

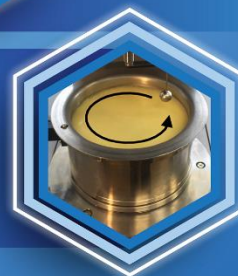
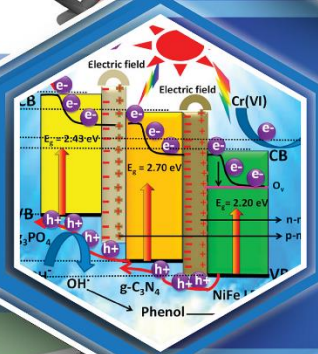
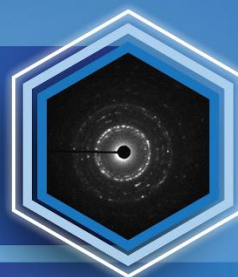
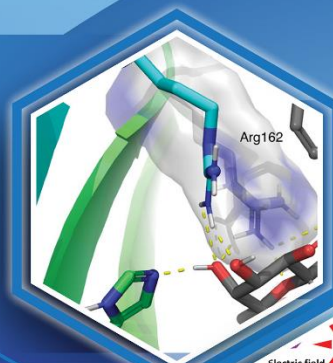


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Selective Adsorption of Hemoglobin in Human Whole Blood with a Nickel Monosubstituted Silicotungstic Acid Hybrid

Qing Chen, Meng-Meng Wang, Yang Zhang, and Dan-Dan Zhang*

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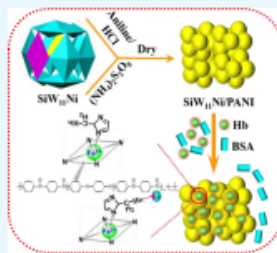
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ABSTRACT: A nickel monosubstituted polyoxometalate (POM)/polyaniline organic–inorganic hybrid $\text{SiW}_{11}\text{Ni}/\text{PANI}$ was synthesized using the liquid-phase method at room temperature to achieve the solidification of water-soluble POMs. The $\text{SiW}_{11}\text{Ni}/\text{PANI}$ hybrid was characterized by scanning electron microscopy, thermogravimetric analysis, Fourier transform infrared spectroscopy, X-ray diffraction, and zeta potential. On the basis of π – π stacking and affinity interaction between the $\text{SiW}_{11}\text{Ni}/\text{PANI}$ hybrid and proteins, the $\text{SiW}_{11}\text{Ni}/\text{PANI}$ hybrid showed good adsorption selectivity to hemoglobin (Hb). At pH 7.0, 0.5 mg of $\text{SiW}_{11}\text{Ni}/\text{PANI}$ resulted in an adsorption efficiency of 92.4% for 1 mL of 100 $\mu\text{g mL}^{-1}$ Hb. The adsorption behavior of Hb on the surface of the hybrid fitted with the Langmuir model, and the maximum adsorption capacity was 692 mg g^{-1} . The adsorbed Hb was eluted by BR (0.04 mol L^{-1} , pH 9), providing a recovery of 94%. Sodium dodecyl sulfate–polyacrylamide gel electrophoresis assay results indicated that the Hb in human whole blood could selectively be adsorbed by the $\text{SiW}_{11}\text{Ni}/\text{PANI}$ hybrid, and the obtained Hb was with high purity. It could expand the application of POMs in life science due to the application of the POM hybrid in protein isolation/purification.



INTRODUCTION

Polyoxometalates (POMs) are a class of polymetallic oxygen cluster compounds, formed by the former transition metal ions (mainly V^{5+} , Mo^{6+} , and W^{6+}) through oxygen linking, with excellent redox characteristics, large size, high negative charge, nucleicity, and thermal stability. Moreover, POMs generally show a cage structure, which is a better receptor molecule and can bind with inorganic molecules, organic molecules, or ions to form the supramolecular compound.^{1,2} Therefore, they have been widely used in many fields, such as drugs, catalysis, electrochemistry, photochromic, magnetism, and medicine, and have attracted the attention of researchers.^{3–5} Moreover, the negative electricity and the oxygen atoms of POMs provide many effective binding sites for their interaction with proteins. For example, through electrostatic interactions between the protein and POMs, the POMs $[\text{Ce}(\alpha\text{-PW}_{11}\text{O}_{39})_2]^{10-}$ of the Keggin type can selectively hydrolyze lysozyme in egg white, the POMs of Zr^{IV} -substituted Keggin, Wells–Dawson, and Lindqvist types can selectively hydrolyze myoglobin under mild acidic and neutral conditions. Therefore, the study of interactions between POMs and different protein molecules has become an interesting topic.^{6–12}

