbed metal ions. By filtration or centrifugation, the polypyrrole solids may be separated. Then through adjusting the pH and ion exchange reactions, the thioanion-functionalized polypyrrole may be regenerated for re-use.

[0028] Thioanion-functionalized polypyrroles, such as $\text{MoS}_4\text{-Ppy}$, are characterized by high acid stability and the ability to adsorb a variety of metal ions from a metal ion-containing sample in acidic aqueous solutions. Acidic pH ranges over which metal ions can be adsorbed by the thioanion-functionalized polypyrroles include a pH range from 0.5 to 6.

This includes adsorption from samples having a pH of 5 or lower, 4 or lower, 3 or lower, 2 or lower, and 1 or lower. The metal ions that can be adsorbed include transition metal ions and, in particular, Hg^{2+} , Ag^+ , Cu^{2+} , Pb^{2+} , Cr^{6+} , Tl^+ , and/or Cd^{2+} ions. Thioanion-functionalized polypyrroles, such as $\text{MoS}_4\text{-Ppy}$, have high adsorption capacities for a variety of metals ions, including Hg^{2+} , Ag^+ , Cu^{2+} , Pb^{2+} , Cr^{6+} , Tl^+ , and/or Cd^{2+} ions and can remove these ions from an aqueous solution quickly. By way of illustration, 95 weight percent (wt.%) or greater of Hg^{2+} , Ag^+ , Cu^{2+} , and/or Pb^{2+} ions can be removed from an aqueous sample in a period of 5 minutes or less using $\text{MoS}_4\text{-Ppy}$, even when the initial sample contains substantial amounts of one or more of these ions – for example when the initial sample has a concentration of one or more of these ions in the range from about 10 ppm to about 3000 ppm.

[0029] Because the rates of metal ion adsorption and the adsorption capacity of the thioanion-functionalized polypyrroles are dependent on solution pH, the pH of the solution can be adjusted to tailor the selectivity of the metal ion adsorption. For example, for certain metal ions, such as silver ions, adsorption is favored at low pH (e.g., pH from ~ 0.5 to ~ 4.5), relative to the adsorption of other metal ions, such as copper ions. As a result, the silver ions can be selectively removed from a sample containing both silver and copper ions when the removal process is conducted at a sufficiently low pH. By way of illustration, the selective removal of silver from a sample containing silver and copper can be carried out at a pH in the range from 0.2 to 1.5, including in the range from about 0.5 to 1.

[0030] In the metal capture applications, the thioanion-functionalized polypyrrole can be provided in particulate form and loaded onto a porous support substrate to facilitate the introduction of the thioanion-functionalized polypyrrole into, and removal from, a sample. Alternatively, the thioanion-functionalized polypyrrole can be packed into a column through which the sample is passed.

[0031] Examples of aqueous samples from which metal ions can be removed using the thioanion-functionalized polypyrroles include drinking water and waste water generated from an industrial plant or from mining processes, such as ore leaching. For example, the thioanion-functionalized polypyrroles can be used to recover silver from silver-containing ores, including low-grade silver ores.

[0032] In the example that follows, anion exchange-based methods of making a molybdenum thioanion-functionalized Ppy and methods of removing metal ions from a sample using the molybdenum thioanion-functionalized Ppy are described. However, it

should be understood that the procedures described in the example can also be used to make and use Ppy functionalized with other thioanions, such as antimony thioanion-functionalized Ppy, tin thioanion-functionalized Ppy, and phosphorus thioanion-functionalized Ppy, by substituting the appropriate thioanion in the anion exchange reaction.

[0033] Unless otherwise indicated, temperature- and/or pressure-dependent values disclosure herein refer to those values at room temperature (23 °C) and atmospheric pressure.

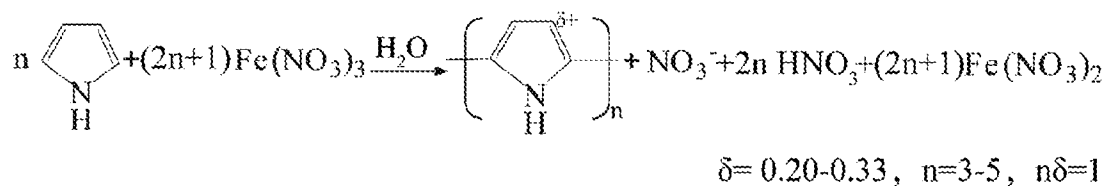
EXAMPLE

[0034] In this example, the synthesis of a Ppy material functionalized with the MoS_4^{2-} ions and its capture ability towards heavy metal ions is described. The MoS_4 -Ppy material exhibited excellent uptake capacity and highly selective removal for Ag^+ , Hg^{2+} , and Pb^{2+} , especially in strongly acidic conditions ($\text{pH} \approx 1$). MoS_4 -Ppy also displayed remarkable selectivity for Ag^+ over Cu^{2+} both in weakly acidic and strongly acidic conditions, making it useful for the direct separation and extraction of silver from low-grade copper minerals. Thus, because of its surprisingly strong chemical stability, MoS_4 -Ppy is an exceptional adsorbent for the remediation of heavy metal polluted water under both weak and strong acidic conditions.

Experimental section

[0035] **Synthesis of NO_3 -Ppy precursor.** NO_3 -Ppy precursor was synthesized *via* a readily oxidation-polymerization method using Fe^{3+} salts as the oxidant and deionized water as solvent. As formed, the pyrrole conjugated backbone is partially oxidized and charge balanced with NO_3^- ions from $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. (See, Zhang, X., *et al.*, *Langmuir* 2003, 19(26), 10703-10709.) The oxidative reaction is shown in Scheme 1, below.

[0036]



Scheme 1. Oxidative reaction of pyrrole doped with NO_3^- .

In detail, 0.69 mL pyrrole (0.01 mol) was firstly mixed with 94 mL deionized water, then an amount of 50 mL $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution (0.023 mol) was added dropwise, with magnetic

stirring in the dark for 24 h. A black precipitate was formed immediately and isolated with filtration, washed several times with deionized water and ethanol, and vacuum dried for about 8 h. Determined by elemental CHN analyses, the as-obtained $\text{NO}_3\text{-Ppy}$ product had a composition of $(\text{C}_4\text{H}_5\text{N})(\text{NO}_3)_{0.25}$.

[0037] Preparation of $\text{MoS}_4\text{-Ppy}$. $\text{MoS}_4\text{-Ppy}$ was prepared by an ion-exchange reaction between the NO_3^- of $\text{NO}_3\text{-Ppy}$ and the MoS_4^{2-} of $(\text{NH}_4)_2\text{MoS}_4$. In detail, 0.15 g of $\text{NO}_3\text{-Ppy}$ was dispersed in 5 mL deionized water with ultrasonic treatment. Then, the $(\text{NH}_4)_2\text{MoS}_4$ solution (0.45 g $(\text{NH}_4)_2\text{MoS}_4$ was dissolved in 10 mL deionized water) was added dropwise into the above dispersion. The mixture was stirred for 72 h to ensure complete ion-exchange. Consequently, 0.275 g of black $\text{MoS}_4\text{-Ppy}$ was obtained by filtration, washing thoroughly and vacuum drying for 24 h. The composition was determined using CHN and Mo analysis by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

[0038] Heavy metal uptake experiments. Adsorption experiments were conducted with solutions of various concentrations containing single metal ions or their mixtures using a batch method. Eight metal ions of Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Ag^+ , Pb^{2+} , Cd^{2+} , and Hg^{2+} were obtained from their nitrate salts. 0.02 g $\text{MoS}_4\text{-Ppy}$ solid was mixed with 20 mL ($V/m = 1000$ mL/g) of each solution and stirred for 6 h. After the adsorption experiments were completed, centrifugation was conducted, and the solid samples were dried in air for further characterization. Meanwhile, the supernatant solutions and their mother solutions were all analyzed using ICP-AES as well as inductively coupled plasma-mass spectroscopy (ICP-MS) for extra low metal ion concentrations.

[0039] Selectivity uptakes towards metal ions (Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Ag^+ , Pb^{2+} , Cd^{2+} , and Hg^{2+}). A solution including the mixture of metal ions (~ 10 ppm for each ion) was used for the study of relative selectivity. The same V/m value of 1000 mL/g and similar operation conditions were used for proper comparison.

[0040] For relative selectivity studies towards Ag^+ , Pb^{2+} and Hg^{2+} under both weak and strong acidic conditions, solutions containing a mixture of Ag^+ , Pb^{2+} and Hg^{2+} were prepared at the concentration of ~ 20 ppm for each ion. For the strong acid case, the as-prepared mixed solution was then adjusted to $\text{pH} \approx 1$ using 0.1 M HNO_3 . Very small amounts of $\text{MoS}_4\text{-Ppy}$ (0.002 g and 0.004 g) were used with 20 mL of the Ag^+ , Pb^{2+} , and Hg^{2+} solutions (V/m is 10000 or 5000 mL/g) and stirred for 6 h.

[0041] For determining the selectivity for Ag^+ and Cu^{2+} under both weak and strong acid conditions, a series of solutions with Ag^+ and Cu^{2+} were prepared. The initial Ag^+ concentration was fixed to ~ 1 ppm in each mixture, and the concentrations of Cu^{2+} were designed to ~ 1 , ~ 2 , ~ 5 , ~ 10 , ~ 20 ppm, respectively, and the local pH values were about 5.3–5.6, meaning the weak acidic condition. For the strong acid case, solutions were prepared as above and then the pH values were adjusted to ~ 1 using 0.1 M HNO_3 . An amount of 0.02 g $\text{MoS}_4\text{-Ppy}$ solid was added to 20 mL ($V/m = 1000$ mL/g) of each solution and stirred for 24 h.

[0042] Equilibrium adsorption isotherm studies for Cu^{2+} , Ag^+ , Pb^{2+} , and Hg^{2+} . The concentrations of the Cu^{2+} , Ag^+ , Pb^{2+} , and Hg^{2+} ions were in the range of 10–2000 ppm to ensure adsorption equilibration was achieved. An amount of 0.02 g $\text{MoS}_4\text{-Ppy}$ powder added in 20 mL solution was used to have a V/m value of 1000 mL/g. The contact time was about 24 h.

[0043] Adsorption kinetics of Ag^+ , Pb^{2+} and Hg^{2+} . An amount of 0.04 g $\text{MoS}_4\text{-Ppy}$ powder was added into the 40 mL ($V/m = 1000$ mL/g) solution with a concentration of ~ 10 ppm, undergoing vigorous stirring continuously for 1 min, 5 min, 10 min, 30 min, 1 h, 3 h, and 6 h. The contact time was varied to check the adsorption kinetics.

[0044] pH effect on the uptake of Ag^+ , Pb^{2+} and Hg^{2+} . Ag^+ solutions with different concentrations adjusted to strong acid condition ($\text{pH} \approx 1$) using 0.1 M HNO_3 were prepared for determining the sorption capacity and kinetics. For Pb^{2+} and Hg^{2+} , the sorption kinetics were measured under strong acid condition ($\text{pH} \approx 1$) using concentrations of ~ 10 ppm for each ion. Solutions of single ions of Ag^+ and Pb^{2+} with a fixed concentration of ~ 20 ppm and varying pH values from 0.5 to 6.0 were prepared for further studies of the pH effect on capture efficiency (% removal). The results obtained of this section involved three parts: (1) sorption capacity of Ag^+ ; (2) sorption kinetics of Ag^+ , Pb^{2+} and Hg^{2+} , respectively; and (3) capture efficiency of Ag^+ and Pb^{2+} within a broad pH range of 0.5 to 6.0. The amount of $\text{MoS}_4\text{-Ppy}$, volume of each solution, and contact time were the same as described above.

[0045] Adsorption capability of $\text{NO}_3\text{-Ppy}$ towards heavy metals. These were carried out as control experiments since this material does not contain MoS_4^{2-} ions. A solution containing eight metal ions together at an initial concentration of ~ 10 ppm for each, and solutions containing single Cu^{2+} , Ag^+ , Pb^{2+} , and Hg^{2+} , were prepared for uptake experiments.

An amount of 0.02 g NO₃-Ppy powder was mixed with 20 mL (V/m = 1000 mL/g) solution and underwent stirring for 6 h.

[0046] Chemical stability of MoS₄-Ppy in strong acid conditions. An amount of 0.1 g MoS₄-Ppy powder was added into a 20 mL H₂O/HNO₃ solution and the pH value was adjusted to 1.0. After 24 h stirring, the solids were isolated and dried for IR spectroscopy and CHN analyses. The supernatant solution was used for UV-Vis spectroscopic analysis.

[0047] Data treatment. The distribution coefficient (K_d) is defined by the equation of $K_d = (V[(C_0 - C_f)/C_f])/m$, where C_0 and C_f are respectively the initial and equilibrium concentrations of M^{n+} (ppm, $\mu\text{g/mL}$) after the contact, V is the solution volume (mL), and m is the solid amount (g). The % removal is calculated with the equation of $100 \times (C_0 - C_f)/C_0$. The removal capacity (q_m) is given by the equation: $q_m = 10^{-3} \times (C_0 - C_f) \cdot V/m$. In general, the adsorption experiments were performed with $V:m$ ratios of 1000 mL/g at ambient temperature.

[0048] Characterization techniques. The XRD patterns of solid samples were collected using a PANalytical X'pert Pro MPD diffractometer with Cu-K α radiation at room temperature, with step size of 0.0167°, scan time of 10s per step, and 2θ ranging from 4.5 to 70°. Fourier transformed infrared (FT-IR) spectra of the samples were recorded on a Nicolet-380 Fourier-Transform infrared spectrometer using the KBr pellet method. Raman spectra were recorded from 100 to 2000 cm^{-1} on a microscopic confocal Raman spectrometer (LabRAMAramis Horiba Jobin Yvon), using a 532 nm He-Ne laser. SEM and Energy disperse spectroscopy (EDS) measurements were carried out using a Hitachi S-4800 microscope. XPS of the solid samples after the adsorption experiments were performed using an ESCALAB 250Xi spectrometer (Thermofisher). The peaks were fitted using the software Advantage.

[0049] The metal ion contents in solid samples were determined by ICP-AES (Jarrel-Ash, ICAP-9000), and a 0.1 M HNO₃ solution was used to dissolve them. The metal ion concentrations in supernatant solutions before and after adsorptions were measured using ICP-AES technique and for extra low concentrations, inductively coupled plasma-mass spectroscopy (ICP-MS, NexION 300X) was used. C, H and N contents of the solid samples were determined using an Elementar Vario EL elemental analyzer. The chemical formulas of the samples were determined from the results of ICP and CHN elemental analyses. The pH of

the solutions was monitored before after the adsorption using a Sartorius universal type pH meter (PB-10).

Results and discussion

[0050] Synthesis and characterization of Ppy-based materials. The NO₃-Ppy polymer precursor was synthesized *via* oxidative polymerization using pyrrole and Fe(NO₃)₃. Here NO₃⁻ ions from Fe(NO₃)₃·9H₂O were retained to maintain the electroneutrality of the partially oxidized polymer conjugated backbone. The MoS₄-Ppy was prepared by an ion-exchange reaction of NO₃-Ppy with a solution of (NH₄)₂MoS₄. Based on ICP and CHN analyses, the stoichiometric compositions of NO₃-Ppy and MoS₄-Ppy were (C₄H₃N)·(NO₃)_{0.25}·0.5H₂O and (C₄H₃N)(MoS₄)_{0.12}(NO₃)_{0.01}·2.8H₂O (see Table 11). The four pyrrole rings carried one positive charge in the Ppy matrix.

Table 11. Chemical compositions for the NO₃-Ppy precursor and the MoS₄-Ppy composite.