However, POMs are well soluble, which make them difficult to be separated from the solution system and limit their application in sample pretreatment. Therefore, the immobilization of POMs is very practical for broadening their application in the field of sample pretreatment. In recent years, organic–inorganic hybrids have promoted the development of functionalized materials and have attracted wide attention.^{13,14}

A combination of POMs and transition metal complexes will form an inorganic–organic hybrid combining the advantages of each component with a complex and attractive structure.¹⁵ There are weak intermolecular interactions, including hydrogen bonds and anion– π interactions in POMs, due to many oxygen atoms of POMs, which is better for constructing high-dimensional supramolecular architectures.¹⁶ Many ligands can be used to build inorganic–organic hybrid materials, for example, *N*-heterocyclic carboxylic acids, H_2PDA (1,10-phenanthroline-2,9-dicarboxylic acid), and pyridine-2,3-dicarboxylic acid (2,3-pydc).^{17–20} POMs possess a variable structure and favorable physical and chemical properties, such as catalytic, photochemical, and electrochemical activity.²¹ For example, Fashapoyeh's group has reported the first example of hydrogen evolution reactivity of lanthanide-substituted Keggin-type polyoxotungstates under photochemical and electrochemical conditions.²² The inorganic–organic functionalized materials can be formed between inorganic anions and organic large cations in aqueous solution through electrostatic interaction and layer by layer self-assembly. Their structural features such as a porous structure and high surface

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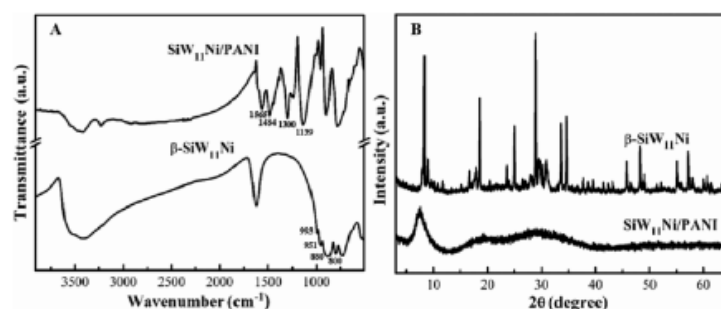


Figure 1. FT-IR (A) and XRD (B) spectra of β -SiW₁₁Ni and SiW₁₁Ni/PANI.

area and special surface activity give it potential applications in solid-phase extraction and separation of proteins.^{25–26} Polyaniline is a polymer compound, with a simple synthesis process, good chemical and environmental stability, and excellent optical, electric, and magnetic properties. Moreover, polyaniline is poorly soluble due to its chain rigidity and strong interchain interaction, which also lays the foundation for the synthesis of solid materials.²⁷ Therefore, the synthesis of POM functionalized materials through the combination of POMs and polyaniline for isolation and purification of proteins is expected to provide effective technical support of protein separation analysis and theoretical support of sample pretreatment for proteomic analysis and disease analysis.

In the present work, the organic–inorganic hybrid SiW₁₁Ni/PANI is synthesized using the liquid-phase method at room temperature, and it shows high selectivity for separation and purification of hemoglobin (Hb) in human whole blood as an adsorbent.

EXPERIMENTAL SECTION

Materials and Reagents. See details in the Supporting Information.

Instruments. See details in the Supporting Information.

Preparation and Characterization of the SiW₁₁Ni/PANI Hybrid. The SiW₁₁Ni/PANI hybrid is prepared by the following procedure. 6.4 g of β -K₈SiW₁₁O₃₉·14H₂O is added into ddH₂O (30 mL), and Ni(NO₃)₂ solution (4 mL, 2 mmol) is added dropwise to the solution after β -K₈SiW₁₁O₃₉·14H₂O dissolved. The reaction is conducted for 10 min under stirring at 40 °C. After reaction, KCl (2 g) is dissolved into the filtrate, the mixture is crystallized at 5 °C, and β -SiW₁₁Ni is obtained. The β -SiW₁₁Ni is dissolved into HCl solution (1 mol L^{−1}, 30 mL); then, aniline (0.93 g) and ammonium peroxydisulfate (2.3 g) are added into the abovementioned solution. Through electrostatic interaction, the β -SiW₁₁Ni inserts into the polyaniline at the −N= position, and the final product SiW₁₁Ni/PANI hybrid is successfully prepared after reaction for 24 h. The product is cleaned with methanol and ddH₂O and dried under vacuum for 48 h.

Protein Adsorption with the SiW₁₁Ni/PANI Hybrid. In this experiment, the performance of the SiW₁₁Ni/PANI hybrid for protein adsorption is evaluated by employing Hb and BSA as the protein model. BR solution (0.04 mol L^{−1}) is used to adjust the pH value of the medium. The SiW₁₁Ni/PANI hybrid (5.0 mg) and 1 mL of deionized water are added to a 2

mL centrifuge tube. After sonication, 100 μ L of the suspension is removed from the 2 mL centrifuge tube, and the supernatant is discarded after centrifugation. Then, the protein solution (100 μ g mL^{−1}, 1.0 mL) is added into the abovementioned centrifuge tube. The mixture oscillates for 10 min to facilitate the adsorption process. After centrifuging (6000 rpm, 5 min), the characteristic absorbance of the protein is determined for deducing the contents of residual proteins in the supernatant using a U-3900 UV–vis spectrophotometer.

Then, the BR solution (0.04 mol L^{−1}, pH = 9) is adopted as a stripping reagent for eluting the adsorbed protein by SiW₁₁Ni/PANI. BR solution (1.0 mL) is mixed with the SiW₁₁Ni/PANI hybrid, and the mixture is vibrated for 10 min to facilitate recovery of the adsorbed protein from the surface of the SiW₁₁Ni/PANI hybrid. The supernatant after centrifugation at 6000 rpm for 5 min is collected for the following study.

RESULTS AND DISCUSSION

Preparation and Characteristics of the SiW₁₁Ni/PANI Hybrid. The Fourier transform infrared spectroscopy (FT-IR) spectrum results of β -SiW₁₁Ni and SiW₁₁Ni/PANI in Figure 1A show that four characteristic bands of the POM structure are identified at 800, 880, 951, and 993 cm^{−1}, which demonstrates that β -SiW₁₁Ni has been inserted into the framework of polyaniline. In the meantime, it is obviously observed that the bands of polyaniline at 1139, 1300, 1484, and 1565 cm^{−1} belong to vibration of benzoquinone, stretching vibrations of C–N, stretching vibrations of phenyl ring modes, and the absorption of quinoid structures, respectively, which demonstrate the formation of the SiW₁₁Ni/PANI hybrid. Figure 1B shows X-ray diffraction (XRD) spectra of β -SiW₁₁Ni and SiW₁₁Ni/PANI. It is seen that the distinct diffraction peaks at $2\theta = 7.5^\circ$, 18.6° , 25° , 29° , and 34.6° are observed in the XRD spectra of prepared β -SiW₁₁Ni. After aniline doping, a diffraction peak is observed at $2\theta = 7.6^\circ$, and the diffraction peaks of β -SiW₁₁Ni are not present in the XRD spectra of the SiW₁₁Ni/PANI hybrid. Moreover, the diffraction figure of SiW₁₁Ni/PANI is completely different from that of β -SiW₁₁Ni, indicating that the new hybrid is prepared after aniline doping and it is not a mechanical mixing of the reactive substances. The diffraction peak of SiW₁₁Ni/PANI indicates that the prepared SiW₁₁Ni/PANI hybrid is non-stereotype powder.