Samples	Chemical formula	Wt.%, found (calcd)			
		C	H	N	Mo
NO ₃ -Ppy	(C ₄ H ₃ N)·(NO ₃) _{0.25} ·0.5H ₂ O	53.32	3.82	19.39	-
		(53.63)	(4.47)	(19.55)	-
MoS ₄ -Ppy	(C ₄ H ₃ N)·(MoS ₄) _{0.12} (NO ₃) _{0.01} ·2.8H ₂ O	32.84	5.86	9.93	9.01
		(33.59)	(6.02)	(9.90)	(8.06)

The *found* data (experimental data) were obtained by CHN and ICP analyses, and the *calcd* data (theoretical data) were determined based on the *chemical formula* to test its rationality.

[0051] Fourier Transform Infrared (FT-IR), Raman, XPS spectroscopy and SEM were used to characterize the compositions and structure of the samples. The IR absorption bands at 1539, 1302, 1036 and 891/921 cm⁻¹ (FIG. 1A) were observed in both NO₃-Ppy and MoS₄-Ppy, corresponding to C=C stretching, ring stretching modes of Ppy, C-H in-plane deformation vibration, and C-H out-of-plane bending. Moreover, the peak at 1383 cm⁻¹ indicated the presence of NO₃⁻ anions of the NO₃-Ppy, and became extremely weak in MoS₄-Ppy (FIG. 1A trace b), revealing a nearly complete ion-exchange. The Raman spectra (FIG. 1B) show additional information about the structure of NO₃-Ppy precursor (FIG. 1B trace a) and the MoS₄-Ppy composite (FIG. 1B trace b). The main peaks at 1563, 1332, 1040, and 979 cm⁻¹ (FIG. 1B trace a) were attributed to C=C backbone stretching, ring stretching mode of Ppy, in-plane and out-of-plane vibration of N-H modes, respectively. The MoS₄-Ppy shows similar peaks (FIG. 1B trace b), as well as new peaks at 550 and 453 cm⁻¹, where the latter

peak belonged to Mo-S stretching according to reference values (477 and 457 cm^{-1}) of free $(\text{NH}_4)_2\text{MoS}_4$. The blue shift of the two peaks was likely caused by the change of chemical environment of Mo-S bonds after the insertion of MoS_4^{2-} into the Ppy structure.

[0052] The chemical states of Mo and S in $\text{MoS}_4\text{-Ppy}$ were determined by XPS spectroscopy (FIG. 1C and FIG. 1D). The spectral peaks at 235.8 eV ($\text{Mo}^{\text{VI}} 3d_{3/2}$) and 233.1 ($\text{Mo}^{\text{VI}} 3d_{5/2}$) eV (FIG. 1C) indicate the Mo^{6+} oxidation state as expected for the presence of the MoS_4^{2-} group. The weak peak at 227.8 eV (FIG. 1C) belongs to the S 2s energy. In addition, the two peaks at 165.2 (S $2p_{1/2}$) and 163.7 eV (S $2p_{3/2}$) deriving from S 2p energy represent the S^{2-} groups (FIG. 1D), and the weak peak at 168.8 eV suggests the presence of a small quantity of SO_4^{2-} impurity originating from adventitious oxidation of S^{2-} . SEM images of the $\text{MoS}_4\text{-Ppy}$ (FIG. 1E) show a granular morphology with a granule size of ~ 300 nm.

[0053] Heavy metal removal. The uptake of heavy metal ions by $\text{MoS}_4\text{-Ppy}$ from aqueous solutions of various concentrations (10-2000 ppm) was studied with the batch method at room temperature (~ 23 °C). The affinity of $\text{MoS}_4\text{-Ppy}$ for the M^{n+} ions can be expressed in terms of the distribution coefficient K_d^{M} . The adsorption behavior towards single ions of Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Ag^+ , Pb^{2+} , Cd^{2+} , and Hg^{2+} (at ~ 10 ppm initial concentration) is shown in Table 1. The removing ability is poor for Co^{2+} , Ni^{2+} , Zn^{2+} , Cd^{2+} but excellent for Cu^{2+} , Pb^{2+} , Ag^+ , and Hg^{2+} (at the local pH during the preparation of the corresponding ion solutions). For Cu^{2+} and Ag^+ , 95.9% and 98.5% removal rates were reached, respectively, and for toxic Pb^{2+} and Hg^{2+} , 99.99% removals were achieved, all of which exhibit high capture ability for these ions.

Table 1. Absorption data of $\text{MoS}_4\text{-Ppy}$ towards eight individual ions. ^a

ions	C_0 (ppm)	C_f (ppm)	Removal (%)	K_d (mL/g)
$\text{Co}^{2+ b}$	9.80	9.00	9.19	88.9
$\text{Ni}^{2+ c}$	9.36	8.51	0.09	99.9
$\text{Cu}^{2+ d}$	9.26	0.28	95.90	2.3×10^4
$\text{Zn}^{2+ e}$	8.94	8.71	2.57	26.4
$\text{Ag}^{+ f}$	7.99	0.12	98.50	6.6×10^4
$\text{Pb}^{2+ g}$	10.46	< 0.001	99.99	$> 1.1 \times 10^7$
$\text{Cd}^{2+ h}$	9.04	7.92	16.37	1.4×10^2
$\text{Hg}^{2+ i}$	11.2	< 0.001	99.99	$> 1.1 \times 10^7$

^a m = 0.02 g, V = 20 mL, V/m = 1000 mL/g; contact time: 6 h.

pH value: ^b5.13→3.34, ^c5.25→3.38, ^d4.60→3.15, ^e5.30→3.38,

^f5.11→3.17, ^g4.74→3.28, ^h5.36→3.44, ⁱ2.07→2.12.

[0054] In order to explore the competitive capture of these ions, uptake experiments were carried out on mixtures of all the eight ions (Table 2). The selectivity order was determined to be Co^{2+} , Ni^{2+} , Zn^{2+} , Cd^{2+} << Cu^{2+} < Pb^{2+} < Hg^{2+} < Ag^+ (pH~3.4, the lower pH resulted from the added nitrate acid when dissolving $\text{Hg}(\text{NO}_3)_2$). For Cu^{2+} and Ag^+ , the K_d values reached 2.2×10^4 and 1.1×10^7 mL/g, respectively, and K_d for Pb^{2+} and Hg^{2+} were $>1.2 \times 10^7$ and $>1.8 \times 10^6$ mL/g. In the mixture of ions, the removal of Ag^+ was increased (99.99 %) and the K_d^{Ag} was 170-fold ($= (1.1 \times 10^7)/(6.6 \times 10^4)$) higher than that in the single ion case. The lower pH value was deduced to favor the capture of Ag^+ , as demonstrated below in the studies of the pH effect.

Table 2. Absorption data of MoS₄-Ppy towards the mixture of eight ions.^{a,b}

single ions	C ₀ (ppm)	C _f (ppm)	Removal (%)	K_d (mL/g)
Co^{2+}	10.39	10.11	2.69	27.7
Ni^{2+}	10.56	10.40	1.52	15.4
Cu^{2+}	10.16	0.44	95.67	2.2×10^4
Zn^{2+}	15.54	14.83	4.57	47.9
Ag^+	11.09	< 0.001	99.99	$>1.1 \times 10^7$
Pb^{2+}	11.65	< 0.001	99.99	$>1.2 \times 10^7$
Cd^{2+}	11.04	10.40	5.80	61.5
Hg^{2+}	13.32	0.008	99.94	1.8×10^6

^a m = 0.04 g, V = 40 mL, V/m = 1000 mL/g; contact time: 6 h.

^b pH value: 3.41→3.05.

[0055] Relative selectivity for Ag^+ , Pb^{2+} and Hg^{2+} . As shown above, the MoS₄-Ppy captured Ag^+ , Pb^{2+} and Hg^{2+} effectively, and the K_d values reached $10^6 \sim 10^7$ mL/g (Table 2). In order to determine the relative selectivity among Ag^+ , Pb^{2+} , and Hg^{2+} , a solution containing only these three ions (~20 ppm for each ion) was investigated. In this case, decreased quantities (0.002 and 0.004 g) of the MoS₄-Ppy adsorbent were used so that the quantity was inadequate to capture all three ions. The separation factors ($\text{SF}_{\text{A/B}}$) defined by $K_d^{\text{A}}/K_d^{\text{B}}$ were used to assess the separation degree of one ion from the other. As shown in

Table 3, when using 0.002 g (1/10 of 0.02 g) MoS₄-Ppy, the $SF_{Ag/Pb}$, $SF_{Hg/Pb}$, and $SF_{Ag/Hg}$ values were about 27.0 ($= (1.7 \times 10^4) / (6.3 \times 10^2)$), 5.1 ($= (3.2 \times 10^3) / (6.3 \times 10^2)$), and 5.3 ($= (1.7 \times 10^4) / (3.2 \times 10^3)$), respectively, showing a higher selectivity for Ag⁺ and Hg²⁺ than for Pb²⁺. When 0.004 g (1/5 of 0.02 g) MoS₄-Ppy was used, the removals of Ag⁺, Hg²⁺ and Pb²⁺ were 82.8%, 62.4% and 13.6%, respectively, confirming the much higher removal efficiency for Ag⁺ and Hg²⁺ than for Pb²⁺. Thus, MoS₄-Ppy possesses its highest affinity and the most efficient removal for Ag⁺ among the three ions, following the selectivity order of Ag⁺ > Hg²⁺ > Pb²⁺.

Table 3. Selective adsorption results of MoS₄-Ppy for Pb²⁺, Ag⁺ and Hg²⁺.^a

MoS ₄ -Ppy	0.002 g ^b			0.004 g ^c		
	Ag ⁺	Pb ²⁺	Hg ²⁺	Ag ⁺	Pb ²⁺	Hg ²⁺
C ₀ (ppm)	23.9	22.1	21.0	23.9	22.1	21.0
C _f (ppm)-6 h	12.2	20.8	15.9	4.1	19.1	7.9
K _d (mL/g)-6 h	1.7×10 ⁴	6.3×10 ²	3.2×10 ³	2.4×10 ⁴	7.9×10 ²	8.3×10 ³
Removal (%)	49.0	1.4	24.3	82.8	13.6	62.4
pH-6 h	2.85→2.84			2.85→2.81		

^a 20-ml solution of AgNO₃, Pb(NO₃)₂ and Hg(NO₃)₂, 20 ppm concentration per ion.
^b V/m = 10000 mL/g, ^c V/m = 5000 mL/g

[0056] Uptake capacity towards Cu²⁺, Ag⁺, Pb²⁺ and Hg²⁺. From the results for single metal ions (Table 1) and mixtures of ions (Table 2) described above, it is clear that the MoS₄-Ppy exhibited efficient removal for Ag⁺, Hg²⁺, Cu²⁺, and Pb²⁺. Thus, the maximum adsorption capacities (q_m) towards the four ions were determined using adsorption equilibrium studies. For Ag⁺ (Table 4), drastically higher q_m^{Ag} of 480 mg/g was observed using a concentration range of 10 to 1200 ppm, showing an outstanding capacity for Ag⁺ by MoS₄-Ppy. The Ag⁺ capacity of 480 mg/g was higher than previously reported absorbents such as S_x-LDH (383 mg/g), MoS₄-LDH (452 mg/g), and KMS-2 (408 mg/g). (See, Ma, S. L., *et al.*, *J. Mater. Chem. A* 2014, 2 (26), 10280-10289; Ma, L. J.; Wang, Q., *et al.*, *J. Am. Chem. Soc.* 2016, 138 (8), 2858-2866; and Hassanzadeh Fard, Z., *et al.*, *Chem. Mater.* 2015, 27 (6), 1925-1928.) The corresponding q_m values for Pb²⁺, Cu²⁺ and Hg²⁺ were 78, 111, and 210 mg/g (Table 12-14). For the highly toxic Hg²⁺, the high removal of > 99.8 % and K_d values of 6×10^5 - 1×10^8 mL/g both indicate excellent uptake. The performance of previously reported absorbents are

listed in Table 5 for comparison. It is apparent from these results that MoS₄-Ppy exhibits a much higher sorption capacity than the reported materials.

Table 4. Sorption data of MoS₄-Ppy towards Ag⁺. ^a

C ₀ (ppm)	C _f (ppm)	Removal (%)	q_m (mg/g)	K_d (mL/g)
8.28 ^b	0.09	98.91	8.2	9.1×10^4
51.0 ^c	0.09	99.80	50.9	5.7×10^5
109 ^d	0.03	99.97	109.0	3.6×10^6
201 ^e	0.004	99.99	201.0	5.0×10^7
383 ^f	37.7	90.16	345.3	9.2×10^3
579 ^g	164	71.68	415.0	2.5×10^3
782 ^h	319	59.21	463.0	1.5×10^3
1167 ⁱ	687	41.13	480.0	28.3

^a m = 0.02 g, V = 20 mL, V/m = 1000 mL/g; Contact time: 24 h.

pH values: ^b5.64→3.79, ^c5.12→3.27, ^d4.63→3.02, ^e4.45→2.81,

^f4.90→2.75, ^g4.45→2.48, ^h4.65→2.34, ⁱ4.71→2.57.

Table 5. Adsorption capacities of various adsorbents for heavy metal ions.

	adsorbents	q_m (mg/g)	References
Cu ²⁺	MoS ₄ -Ppy	111	this work
	E. crassipes ^a	11.6/27.7	Komy, Z. R., <i>et al.</i> , <i>J. King Saud. Univ. -Sci.</i> , 2013, 25 (1), 47-56.
	EDTA-silica ^b	79	Kumar, R., <i>et al.</i> , <i>J. Colloid Interf. Sci.</i> 2013, 408, 200-205.
	MMT ^c	4.4	Ijagbemi, C. O., <i>et al.</i> , <i>J. Hazard. Mater.</i> 2009, 166 (1), 538-546.
	PEI-modified biomass ^d	92	Deng, S., <i>et al.</i> , <i>Water Res.</i> 2005, 39 (10), 2167-2177.
	Cell 2, 4 ^e	56.8/69.4	Gurgel, L. V. A., <i>et al.</i> , <i>Carbohydr. Polym.</i> 2009, 77 (1), 142-149.
	MS ^f	62.9	Lim, S. F., <i>et al.</i> , <i>Environ. Sci. Technol.</i> 2008, 42 (7), 2551-2556.
Ag ⁺	MoS ₄ -Ppy	480 (pH~5)/725 (pH~1)	this work

	APAN nanofiber mats ^g	155	Kampalanonwat, P., <i>et al.</i> , <i>ACS Appl. Mater. Interfaces</i> 2010, 2 (12), 3619-3627
	Fe ₃ O ₄ @EDTA ^h	112	Ghasemi, E., <i>et al.</i> , <i>Microchem. J.</i> 2017, 131, 51-56
	Fe ₃ O ₄ -decorated MEG-NH ₂ ⁱ	100	Ma, Y. X., <i>et al.</i> , <i>J. Nanomater.</i> 2017, 2017, 1-11.
	Nano-TiO ₂ -MBF ^j	128	Pourreza, N., <i>et al.</i> , <i>J. Ind. Eng. Chem.</i> 2014, 20 (1), 127-132.
	Cercis siliquastrum tree leave ^k	94	Zolgharnein, J., <i>et al.</i> , <i>Clean: Soil, Air, Water</i> 2013, 41 (12), 1183-1195
	MCX ^l	166	Beyki, M. H., <i>et al.</i> , <i>Ind. Eng. Chem. Res.</i> 2014, 53 (39), 14904-14912.
	S _x -LDH ^m	383	Ma, S. L., <i>et al.</i> , <i>J. Mater. Chem. A</i> 2014, 2 (26), 10280-10289.
	KMS-2 ⁿ	408	Hassanzadeh Fard, Z., <i>et al.</i> , <i>Chem. Mater.</i> 2015, 27 (6), 1925-1928.
	MoS ₄ -LDH ^o	450	Ma, L. J., <i>et al.</i> , <i>J. Am. Chem. Soc.</i> 2016, 138 (8), 2858-2866.
Pb ²⁺	MoS ₄ -Ppy	78	this work
	Cl-LDH ^p	40	Liang, X., <i>et al.</i> , <i>Colloids Surf., A</i> 2010, 366 (1-3), 50-57.
	Fe ₃ O ₄ -GS ^q	28	Guo, X., <i>et al.</i> , <i>Hazard. Mater.</i> 2014, 278, 211-220
	Ethylenediamine-modified MWCNT ^r	54	Zang, Z. P., <i>et al.</i> , <i>J. Hazard. Mater.</i> 2009, 172, 958-963.
	APAN nanofiber mats	60	Kampalanonwat, P., <i>et al.</i> , <i>ACS Appl. Mater. Interfaces</i> 2010, 2 (12), 3619-3627.
	CDpoly-MNPs ^s	64	Badrudodoza, A. Z. M., <i>et al.</i> , <i>Carbohydr. Polym.</i> 2013, 91 (1), 322-332.
	XMCS ^t	77	Zhu, Y. H., <i>et al.</i> , <i>J. Hazard. Mater.</i> 2012, 221, 155-161
Hg ²⁺	MoS ₄ -Ppy	210	this work
	Fe ₃ O ₄ -GS	23	Guo, X., <i>et al.</i> , <i>J. Hazard. Mater.</i> 2014, 278, 211-220.
	Fe ₃ O ₄ @EDTA	112	Ghasemi, E., <i>et al.</i> , <i>Microchem. J.</i> 2017, 131, 51-56.

SH-Fe ₃ O ₄ -NMPs ^u	132	Pan, S., <i>et al.</i> , <i>J. Colloid Interface Sci.</i> 2012, 365 (1), 204-212.
Carbon A, B, C ^v	174/154/134	Budinova, T., <i>et al.</i> , <i>Ind. Eng. Chem. Res.</i> 2003, 42 (10), 2223-2229.
M-ATP ^w	90	Cui, H., <i>et al.</i> , <i>Appl. Clay Sci.</i> 2013, 72, 84-90.
SWCNT-SH ^x	131	Bandaru, N. M., <i>et al.</i> , <i>J. Hazard. Mater.</i> 2013, 261, 534-541
SG-TEOS (-BTESPT and -MPTMS) ^y	41/93/102	Johari, K., <i>et al.</i> , <i>Mat. H. Can. J. Chem. Eng.</i> 2014, 92 (6), 1048-1058.

^aEichhornia crassipes (E. crassipes). ^bEthylenediaminetetraacetic acid (EDTA) functionalized silica (EDTA-silica). ^cMontmorillonite (MMT). ^dPolyethylenimine (PEI) modified with biomass of penicillium chrysogenum (PEI-modified biomass). ^eSuccinylated mercerized cellulose modified with triethylenetetramine (Cell 2, 4). ^fCalcium alginate encapsulated magnetic sorbent (MS). ^gAminated electrospun polyacrylonitrile nanofiber mats (APAN nanofiber mats). ^hEDTA functionalized Fe₃O₄ nanoparticles (Fe₃O₄@EDTA). ⁱAmino functionalized magnetic expanded graphite nanohybrids (Fe₃O₄-decorated MEG-NH₂). ^jNano-TiO₂ modified with 2-mercaptobenzimidazole (Nano-TiO₂-MBI). ^kCercis siliquastrum tree leaves. ^lMagnetic cellulose xanthate (MCX). ^mMgAl layered double hydroxide intercalated by polysulfide S_x²⁻ (MgAl-S_x-LDH). ⁿLayered metal sulfides of K_{2x}Mg_xSn_{3-x}S₆ (KMS-2). ^oMgAl layered double hydroxide intercalated with the MoS₄²⁻ ion (MgAl-MoS₄-LDH). ^pLayered double hydroxide intercalated by chloride (Cl-LDH). ^qGraphene sheet composited with ferroferric oxide (Fe₃O₄-GS). ^rEthylenediamine-modified multiwalled carbon nanotubes (MWCNT). ^sCarboxymethyl-cyclodextrin polymer modified Fe₃O₄ nanoparticles (CDpoly-MNPs). ^tXanthate-modified magnetic chitosan (XMCS). ^uMercapto-functionalized nano-Fe₃O₄ magnetic polymers (SH-Fe₃O₄-NMPs). ^vSteam-activated furfural carbon (carbon A), steam-activated carbon from a mixture of furfural and tar from apricot stones (carbon B), air-oxidized furfural carbon (carbon C). ^wNatural attapulgite (ATP) modified with an amino-terminated organosilicon (3-aminopropyltriethoxysilane, APTES) (M-ATP). ^xThiol-derivatized single walled carbon nanotube (SWCNT-SH) powders. ^ySilica gel synthesised with tetraethyl orthosilicate (TEOS) as a precursor (SG-TEOS), sulfur-functionalized silica gel using TEOS as a precursor with bis(triethoxysilylpropyl)tetrasulfide (BTESPT) (SG-BTESPT), and silica gel synthesized with TEOS as a precursor and 3-mercaptopropyl trimethoxysilane (MPTMS) as sulfur ligands (SG-MPTMS).

Table 12. Sorption data of MoS₄-Ppy towards Cu²⁺.^a

C ₀ (ppm)	C _f (ppm)	Removal (%)	q _m (mg/g)	K _d (mL/g)
8.75 ^b	0.16	98.17	8.6	5.4×10 ⁴
53.3 ^c	30.5	42.78	22.8	7.5×10 ²
111 ^d	71.6	35.50	39.4	5.5×10 ²
197 ^e	150.0	23.86	47.0	3.1×10 ²
401 ^f	344.0	11.97	57.0	1.7×10 ²
608 ^g	537.0	9.38	71.0	1.3×10 ²
824 ^h	737.0	7.40	87.0	1.2×10 ²

1218 ⁱ	1107.0	6.16	111.0	1.0×10 ²
^a m = 0.02 g, V = 20 mL, V/m = 1000 mL/g; contact time: 24 h. pH value: ^b 5.32→3.66, ^c 5.19→3.32, ^d 4.76→3.00, ^e 4.76→2.88, ^f 4.81→3.02, ^g 4.76→3.14, ^h 4.58→2.71, ⁱ 4.43→2.82.				

Table 13. Sorption data of MoS₄-Ppy towards Pb²⁺. ^a

C ₀ (ppm)	C _f (ppm)	Removal (%)	q _m (mg/g)	K _d (mL/g)
10.2 ^b	0.001	99.96	10.2	2.6×10 ⁶
67.5 ^c	14.5	78.52	53.0	3.7×10 ³
171 ^d	108.0	36.84	63.0	5.8×10 ²
376 ^e	311.0	17.29	65.0	2.1×10 ²
629 ^f	557.0	11.45	72.0	1.3×10 ²
821 ^g	743.0	9.50	78.0	1.1×10 ²

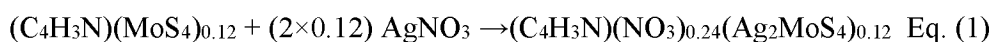
^am = 0.02 g, V = 20 mL, V/m = 1000 mL/g; contact time: 24 h.
pH value: ^b5.51→3.84, ^c5.24→3.65, ^d4.42→3.29, ^e5.07→3.14, ^f4.41→3.52,
^g4.45→3.62.

Table 14. Sorption data of MoS₄-Ppy towards Hg²⁺. ^a

C ₀ (ppm)	C _f (ppm)	Removal (%)	q _m (mg/g)	K _d (mL/g)
14.79 ^b	0.001	99.99	14.8	1.5×10 ⁷
48.5 ^c	0.001	99.99	48.5	4.9×10 ⁷
105 ^d	0.001	99.99	105.0	1.1×10 ⁸
170 ^e	0.004	99.99	167.0	4.3×10 ⁷
211 ^f	0.33	99.84	210.6	6.4×10 ⁵

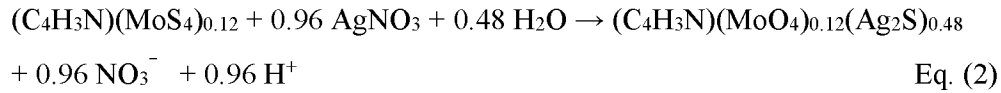
^am = 0.02 g, V = 20 mL, V/m = 1000 mL/g; contact time: 24 h.
pH value: ^b2.03→1.99, ^c1.84→1.76, ^d2.06→2.10, ^e2.80→2.90, ^f2.22→2.07.

[0057] The chemical formula of as-prepared MoS₄-Ppy is (C₄H₃N)(MoS₄)_{0.12}(NO₃)_{0.01}·2.8H₂O (molecular weight ~142.9), which means 1 g of MoS₄-Ppy has 8.4×10⁻⁴ (= 1/142.9×0.12) mol of MoS₄²⁻. If the MoS₄²⁻ binds to Ag⁺ in a ratio of 1:2, according to Eq. (1):



then the calculated q_m^{Ag} value for adsorbed Ag⁺ amount is 181 mg/g (= (8.4×10⁻⁴)×2×108×1000).

[0058] Alternatively, if the MoS₄²⁻ anions reacted with Ag⁺ to form Ag₂S according to Eq. (2), then the calculated q_m^{Ag} value for Ag⁺ is 725 mg/g (= (8.4×10⁻⁴)×8×108×1000).



[0059] The observed experimental q_{m}^{Ag} value of 480 mg/g is between the two cases, suggesting that $\text{MoS}_4\text{-Ppy}$ traps Ag^+ ion by means of both binding modes as indicated by Eq. (1) and Eq. (2).

[0060] Langmuir isotherm curves are generally used to present experimental data of uptake capacity. The Langmuir isotherm model is defined as:

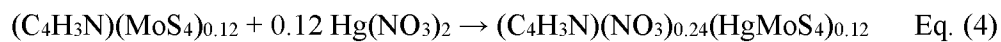
$$q = q_{\text{m}} \frac{bC_{\text{e}}}{1+bC_{\text{e}}} \quad \text{Eq. (3)}$$

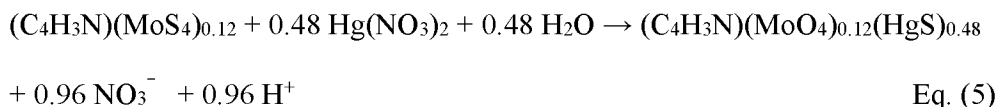
where q (mg/g) is the equilibrium adsorption capacity, c_{e} (mg/L) is the ion concentration at equilibrium, q_{m} (mg/g) is the theoretical maximum sorption capacity. In this model, the adsorbed substance is supposed to achieve monolayer type coverage of the sorbent on an adsorbent surface and indicates that there is a one-to-one correspondence between the sorption capacity and the adsorption site. The equilibrium adsorption isotherms of Pb^{2+} and Hg^{2+} are shown in FIG. 10A and 10B. For Pb^{2+} (FIG. 10A), the data points were well-fitted with the Langmuir model with a correlation coefficient (R^2) of ~ 0.98 (Table 15), suggesting a monolayer adsorption ($R^2 > 0.97$) on the $\text{MoS}_4\text{-Ppy}$. A q_{m}^{Pb} of 111.6 mg/g was determined by the Langmuir isotherm model. Based on the 1:1 $\text{MoS}_4^{2-}:\text{Pb}^{2+}$ coordination, the calculated q_{m}^{Pb} was 174 mg/g ($= (8.4 \times 10^{-4}) \times 1 \times 207 \cdot 1000$). The fitted experimental q_{m}^{Pb} of 111.6 mg/g was lower than the calculated q_{m}^{Pb} (174 mg/g), meaning a different binding mode of Pb^{2+} .

Table 15. Fitting results from Langmuir isotherm model.

Ions	q_{m} (mg/g)	b (L/mg)	R^2
Pb^{2+}	111.6	0.4755	0.98
Hg^{2+}	210.7	7.0×10^4	0.69
Ag^+ (pH $\sim$ 1)	666	5.8×10^{-5}	0.98

[0061] For Hg^{2+} (FIG. 10B), the expected q_{m}^{Hg} of 210.7 mg/g was also obtained from its Langmuir isotherm model, which was fitted quite well with the experimental value of 210.6 mg/g (Table 14). From 1:1 $\text{MoS}_4^{2-}:\text{Hg}^{2+}$ binding (Eq. (4), shown below), the calculated q_{m}^{Hg} was 168.5 mg/g ($= (8.4 \times 10^{-4}) \times 1 \times 200.6 \cdot 1000$). The larger experimental q_{m}^{Hg} of 210.6 mg/g illustrates that Hg^{2+} may combine with MoS_4^{2-} to form HgS (1:4 mode, i.e., 1 MoS_4^{2-} binds to 4 Hg^{2+}) according to Eq. (5).



**Table 14.** Sorption data of MoS₄-Ppy towards Hg²⁺. ^a

C ₀ (ppm)	C _f (ppm)	Removal (%)	q _m (mg/g)	K _d (mL/g)
14.79 ^b	0.001	99.99	14.8	1.5×10 ⁷
48.5 ^c	0.001	99.99	48.5	4.9×10 ⁷
105 ^d	0.001	99.99	105.0	1.1×10 ⁸
170 ^e	0.004	99.99	167.0	4.3×10 ⁷
211 ^f	0.33	99.84	210.6	6.4×10 ⁵

^a m = 0.02 g, V = 20 mL, V/m = 1000 mL/g; contact time: 24 h.

pH value: ^b2.03→1.99, ^c1.84→1.76, ^d2.06→2.10, ^e2.80→2.90, ^f2.22→2.07.

[0062] Adsorption kinetics. The adsorption kinetics of Ag⁺, Pb²⁺, and Hg²⁺ by MoS₄-Ppy were investigated to assess the adsorption efficiency and explore the possible pathways of adsorption before equilibrium. The results (Table 6, Table 16, Table 17) and sorption kinetics curves (FIG. 2A -2D) show rapid uptake rates and high removal efficiency. For toxic Pb²⁺ (initial pH value of 4.7), the absorption was extremely rapid, with > 99.7% removal rates, and K_d^{Pb} > 10⁵ mg/L only within 5 min and even > 10⁷ mg/L eventually. The % removal for Hg²⁺ (initial pH value of 2.1) can reach > 98% within 30 min, and K_d values were > 10⁴ mg/L within 1 h and up to >10⁶ mg/L during the further contact time.

Table 6. Kinetics data of Pb²⁺ using MoS₄-Ppy. ^a

C ₀ (ppm)	time (min)	C _f (ppm)	Removal (%)	K _d (mL/g)
10.46	1	0.007	99.93	1.5×10 ⁶
	5	0.017	99.83	6.1×10 ⁵
	10	0.011	99.89	9.5×10 ⁵
	60	0.007	99.93	1.5×10 ⁶
	180	0.031	99.70	3.6×10 ⁶
	360	0.001	99.99	1.1×10 ⁷

^a m = 0.04 g, V = 40 mL, V/m = 1000 mL/g; pH value: 4.74→4.47.

Table 16. Kinetics data of Ag⁺ using MoS₄-Ppy. ^a

C ₀ (ppm)	time (min)	C _f (ppm)	Removal (%)	K _d (mL/g)
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	1	0.040	99.6	2.7×10^5
	5	0.030	99.7	3.7×10^5
11.0	10	0.030	99.7	3.7×10^5
	30	0.030	99.7	3.7×10^5
	60	0.040	99.6	2.7×10^5

^a m = 0.04 g, V = 40 mL, V/m = 1000 mL/g; pH value: 4.57→3.87.