The thermogravimetric analysis (TG) result of the SiW₁₁Ni/PANI hybrid is shown in Figure 2A. The result indicates that

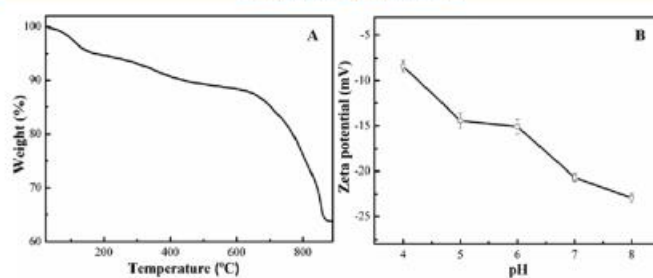


Figure 2. TG result (A) and zeta potential (B) of $\text{SiW}_{11}\text{Ni}/\text{PANI}$.

there are three weightlessness stages along with the temperature increase between 25 and 900 °C. The first weightlessness is observed between 25 and 100 °C due to the loss of crystal water. Another weightlessness is followed between 100 and 520 °C which is surely attributed to the decomposition of the PANI framework in the hybrid. With the temperature being further increased to 900 °C, the third weightlessness is obtained due to decomposition of the POMs. The zeta potential of the $\text{SiW}_{11}\text{Ni}/\text{PANI}$ hybrid is shown in Figure 2B. The hybrid is negatively charged at pH 4–8.

The scanning electron microscopy (SEM) images of β - SiW_{11}Ni and $\text{SiW}_{11}\text{Ni}/\text{PANI}$ are shown in Figure 3, and the results reveal that β - SiW_{11}Ni exhibits a block structure and the prepared $\text{SiW}_{11}\text{Ni}/\text{PANI}$ is a hybrid stacked by multiple particles with a smooth surface and micron size.

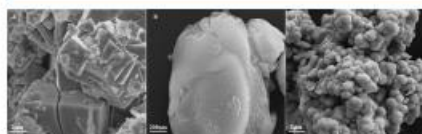


Figure 3. SEM images of SiW_{11}Ni (A) and $\text{SiW}_{11}\text{Ni}/\text{PANI}$ (B, C).

Protein Adsorption by the $\text{SiW}_{11}\text{Ni}/\text{PANI}$ Hybrid. Albumin (BSA, pI 5) and Hb (pI 7) are used as protein models to investigate the adsorption properties of the SiW_{11}Ni

PANI hybrid. First, the effect of pH on adsorption efficiency of proteins on the surface of the $\text{SiW}_{11}\text{Ni}/\text{PANI}$ is studied, and the results are shown in Figure 4A. It is seen that the adsorption efficiency of Hb and BSA first increases and then decreases. The maximum adsorption efficiency is obtained when the pH is at the isoelectric point (pI) of a protein. When the pH approaches to the pI of a protein, hydrogen bonds between the hybrid and protein are the main driving force to prompt protein adsorption to the surface of the hybrid. When the pH is below the pI of a protein, the protonation of O and NH_2 on the surface of the hybrid is detrimental to form hydrogen bonds, so adsorption efficiency of proteins decreases. However, when pH is higher than pI of a protein, the hybrid and the protein are both negatively charged, and the electrostatic repulsion causes a decrease in adsorption efficiency.

The adsorption efficiency of the $\text{SiW}_{11}\text{Ni}/\text{PANI}$ hybrid is 92.4 and 5.7% for Hb and BSA, respectively, which illustrates a favorable selectivity toward Hb at pH 7. Hb is a globular protein with two kinds of existence forms, that is, loose oxygenation form and tight deoxygenation form. With increasing pH, Hb molecules could bind oxygen molecules, which makes the structure of Hb change into an oxygenation form, and Fe^{2+} in heme enters the porphyrin ring to form a planar structure. Meanwhile, the position of the histidine residue changes, which makes the structure of Hb become loose.²⁸ When the pH approaches to pI of Hb, the Hb residues are better exposed and the affinity interactions between the

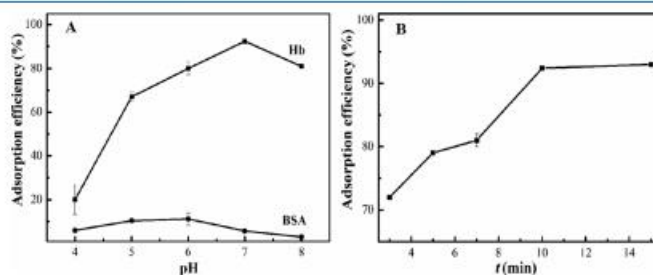


Figure 4. Effect of pH (A) and adsorption time (B) on adsorption efficiencies of proteins onto the surface of the $\text{SiW}_{11}\text{Ni}/\text{PANI}$ hybrid. Amount of the $\text{SiW}_{11}\text{Ni}/\text{PANI}$ hybrid: 0.5 mg and protein: $100 \mu\text{g mL}^{-1}$, 1 mL.

exposed histidine residues and the nickel ions on the hybrid and the π - π interactions between the porphyrin ring and the hybrid promote Hb adsorption to the surface of the hybrid. However, due to the framework structure of BSA without the heme group, the affinity interactions and π - π interactions between the hybrid and BSA are much weaker than those of Hb. Therefore, inferior adsorption capability is obtained at pH 7.