Table 17. Kinetics data of Hg²⁺ using MoS₄-Ppy.^a

C ₀ (ppm)	time (min)	C _f (ppm)	Removal (%)	K _d (mL/g)	q _t (mg/g)
	1	0.190	98.30	5.8×10^4	11.01
	30	0.169	98.49	6.5×10^4	11.03
11.2	60	0.138	98.77	8.0×10^4	11.06
	180	0.006	99.95	1.9×10^6	11.19
	360	0.002	99.98	5.6×10^6	11.20

^a m = 0.04 g, V = 40 mL, V/m = 1000 mL/g; pH value: 2.07→2.35.

[0063] The removal rate can be determined in two different ways: pseudo-first-order and pseudo-second-order mechanisms, which were defined as follows:

Pseudo-first-order:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad \text{Eq. (6)}$$

Pseudo-second-order:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \text{Eq. (7)}$$

where q_e (mg/g) is the adsorbed amount per unit mass of adsorbent at equilibrium and q_t (mg/g) is the adsorbed mass at time t , while k_1 (min⁻¹) and k_2 (g/mg min⁻¹) are corresponding equilibrium rate constants. (See, Azizian, S. J. *Colloid Interface Sci.* 2004, 276 (1), 47-52.) The k_1 value was obtained by plotting $\ln(q_e - q_t)$ against t and the k_2 by plotting t/q_t against t . The linear relationship of t/q_t versus t is presented in FIG. 2D. From the kinetic parameters of Ag⁺, Pb²⁺, and Hg²⁺ (Table 18), the calculated sorption capacities ($q_{e,cal}$) derived from the

pseudo-second-order model were quite close to corresponding experimental values ($q_{e,exp}$). The fit coefficient (R^2) was close to 1, indicating the adsorption was well fitted with the pseudo-second-order kinetic model, suggesting a chemisorption process.

Table 18. Kinetics parameters (pseudo-second-order-model) for adsorbing metal ions onto MoS₄-Ppy.

	$q_{e, exp}$	k_2	$q_{e, cal} (mg/g)$	R^2
Ag ⁺	10.97	8.28×10^{-3}	10.99	0.999
Pb ²⁺	10.45	1.77	10.45	1
Hg ²⁺	11.19	0.309	11.21	0.999

[0064] Uptake capacity for Ag⁺ in strong acid (SA) conditions (pH~1). As discussed above, the capture ability of MoS₄-Ppy for Ag⁺ was markedly enhanced in the ionic mixture (pH = 3.4) compared to the individual ion case (pH = 5.1). This prompted the study of the uptake capacity for Ag⁺ in strong acid (SA) condition. As shown in Table 7, at pH ≈ 1, an exceptionally high q_m^{SA-Ag} of 725 mg/g was obtained (with initial concentrations of 10-2000 ppm), being ~1.5 times (= 725/480) of the q_m^{Ag} of 480 mg/g in the weak acid case. This clearly indicates the enhanced effect at lower pH. The experimental data of uptake capacity for Ag⁺ were fitted well with the Langmuir isotherm model of Eq. (3). See FIG. 3A and 3B, with correlation coefficient (R^2) of 0.98. According to the Langmuir isotherm model, the expected capacity q_m^{SA-Ag} of 666 mg/g is close to the experimental value of 725 mg/g. The much larger value of 725 mg/g corresponds to the value based on Eq. (2), which suggests that in strongly acidic conditions, one MoS₄²⁻ binds to 8 Ag⁺ ions, forming 4Ag₂S. In this case, the MoO₄²⁻ may act as the counter-anion to balance the charge in the Ppy backbone. Mo was not detected in the filtrates after sorption, which indicates that the Mo remained in the solids.

Table 7. Sorption data of MoS₄-Ppy towards Ag⁺ at strong acidic conditions.^a

C ₀ (ppm)	C _f (ppm)	Removal (%)	q_m (mg/g)	K_d (mL/g)
9.96 ^b	0.01	99.90	9.9	1.0×10^6
47.3 ^c	2.95	93.76	44.4	1.5×10^4
198 ^d	17.4	91.21	180.6	1.0×10^4
485 ^e	30.6	93.69	454.4	1.5×10^4
981 ^f	329	66.46	652.0	2.0×10^3
1439 ^g	820	43.02	619.0	7.5×10^2
1902 ^h	1177	38.12	725.0	6.2×10^2

^a m = 0.02 g, V = 20 mL, V/m = 1000 mL/g; contact time: 24 h.

pH value: ^b0.91→1.03, ^c0.82→0.88, ^d0.68→0.77, ^e0.63→0.78, ^f0.67→0.82,

^g0.60→0.75, ^h0.80→0.80.

[0065] Adsorption kinetics of Ag⁺, Pb²⁺ and Hg²⁺ in strong acid (SA) conditions

(pH~1). The kinetic behavior for Ag⁺, Pb²⁺, and Hg²⁺ was subsequently investigated in strongly acidic conditions in order to further understand the pH effect on the adsorption. For Ag⁺ (Table 8), >99.9% removal and $K_d > 10^6$ mL/g within 5 min were observed, exhibiting a more efficient capture than under weak acid conditions (Table 16). For the highly toxic Hg²⁺ (Table 9), the concentration decreased from 10 ppm to 8 ppb within 5 min, and then even lower than the officially set safety level of 2 ppb. Therefore, MoS₄-Ppy exhibited better Hg²⁺ removal in strongly acidic conditions than in weakly acidic ones. Interestingly, the MoS₄-Ppy exhibited nearly no adsorption for Pb²⁺ (Table 19) under strong acid conditions (pH ≈ 1), and this could be used to separate Pb²⁺ from other heavy metal ions. The kinetics curves for Ag⁺ and Hg²⁺ (FIG. 4A – 4D) and kinetic parameters (Table 20) clearly demonstrate the rapid removal of Ag⁺ than Hg²⁺ in strongly acidic conditions.

Table 8. Kinetics data of Ag⁺ using MoS₄-Ppy under strong acid conditions.^{a,b}

C ₀ (ppm)	time (min)	C _f (ppm)	Removal (%)	K _d (mL/g)
17.0	1	0.064	99.62	2.6×10 ⁵
	5	0.013	99.92	1.3×10 ⁶
	10	0.008	99.95	2.1×10 ⁶
	30	0.001	99.99	1.7×10 ⁷
	60	0.001	99.99	1.7×10 ⁷
	360	0.001	99.99	1.7×10 ⁷

^a m = 0.04 g, V = 40 mL, V/m = 1000 mL/g; pH value: ^b0.83→1.18.

Table 9. Kinetics data of Hg²⁺ using MoS₄-Ppy under strong acid conditions.^a

C ₀ (ppm)	time (min)	C _f (ppm)	Removal (%)	K _d (mL/g)
11.2	1	0.039	99.65	2.86×10 ⁵
	5	0.008	99.93	1.40×10 ⁶
	30	0.005	99.96	2.24×10 ⁶
	60	0.005	99.96	2.24×10 ⁶

180	0.002	99.98	5.60×10^6
360	0.001	99.99	1.12×10^7

^a m = 0.04 g, V = 40 mL, V/m = 1000 mL/g; pH value: 0.93→1.25.

Table 16. Kinetics data of Ag⁺ using MoS₄-Ppy.^a

C ₀ (ppm)	time (min)	C _f (ppm)	Removal (%)	K _d (mL/g)
11.0	1	0.040	99.6	2.7×10^5
	5	0.030	99.7	3.7×10^5
	10	0.030	99.7	3.7×10^5
	30	0.030	99.7	3.7×10^5
	60	0.040	99.6	2.7×10^5

^a m = 0.04 g, V = 40 mL, V/m = 1000 mL/g; pH value: 4.57→3.87.

Table 19. Kinetics data of Pb²⁺ using MoS₄-Ppy under strong acid conditions.^a

C ₀ (ppm)	time (min)	C _f (ppm)	Removal (%)	K _d (mL/g)	q _t (mg/g)
11.7	1	11.0	5.98	63.6	0.7
	5	11.0	5.98	63.6	0.7
	10	11.2	4.27	44.6	0.5
	30	11.2	4.27	44.6	0.5
	60	11.3	3.42	35.4	0.4
	180	11.2	4.27	44.6	0.5
	360	11.3	3.42	35.40	0.4

^a m = 0.04 g, V = 40 mL, V/m = 1000 mL/g; pH value: 0.83→1.18.

Table 20. Kinetics parameters (pseudo-second-order-model) for adsorbing metal ions onto MoS₄-Ppy under strong acid condition.

	q _{e,exp}	k ₂	q _{e,cal} (mg/g)	R ²
Ag ⁺	16.99	21.63	17.00	1
Hg ²⁺	11.19	8.39	11.20	1

[0066] Relative selectivity towards Pb^{2+} , Ag^+ and Hg^{2+} in strongly acidic conditions.

Selectivity experiments towards Ag^+ , Pb^{2+} , and Hg^{2+} were conducted under strong acid conditions ($\text{pH} < 1$), using a solution of Ag^+ , Pb^{2+} , and Hg^{2+} mixture with an initial concentration of ~ 20 ppm for each ion. The quantities of solid $\text{MoS}_4\text{-Ppy}$ used were 0.002 g and 0.004 g. As shown in Table 21, in the case of the reduced amount of $\text{MoS}_4\text{-Ppy}$ (0.002 g), there was nearly no adsorption for Pb^{2+} . For Ag^+ and Hg^{2+} , the separation factor ($\text{SF}_{\text{Ag/Hg}}$) defined by $K_d^{\text{Ag}}/K_d^{\text{Hg}}$ was further studied. When the amount of $\text{MoS}_4\text{-Ppy}$ was decreased to 0.004 g (1/5 of 0.02 g) and then to 0.002 g (1/10 of 0.02 g), the $\text{SF}_{\text{Ag/Hg}}$ values were 2.8 ($= (7.4 \times 10^3)/(2.6 \times 10^2)$) and 2.4 ($= (5.6 \times 10^3)/(2.36 \times 10^2)$), respectively, showing a somewhat higher affinity for Ag^+ than for Hg^{2+} . All these results show the $\text{MoS}_4\text{-Ppy}$ can work as an effective material for separating Pb^{2+} from mixtures of $\text{Pb}^{2+}/\text{Ag}^+/\text{Hg}^{2+}$ in strongly acidic conditions.

Table 21. Adsorption results of $\text{MoS}_4\text{-Ppy}$ for Pb^{2+} , Ag^+ and Hg^{2+} under strong acid condition. ^a

MoS ₄ -Ppy	0.002 g			0.004 g		
	Ag ⁺	Pb ²⁺	Hg ²⁺	Ag ⁺	Pb ²⁺	Hg ²⁺
C ₀ (ppm)	24.7	21.3	28.4	24.7	21.3	28.4
C _f (ppm)-6 h	15.8	21.3	23.0	10.0	21.3	18.6
K _d (mL/g)-6 h	5.6×10 ³	0	2.3×10 ³	7.4×10 ³	0	2.6×10 ³
Removal (%)	36.0	0	19.0	59.5	0	35.5
pH	0.85→0.90			0.85→0.93		

^a 20 ml solution of AgNO_3 , $\text{Pb}(\text{NO}_3)_2$ and $\text{Hg}(\text{NO}_3)_2$, 20 ppm concentration per ion.

[0067] pH effect on removal of Ag^+ and Pb^{2+} by $\text{MoS}_4\text{-Ppy}$. Based on the sensitive pH effect discussed above on the adsorption of Ag^+ and Pb^{2+} , pH ranges favorable for trapping Pb^{2+} and Ag^+ were investigated by varying the pH. As shown in Table 22, Ag^+ maintained >99.9% removal rates and >10⁶ mg/L of K_d within a wide pH range of 0.6~4.36, demonstrating the outstanding capacity for Ag^+ removal at a broad pH range. For Pb^{2+} (Table 23), the adsorption at the initial pH~0.9 was poor, in good agreement with the results of Pb^{2+} removal in strong acid conditions (Table 19). However, > 98% removal rates and $K_d^{\text{Pb}} > 10^4$ mg/L could be obtained at pH = 2.5~6, suggesting different uptakes towards Pb^{2+} in different conditions. The best pH value for Pb^{2+} removal was determined to be ~3, giving nearly

complete removal (100%) and the highest K_d ($>2.6 \times 10^7$ mg/L). The pH effect on the two ions is shown in FIG. 5.

Table 22. pH effect on sorption data of MoS₄-Ppy towards Ag⁺. ^a

pH	C ₀ (ppm)	C _f (ppm)	Removal (%)	q _m (mg/g)	K _d (mL/g)
0.60→0.72	17.0	0.001	99.99	16.9	1.7×10^7
1.90→2.03	18.9	0.004	99.98	18.9	4.7×10^6
2.85→3.23	20.8	0.01	99.95	20.8	2.1×10^6
4.36→3.88	20.5	0.01	99.95	20.5	2.0×10^6
6.47→3.73	15.6	0.69	95.66	15.2	2.2×10^4

^a m = 0.02 g, V = 20 mL, V/m = 1000 mL/g; contact time: 24 h.

Table 23. pH effect on sorption data of MoS₄-Ppy towards Pb²⁺. ^a

pH	C ₀ (ppm)	C _f (ppm)	Removal (%)	q _m (mg/g)	K _d (mL/g)
0.96→0.93	22.5	21.6	4.00	0.9	41.7
1.85→1.78	24.0	2.75	88.54	21.3	7.7×10^3
2.47→2.47	25.4	0.06	99.76	25.3	4.2×10^5
3.18→3.25	26.3	<0.001	100.0	26.3	$>2.6 \times 10^7$
4.10→3.85	21.9	0.04	99.98	21.9	5.5×10^5
6.12→3.58	21.8	0.31	98.58	21.5	6.9×10^4

^a m = 0.02 g, V = 20 mL, V/m = 1000 mL/g; contact time: 24 h.

Table 19. Kinetics data of Pb²⁺ using MoS₄-Ppy under strong acid conditions. ^a

C ₀ (ppm)	time (min)	C _f (ppm)	Removal (%)	K _d (mL/g)	q _t (mg/g)
11.7	1	11.0	5.98	63.6	0.7
	5	11.0	5.98	63.6	0.7
	10	11.2	4.27	44.6	0.5
	30	11.2	4.27	44.6	0.5
	60	11.3	3.42	35.4	0.4
	180	11.2	4.27	44.6	0.5
	360	11.3	3.42	35.40	0.4

^a m = 0.04 g, V = 40 mL, V/m = 1000 mL/g; pH value: 0.83→1.18.

[0068] Selectivity for Ag⁺ and Cu²⁺ in weak and strong acid conditions. The remarkably high selectivity towards Ag⁺ suggests MoS₄-Ppy could be an ideal material for the selective extraction of low-grade silver from some ores that are rich in copper. A batch of

experiments focusing on the exploration of relative selectivity towards a mixture of Ag^+ and Cu^{2+} were conducted under weak and strong acid conditions. The Ag^+ concentration was fixed at ~ 1 ppm while Cu^{2+} concentrations were set at ~ 1 , ~ 2 , ~ 5 , ~ 10 , and ~ 20 ppm (Table 10, FIG. 6A and 6B). In weak acid conditions ($\text{pH} = 3.3\text{--}5.7$), the removals of Ag^+ and Cu^{2+} both reached 96–99.9% at the molar ratios ($n(\text{Cu}^{2+})/n(\text{Ag}^+)$) from 1.1 to 19.1 (FIG. 6A). When the $n(\text{Cu}^{2+})/n(\text{Ag}^+)$ ratio increased to 38.7 ($C_0^{\text{Ag}} = 0.74$ ppm, $C_0^{\text{Cu}} = 20.04$ ppm), the removal of Cu^{2+} decreased to 79.1% while that of Ag^+ kept 99.8% (FIG. 6B). Generally, good separation factors ($\text{SF}_{\text{A/B}}$) are considered to be >100 . The $\text{SF}_{\text{Ag/Cu}}$ ($K_d^{\text{Ag}}/K_d^{\text{Cu}}$) of 163.2 ($= (6.2 \times 10^5)/(3.8 \times 10^3)$) suggests excellent separation capability of Ag^+ from Cu^{2+} by the $\text{MoS}_4\text{-Ppy}$ (FIG. 6C). In the strong acid case ($\text{pH} \sim 1$) (Table 8, FIG. 6B), the $\text{MoS}_4\text{-Ppy}$ retained the excellent removal of Ag^+ ($> 99.8\%$), at $n(\text{Cu}^{2+})/n(\text{Ag}^+)$ ratios of 1.6–35.7 ($C_0^{\text{Ag}} \sim 1$ ppm), while worse adsorption for Cu^{2+} was observed with only 8.2–25.1% removal (FIG. 6B). In addition, the $\text{SF}_{\text{Ag/Cu}}$ increased sharply to $3.1 \times 10^3 \sim 1.1 \times 10^5$ (FIG. 6D). The high $\text{SF}_{\text{Ag/Cu}}$ found in strong acid conditions indicate that $\text{MoS}_4\text{-Ppy}$ could be an outstanding material for the extraction of silver from copper-rich low-grade minerals.

Table 10. Removal results using $\text{MoS}_4\text{-Ppy}$ towards mixtures of Cu^{2+} and Ag^+ . ^a

	$n(\text{Cu}^{2+})/n(\text{Ag}^+)$	C_0 (ppm)	C_f (ppm)	Removal (%)	K_d (mL/g)
weak acid case	1.1	Cu^{2+} : 0.53	0.019	96.4	2.7×10^4
	(pH: 5.69→3.95)	Ag^+ : 0.82	0.033	96.0	2.4×10^4
	3.5	Cu^{2+} : 1.75	0.006	99.7	2.9×10^5
	(pH: 5.52→3.82)	Ag^+ : 0.84	0.0021	99.8	4.0×10^5
	8.6	Cu^{2+} : 4.38	0.013	99.7	3.4×10^5
	(pH: 5.38→3.92)	Ag^+ : 0.86	0.0018	99.8	4.8×10^5
strong acid case	19.1	Cu^{2+} : 9.89	0.205	97.9	4.7×10^4
	(pH: 5.29→3.52)	Ag^+ : 0.88	0.0011	99.9	8.0×10^5
	38.7	Cu^{2+} : 20.0	4.19	79.1	3.8×10^3
	(pH: 5.38→3.33)	Ag^+ : 0.74	0.0012	99.8	6.2×10^5
	1.6	Cu^{2+} : 0.93	0.74	20.4	2.6×10^2
	(pH: 0.78→0.75)	Ag^+ : 1.00	0.0008	99.9	1.2×10^6
strong acid case	3.2	Cu^{2+} : 1.91	1.43	25.1	3.4×10^2
	(pH: 0.88→0.83)	Ag^+ : 1.03	0.0005	99.99	2.1×10^6

	8.5 (pH: 0.86→0.84)	Cu ²⁺ : 4.94 Ag ⁺ : 0.99	4.25 0.002	14.0 99.8	1.6×10 ² 4.9×10 ⁵
	18.1 (pH: 0.74→0.75)	Cu ²⁺ : 9.36 Ag ⁺ : 0.97	8.51 0.001	9.1 99.9	99.9 9.7×10 ⁵
	35.7 (pH: 1.03→1.03)	Cu ²⁺ : 19.74 Ag ⁺ : 0.94	18.12 0.0002	8.2 99.9	89.4 9.7×10 ⁶

^a m = 0.02 g, V = 20 mL, V/m = 1000 mL/g; Contact time: 24 h.

[0069] Structural characterization of the post-adsorption solid samples. The solid samples after adsorption were centrifuged and air-dried for XRD, IR spectroscopy and XPS analyses. After Cu²⁺ removal, the sample was X-ray amorphous (FIG. 7A trace b, FIG. 7A trace c) as the Ppy-MoS₄ precursor. For Ag⁺, the XRD pattern of the 10-ppm adsorbed sample (FIG. 7A trace d) was also amorphous. However, with the increasing concentrations of Ag⁺ (FIG. 7A trace e, FIG. 7A trace f), the solid samples presented weak diffraction peaks at 0.29, 0.26, 0.24 and 0.21 nm, suggesting the presence of Ag₂S (PDF #04-0774).

Interestingly, for the Pb²⁺ adsorbed samples (FIG. 7A trace g- FIG. 7A trace i), a set of new diffraction peaks were observed, which were attributed to the tetragonal phase of PbMoO₄ (PDF #44-1486). FIG. 7B and FIG. 7C show the XRD patterns at slow scan rates of the 200 ppm Pb²⁺ and 1200 ppm Ag⁺ post-adsorption samples and standard patterns of Ag₂S and PbMoO₄. For Hg²⁺ (FIG. 7A trace j, FIG. 7A trace k), similar XRD patterns to those of Cu²⁺ were observed.

[0070] The mechanism of Hg²⁺ removal was further investigated by IR (FIG. 11A, 11B) and XPS spectroscopy. XPS spectra of the post-adsorption samples are shown in FIG. 8A – 8L. The Mo^{VI} 3d energies observed at ~235 and ~233 eV, S 2s energy at ~227 eV, and S 2p peaks at ~163 eV were much closer to the corresponding values for MoS₄-Ppy precursor (FIG. 1C, FIG. 1D), indicating that the MoS₄²⁻ groups were stable during the adsorption process. The presence of the weak peaks at ~168 eV (FIG. 8B, FIG. 8E, FIG. 8H, FIG. 8K) were from SO₄²⁻ impurity as found above, considering some oxidation of S²⁻ in air. For the Cu²⁺ adsorbed sample, two characteristic peaks occurred at 952.8 (Cu 2p_{1/2}) and 933.0 eV (Cu 2p_{3/2}) (Δ = 19.9 eV) (FIG. 8C), arising from the Cu 2p energy of Cu²⁺. As shown in FIG. 8F, the Ag 3d_{3/2} and Ag 3d_{5/2} energies at 374.5 and 368.5 eV respectively, were assigned to Ag⁺. In FIG. 8I, the peaks at 143.9 (Pb 4f_{5/2}) and 139.0 eV (Pb 4f_{7/2}) correspond to Pb 4f

levels of Pb^{2+} . For Hg^{2+} (FIG. 8L), the Hg 4f levels were observed at 105.2 (Hg 4f_{5/2}) and 101.1 (Hg 4f_{7/2}) eV, indicating the presence of Hg^{2+} in the post-adsorption sample.

[0071] To probe the stability of MoS₄-Ppy in strong acid environment (*abbr.* MoS₄-Ppy-SA), the material was soaked in strong acid ($\text{H}_2\text{O}/\text{HNO}_3$ solution, pH~1) for 24 h. There was no obvious difference before and after soaking in the IR spectra (FIG. 12A). The increased intensity of 1383 cm^{-1} band of NO_3^- (FIG. 12A trace b), was due to the insertion of additional NO_3^- in the structure and back ion-exchange. After acid soaking of MoS₄-Ppy, no UV-Vis absorptions attributed to MoS₄²⁻ (241, 317, 468 nm) or MoO_xS_{4-x}²⁻ (289, 393, 470 nm) were observed in the supernatant (FIG. 12B). In addition, XRD, IR, and XPS analyses of the Ag⁺ post-adsorption samples were performed from the strong acid case (FIG. 13A - FIG. 13E). These experiments suggested that MoS₄-Ppy did not undergo dissolution, oxidation, or hydrolysis in the strong acid environment. Thus, MoS₄-Ppy is an acid durable and chemically stable material, and it is promising for the removal of heavy metal ions, especially from strongly-acidic polluted water.

[0072] MoS₄-Ppy is a novel material that exhibits highly selective and effective removal of heavy metal ions such as Cu^{2+} , Ag^+ , and Hg^{2+} , relying mainly on the coordination interactions of S²⁻ sites and these metal ions. The key findings were: (a) in the weak acid case, highly efficient removal of Ag^+ , Pb^{2+} , Hg^{2+} was rapidly achieved with > 99% for Ag^+ (pH = 4.6), > 99.7% for Pb^{2+} (pH = 4.7), and > 98% for Hg^{2+} (pH = 2.1); (b) in strongly acidic conditions (pH~1), MoS₄-Ppy had an enhanced removal efficiency for Ag^+ and Hg^{2+} (>99.9%) and can achieve a final Hg^{2+} concentration of ≤ 2 ppb, which is the limit value of Hg^{2+} in drinking water; (c) enormous record-high uptake capacities (q_m) of 480 mg/g (pH ≈ 5) and 725 mg/g (pH ≈ 1) for Ag^+ were obtained; (d) wide pH range was available for efficient Ag^+ and Pb^{2+} removal: nearly complete Ag^+ removal (>99.99%) at a pH = 0.6-5.0, and > 98% removal for Pb^{2+} at pH = 2.5-6.0; (e) successful separation of Ag^+ from high concentrations of Cu^{2+} . Under strong acidic conditions (pH~1), very large $\text{SF}_{\text{Ag}/\text{Cu}}$ values ($3.1 \times 10^3 \sim 1.1 \times 10^5$) were achieved, which demonstrate the usefulness of MoS₄-Ppy for extraction of silver from copper-rich minerals. Therefore, because of its excellent chemical stability and the outstanding removal abilities for heavy metal ions, MoS₄-Ppy is well-suited for the remediation of heavy metal polluted acidic water as well as for separating silver from raw Cu/Ag mixtures in strongly acidic media.

[0073] The word "illustrative" is used herein to mean serving as an example, instance, or illustration. Any aspect or design described herein as "illustrative" is not necessarily to be construed as preferred or advantageous over other aspects or designs. Further, for the purposes of this disclosure and unless otherwise specified, "a" or "an" means "one or more."

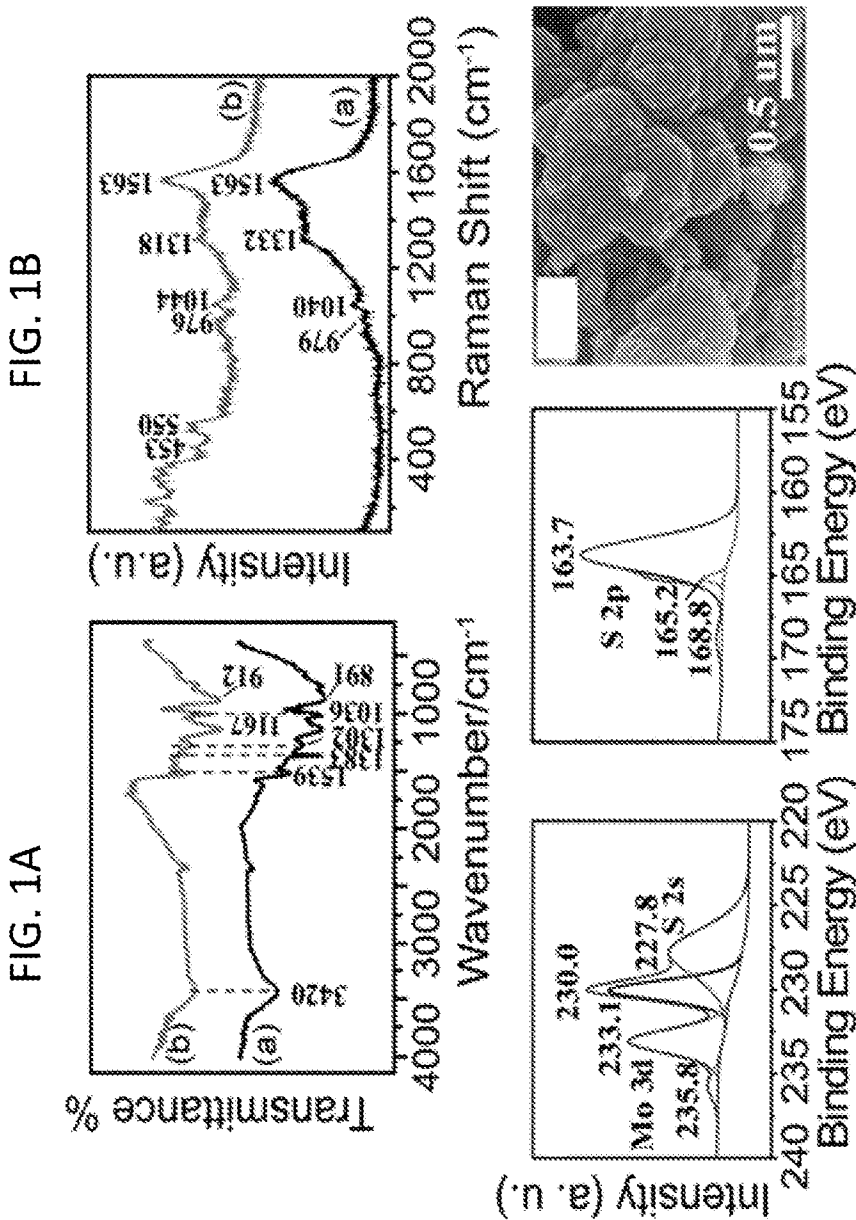
[0074] The foregoing description of illustrative embodiments of the invention has been presented for purposes of illustration and of description. It is not intended to be exhaustive or to limit the invention to the precise form disclosed, and modifications and variations are possible in light of the above teachings or may be acquired from practice of the invention. The embodiments were chosen and described in order to explain the principles of the invention and as practical applications of the invention to enable one skilled in the art to utilize the invention in various embodiments and with various modifications as suited to the particular use contemplated. It is intended that the scope of the invention be defined by the claims appended hereto and their equivalents.

WHAT IS CLAIMED IS:

1. A thioanion-functionalized polypyrrole comprising:
a conjugated, positively charged backbone of pyrrole units; and
charge-balancing thioanions associated with the conjugated, positively charged backbone of pyrrole units.
2. The thioanion-functionalized polypyrrole of claim 1, wherein the thioanions comprise molybdenum thioanions.
3. The thioanion-functionalized polypyrrole of claim 2, wherein the molybdenum thioanions comprise MoS_4^{2-} anions.
4. The thioanion-functionalized polypyrrole of claim 1, wherein the thioanions comprise antimony thioanions.
5. The thioanion-functionalized polypyrrole of claim 1, wherein the thioanions comprise tin thioanions.
6. The thioanion-functionalized polypyrrole of claim 1, wherein the thioanions comprise phosphorus thioanions.
7. The thioanion-functionalized polypyrrole of claim 2, wherein the thioanions comprise $\text{Mo}_3\text{S}_{13}^{2-}$ anions, SbS_3^{3-} anions, SbS_4^{3-} anions, S_x^{2-} anions, wherein $x = 1, 2, 3, 4, 5,$ or 6), SH^{1-} anions, $\text{Sb}_2\text{S}_4^{4-}$ anions, SnS_4^{4-} anions, $\text{Sn}_2\text{S}_6^{4-}$ anions, $\text{Sn}_4\text{S}_{10}^{4-}$ anions, WS_4^{2-} anions, $\text{PS}_{4-x}\text{O}^{3-}$ anions, wherein ($x = 1, 2,$ or 3), or a mixture of two or more thereof.
8. A method of removing metal ions from a sample comprising the metal ions, using a thioanion-functionalized polypyrrole comprising:
a conjugated, positively charged backbone of pyrrole units; and
charge-balancing thioanions associated with the conjugated, positively charged backbone of pyrrole units,
the method comprising:
exposing the thioanion-functionalized polypyrrole to the sample, wherein metal ions are adsorbed by the thioanion-functionalized polypyrrole; and

removing the thioanion-functionalized polypyrrole and the absorbed metal ions from the sample.

9. The method of claim 8, wherein the thioanions comprise molybdenum thioanions.
10. The method of claim 9, wherein the molybdenum thioanions comprise MoS_4^{2-} anions.
11. The method of claim 8, wherein the thioanions comprise antimony thioanions.
12. The method of claim 8, wherein the thioanions comprise tin thioanions.
13. The method of claim 8, wherein the thioanions comprise phosphorus thioanions.
14. The method of claim 8, wherein the sample is an aqueous solution having a pH of no greater than 6.
15. The method of claim 8, wherein the sample is an aqueous solution having a pH of no greater than 5.
16. The method of claim 8, wherein the sample is an aqueous solution having a pH in the range from 0.5 to 1.5.
17. The method of claim 8, wherein the metal ions include Ag^+ ions, Hg^{2+} ions, Pb^{2+} ions, Cu^{2+} ions, Cr^{6+} ions, Tl^+ ions, Cd^{2+} ions, or a combination of two or more thereof.
18. The method of claim 8, wherein the metal ions include Ag^+ ions.
19. The method of claim 10, wherein the sample is an aqueous solution having a pH in the range from 0.5 to 1.5 and the sample comprises Ag^+ ions and Cu^{2+} ions.



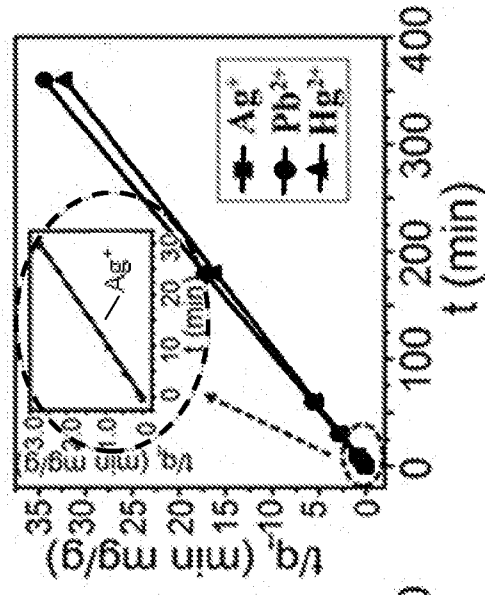
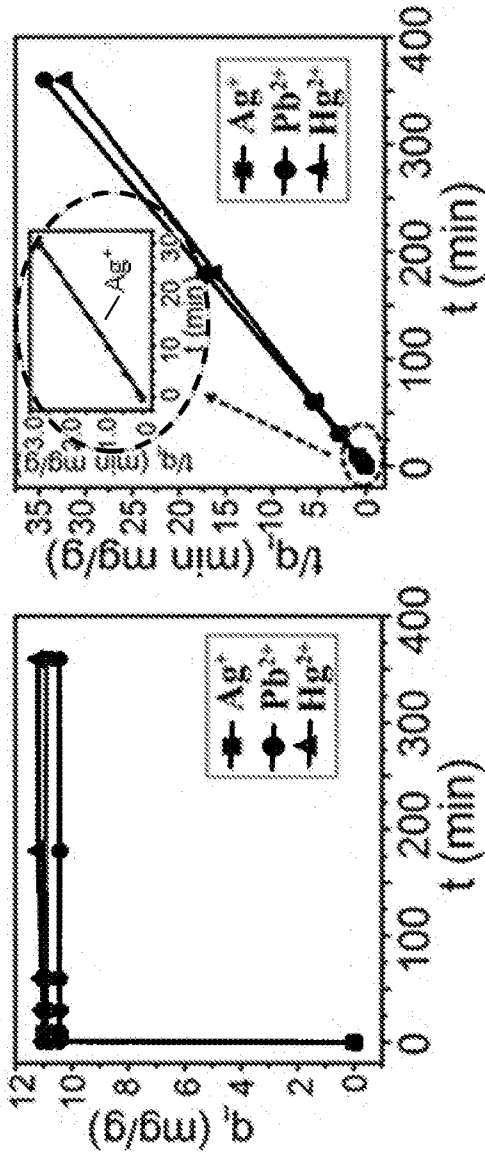
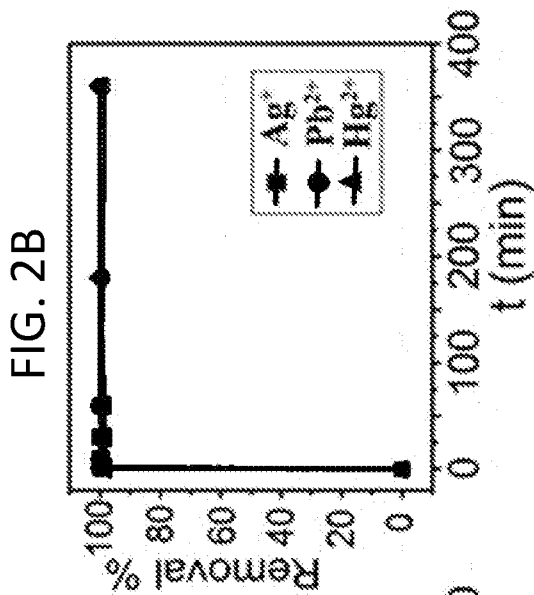
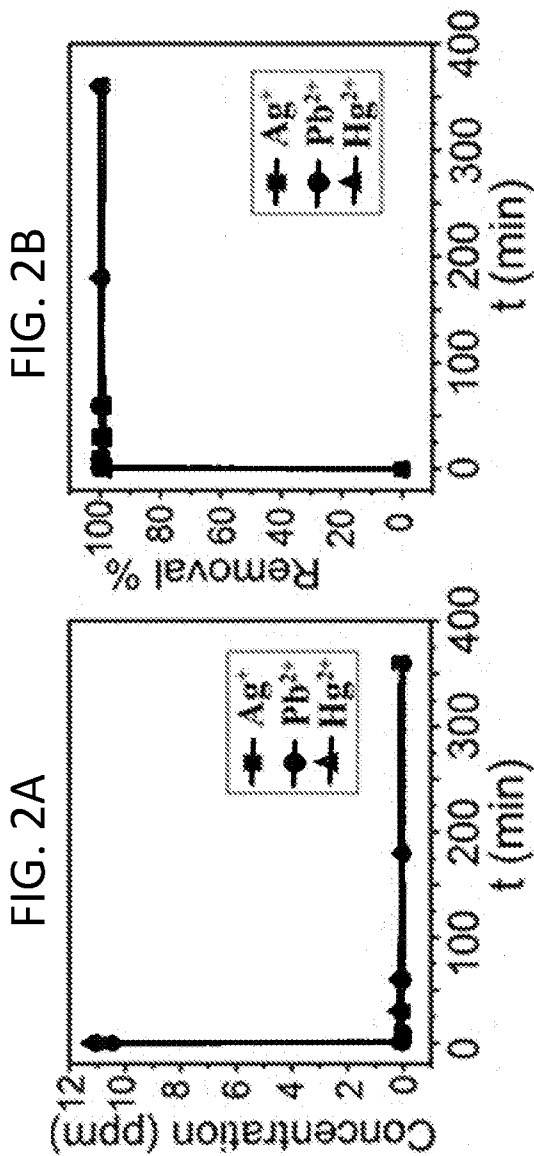


FIG. 2D

FIG. 2C

FIG. 3B

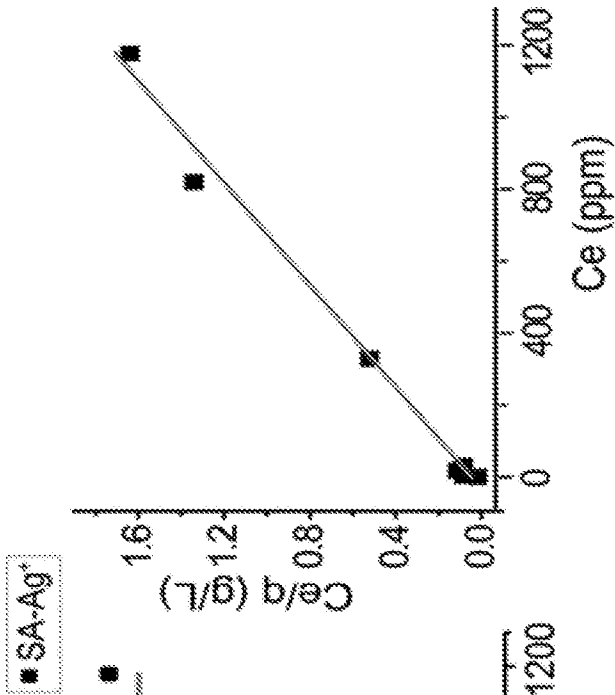


FIG. 3A

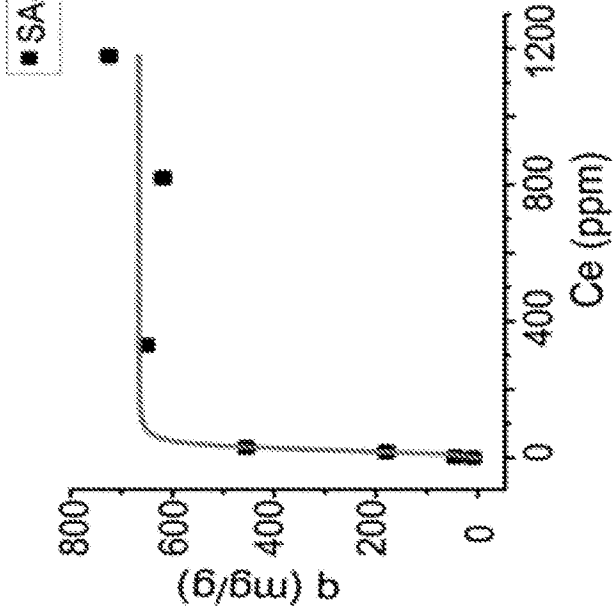


FIG. 4B

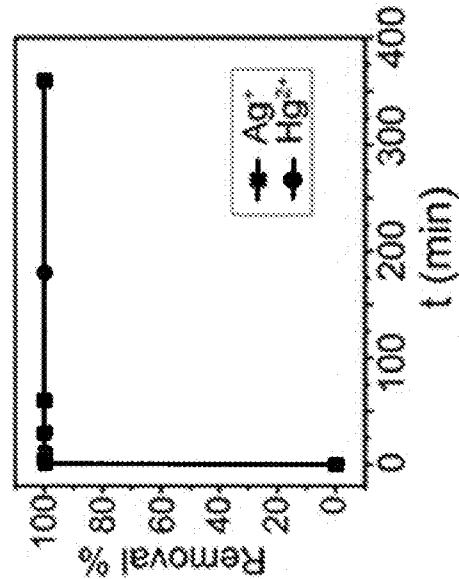


FIG. 4A

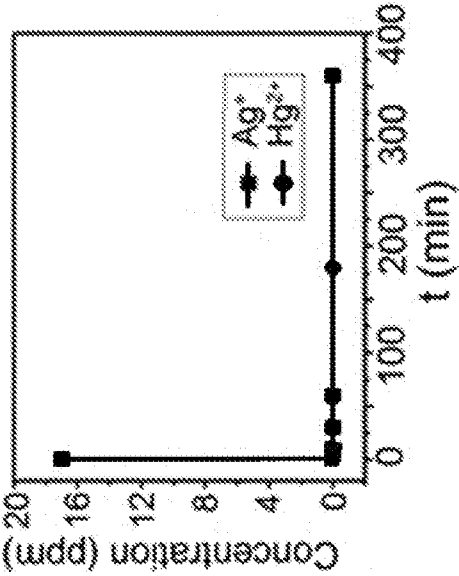


FIG. 4D

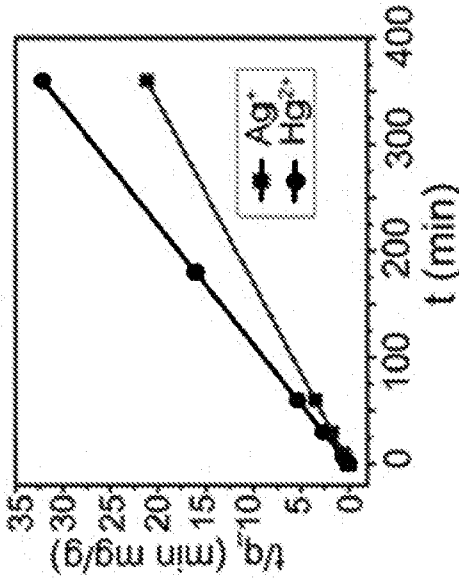


FIG. 4C

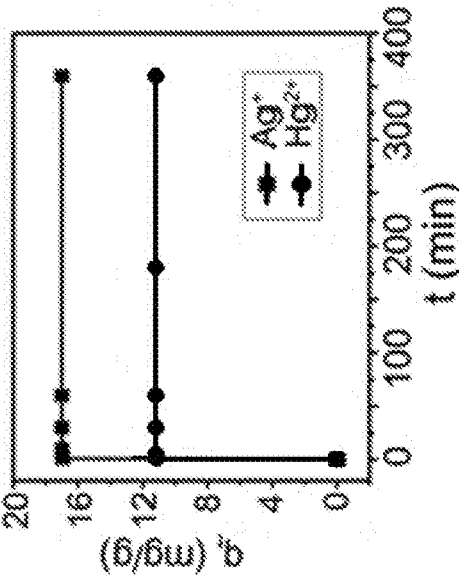
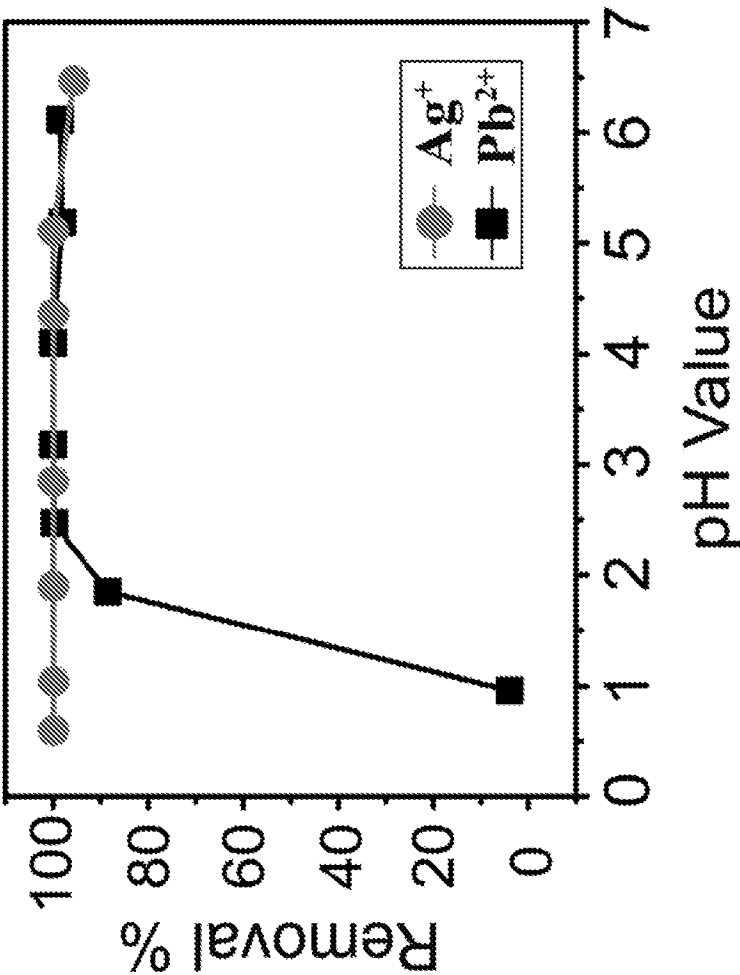
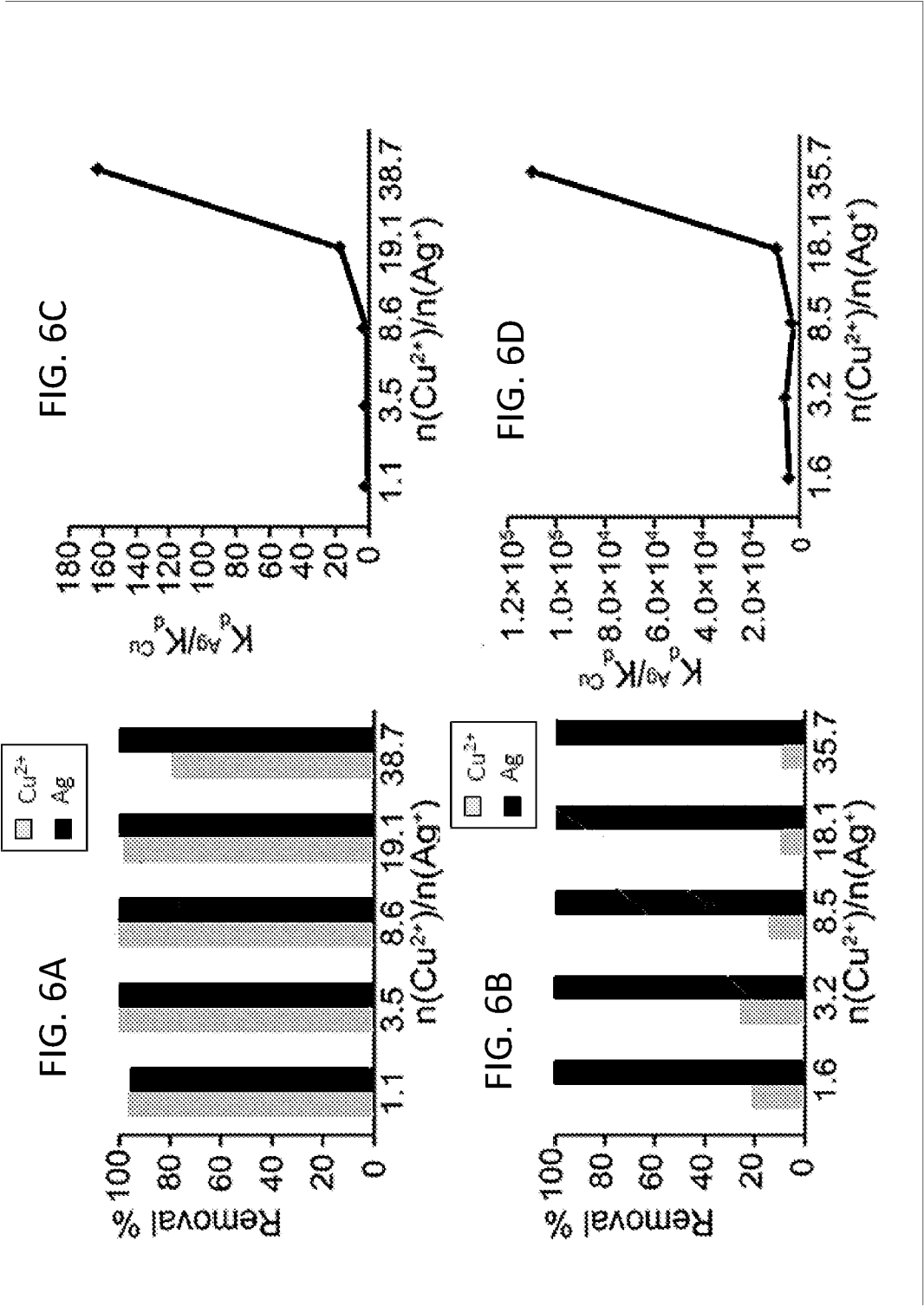
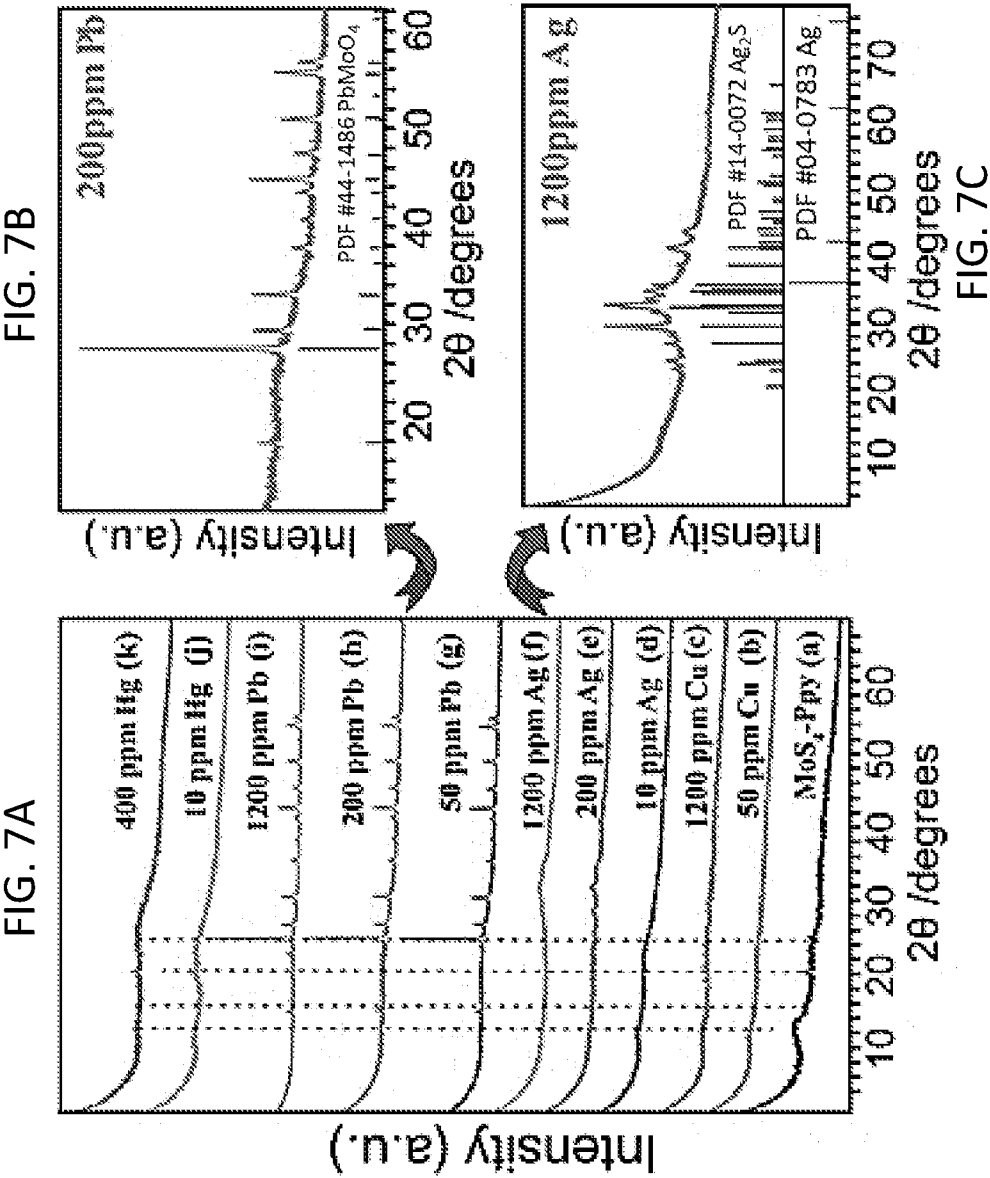


FIG. 5







after MoS₄-Ppy adsorbed Cu²⁺

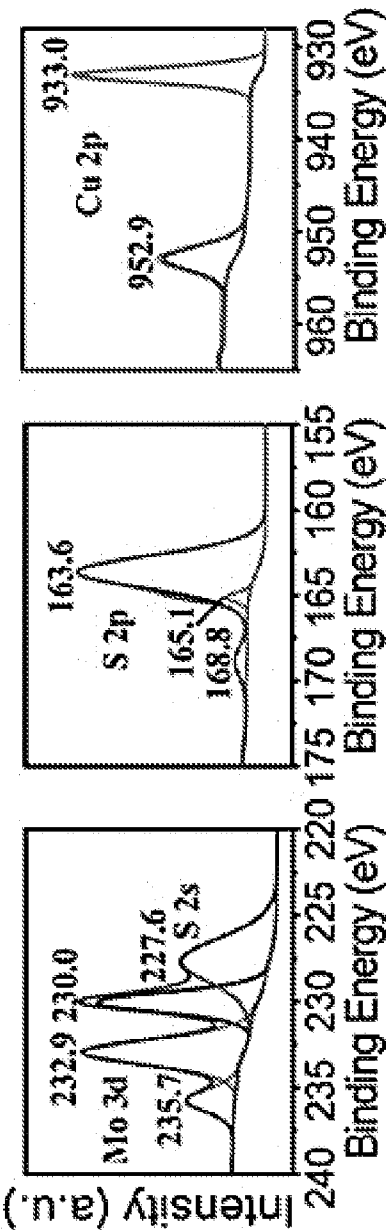


Fig. 8A

Fig. 8B

Fig. 8C

after MoS₄-Ppy adsorbed Ag⁺

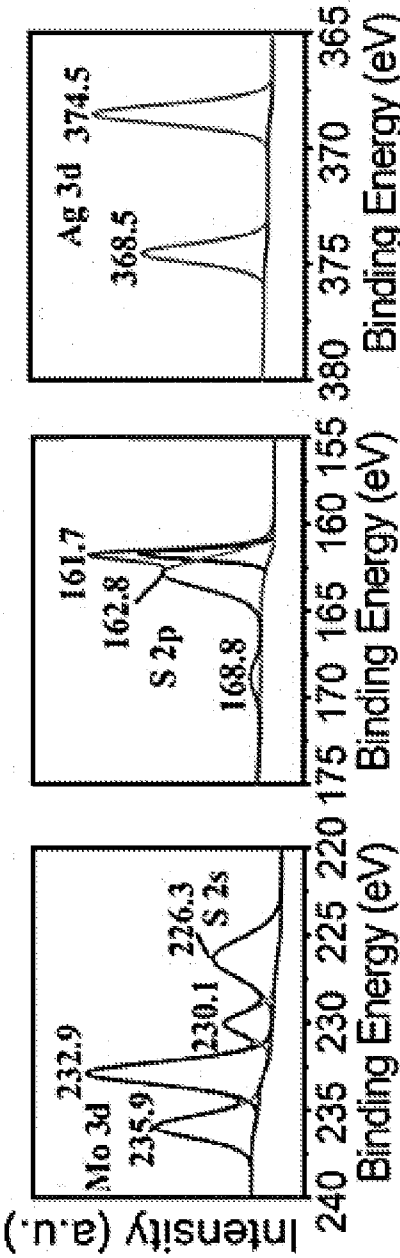


FIG. 8D

FIG. 8E

FIG. 8F

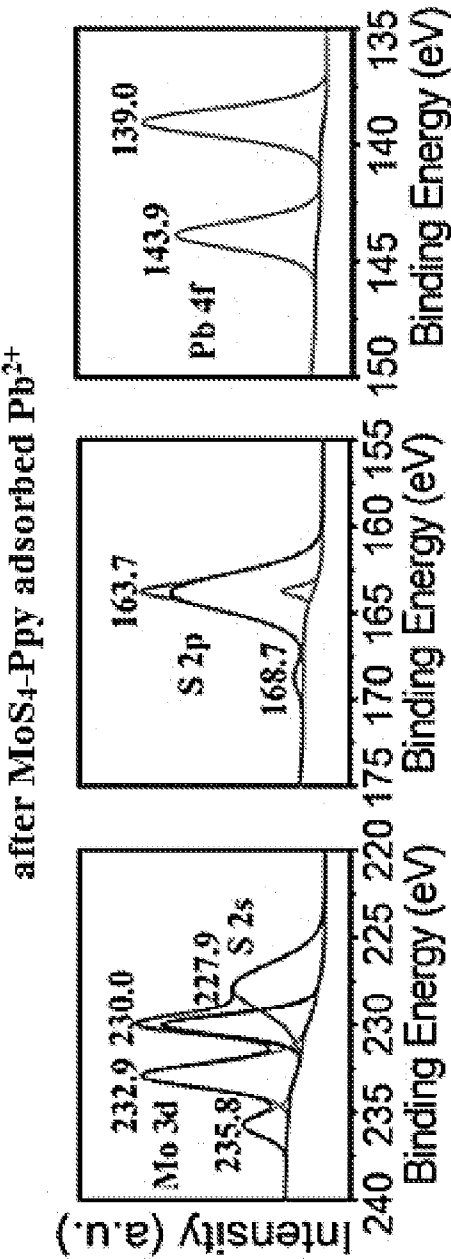


FIG. 8I

FIG. 8H

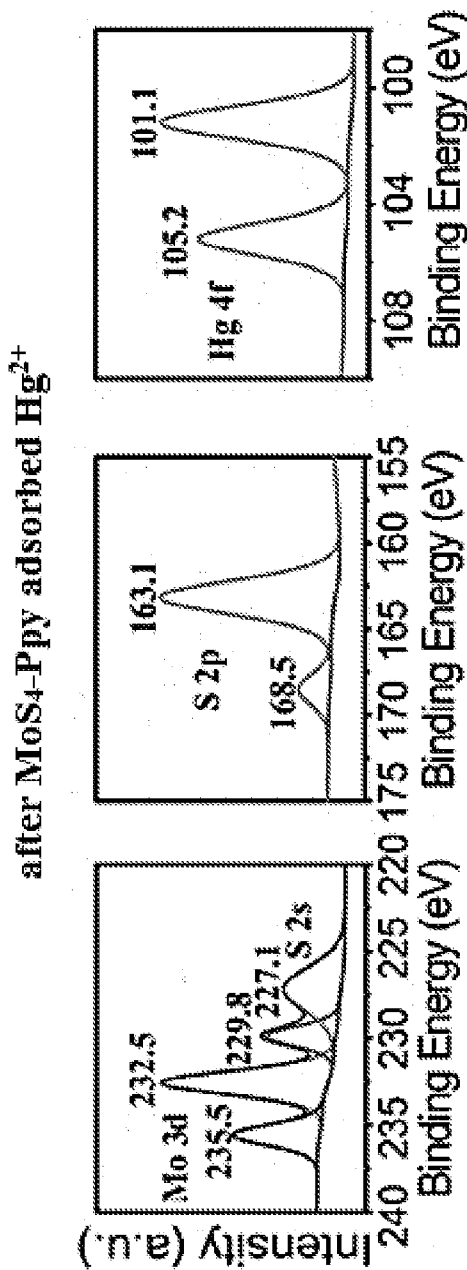


FIG. 8L

FIG. 8K

FIG. 8J

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FIG. 9

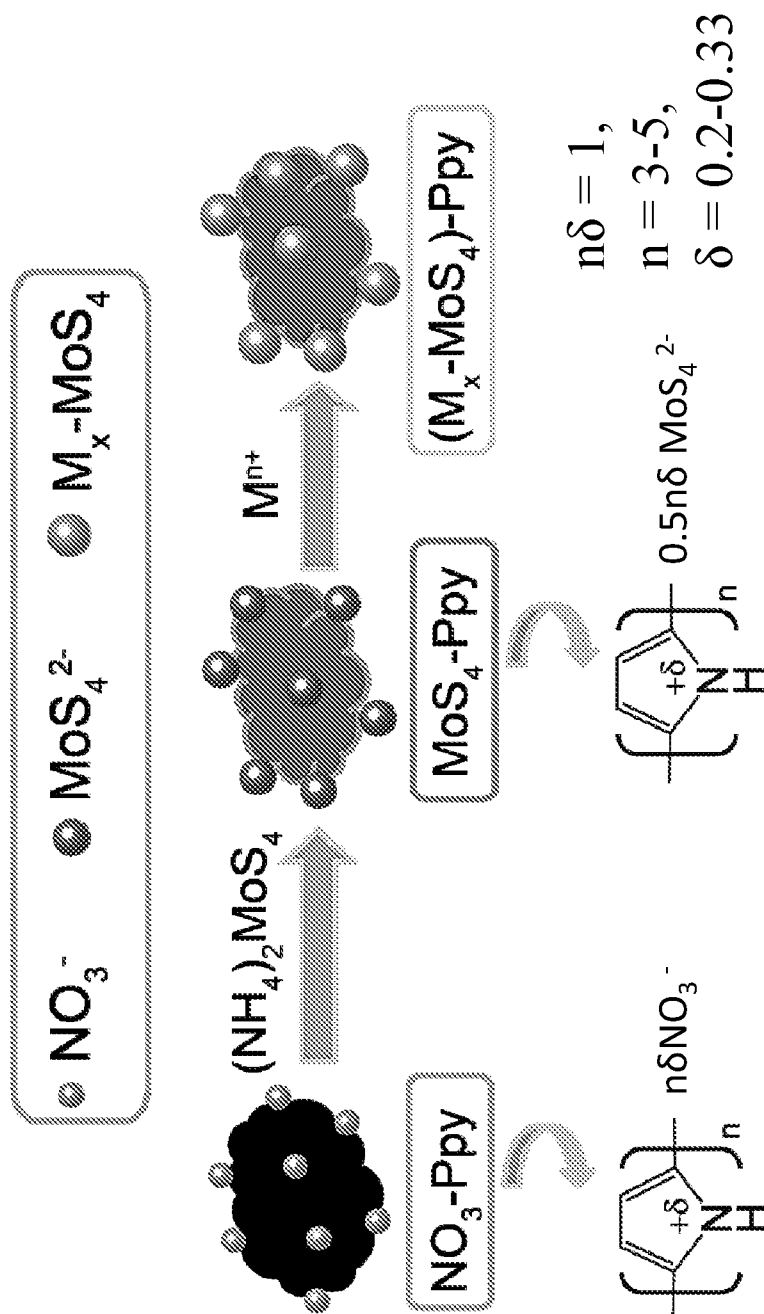


FIG. 10B

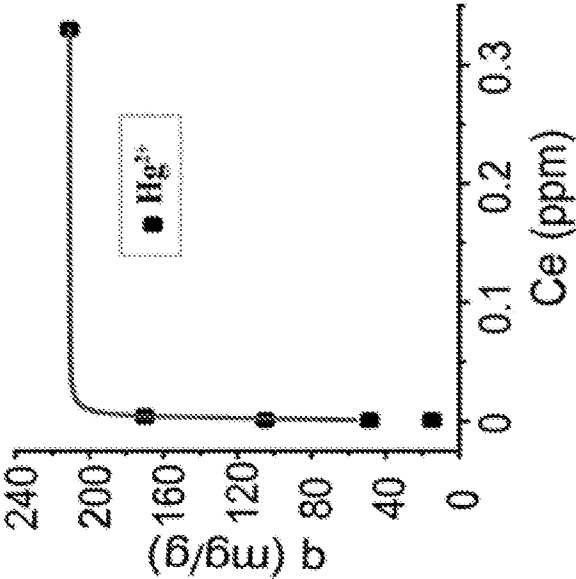
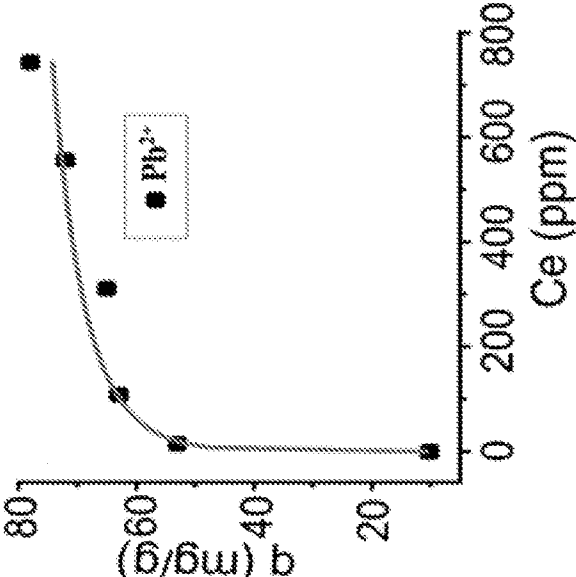


FIG. 10A



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FIG. 11B

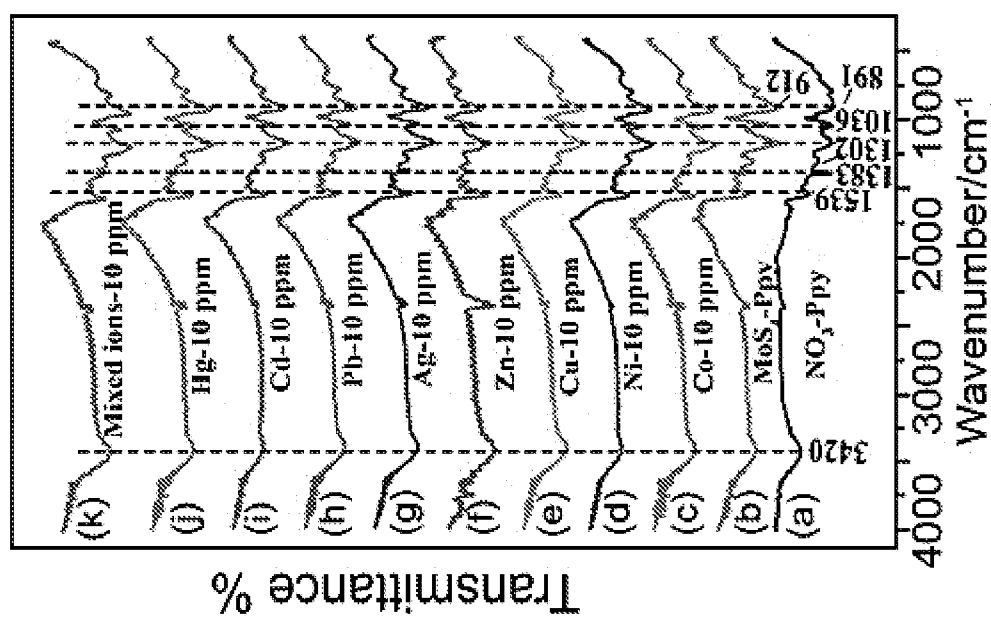


FIG. 11A

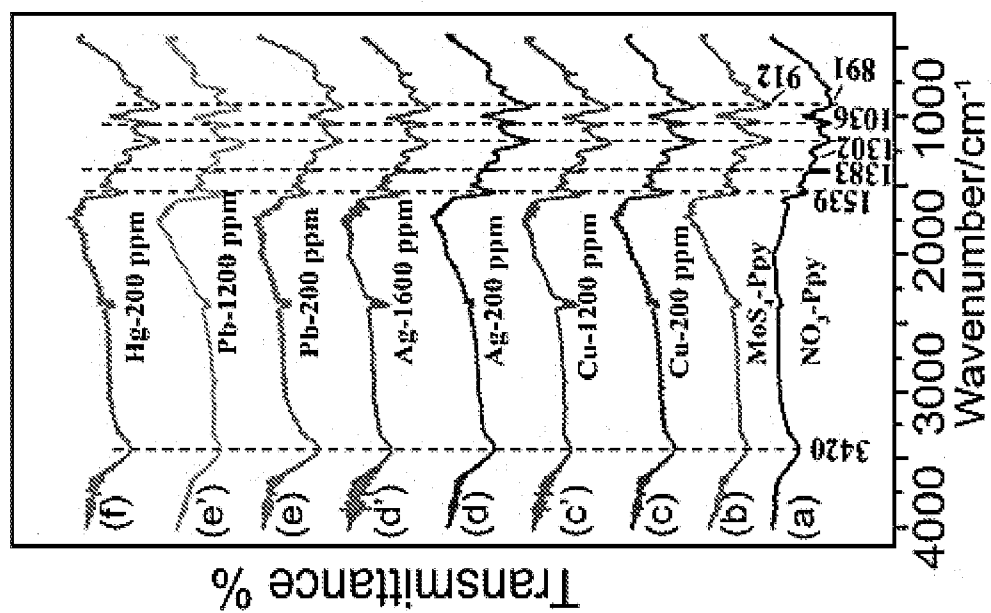


FIG. 12B

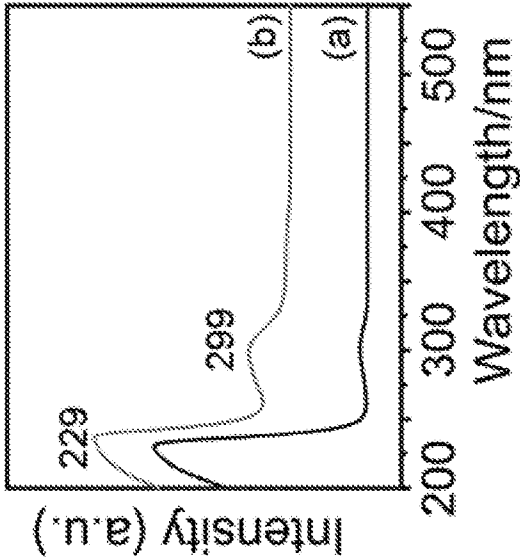


FIG. 12A

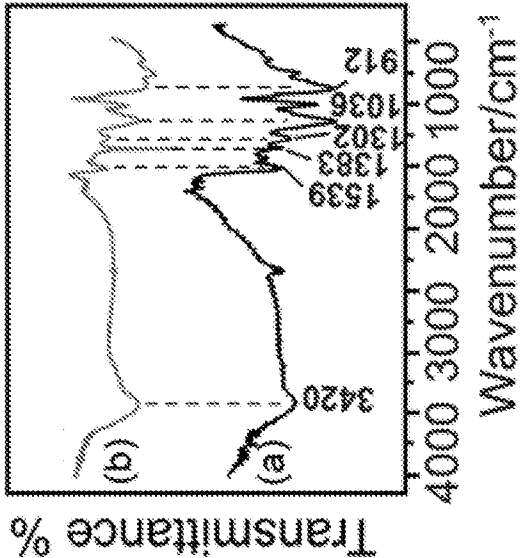


FIG. 13A

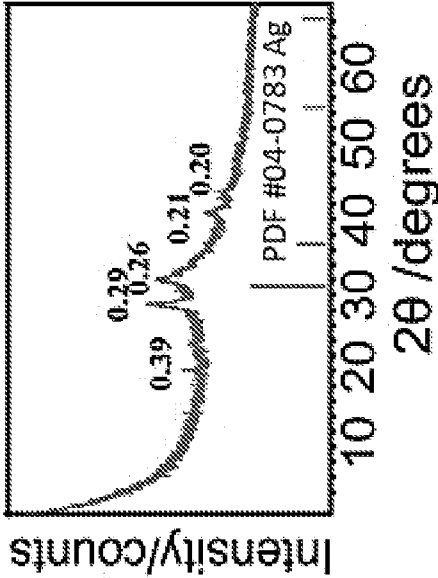


FIG. 13B

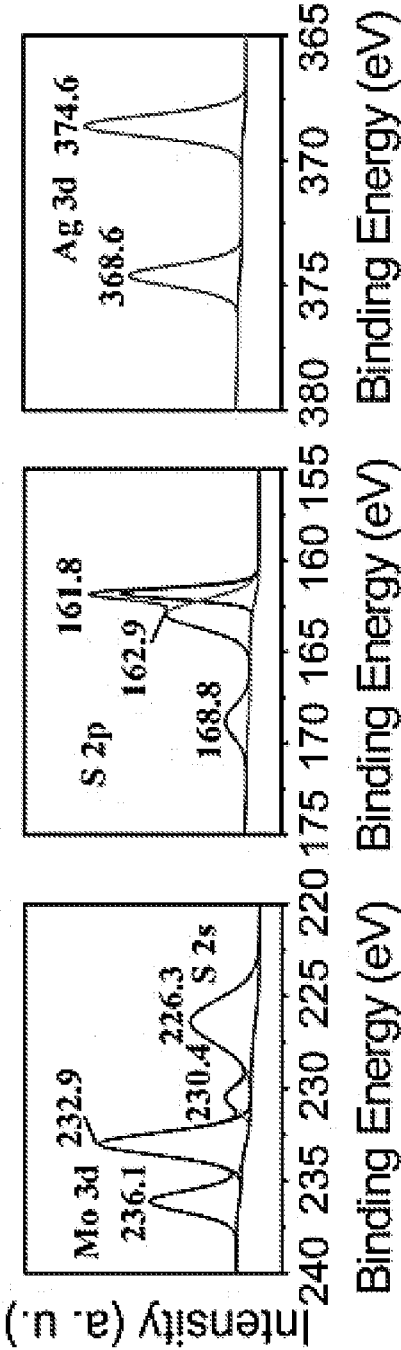
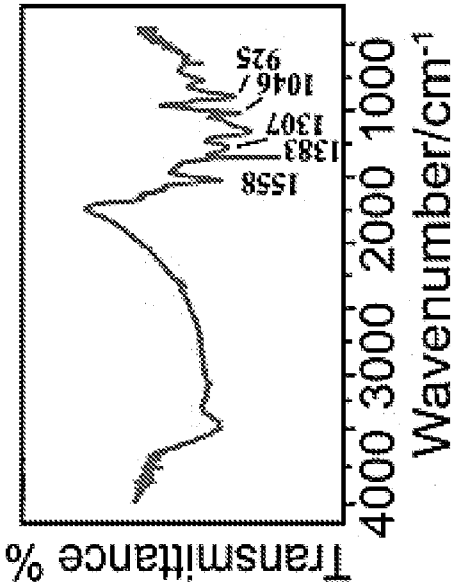


FIG. 13C

FIG. 13D

FIG. 13E

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2018/065614

A. CLASSIFICATION OF SUBJECT MATTER
 IPC(8) - B01J 20/26; C02F 1/28; C08F 26/06 (2019.01)
 CPC - B01J 20/226; C02F 1/285; C08F 26/06 (2019.01)

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)

See Search History document

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

USPC - 210/688; 502/402; 526/258; 528/487 (keyword delimited)

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

See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,233,000 A (YODICE) 03 August 1993 (03.08.1993) entire document	1-3, 7
A	US 9,536,633 B2 (HIGASHIMURA et al) 03 January 2017 (03.01.2017) entire document	1-19
A	US 5,108,573 A (RUBINSTEIN et al) 28 April 1992 (28.04.1992) entire document	1-19
A	US 2004/0146786 A1 (SATO et al) 29 July 2004 (29.07.2004) entire document	1-19

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:

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"E" earlier application or patent but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"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

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Date of the actual completion of the international search

29 January 2019

Date of mailing of the international search report

14 FEB 2019

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