In order to make the protein more completely adsorbed on the surface of the hybrid and make the adsorption process reach equilibrium, the effect of the adsorption time on adsorption efficiency of Hb is studied. The results are shown in Figure 4B. It is seen that adsorption efficiency of Hb gradually increases with the increase in time. The adsorption efficiency of Hb reaches the maximum at an adsorption time of 10 min, and the further increase in adsorption time has little effect on adsorption efficiency of Hb.

Adsorption Isotherm of Proteins and Recovery of Retained Proteins. To investigate adsorption behavior of Hb on the surface of the SiW₁₁Ni/PANI hybrid, a series of Hb solutions with different concentrations are treated with the hybrid. After adsorption, the content of Hb in the supernatant is quantified, and dynamic adsorption isotherm of Hb is obtained, as shown in Figure 5, by deriving IgG adsorption

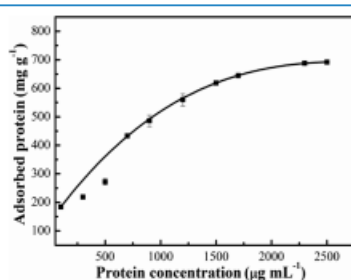


Figure 5. Adsorption isotherm for Hb on the SiW₁₁Ni/PANI hybrid. Volume of Hb solution: 1.0 mL, pH 7.0; adsorption time: 10 min; and amount of SiW₁₁Ni/PANI hybrid: 0.5 mg.

capacity from the following equation, where K_d ($\mu\text{g mL}^{-1}$) attributes to the equilibrium constant, Q_{max} (mg g^{-1}) is the theoretical maximum adsorption capacity, C_e ($\mu\text{g mL}^{-1}$) represents the equilibrium concentration, and Q_e (mg g^{-1}) is the adsorption capacity.

By fitting the data into the abovementioned equation, the theoretical maximum adsorption capacity of Hb is concluded to be 692.0 mg g^{-1} , and adsorption behaviors of Hb fit well with the Langmuir model.

For subsequent biological analysis and studies, the adsorbed protein on the SiW₁₁Ni/PANI hybrid surface needs to be eluted into aqueous medium using stripping reagents. According to Figure 4A, the adsorption efficiency of Hb is low under acidic and alkaline conditions. Therefore, the acidic or alkaline buffer solution may be chosen as stripping reagents. For this purpose, the recovery of Hb from the surface of SiW₁₁Ni/PANI is investigated using different stripping reagents, which includes NaCl (0.1 mol L^{-1}), BR buffer (0.04 mol L^{-1} , pH 4, 9), sodium dodecyl sulfate (SDS) (0.1

mol L^{-1}), and so on. The results in Figure 6 indicated that BR buffer (0.04 mol L^{-1} , pH 9) offers favorable recoveries of 94% for Hb, while other stripping reagents mentioned lead to virtually no recovery of adsorbed Hb.

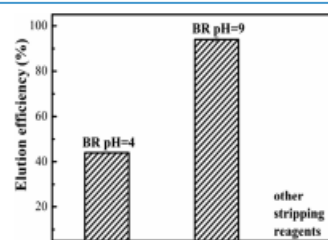


Figure 6. Elution efficiency of Hb using different kinds of stripping reagents. Volume of Hb solution: 1.0 mL, pH 7.0; adsorption time: 10 min; amount of SiW₁₁Ni/PANI hybrid: 0.5 mg.

Isolation of Proteins from Human Whole Blood. The practicability of the SiW₁₁Ni/PANI hybrid is investigated by separation and purification of Hb in human whole blood. In practice, human whole blood is diluted 100 times, and the pH value of solution is adjusted to 7. Subsequently, the sample solution is added into the hybrid following the process described in the Experimental Section. The adsorbed Hb is eluted by BR buffer solution (0.04 mol L^{-1} , pH 9) for the following analysis of SDS-PAGE assay, and the results are shown in Figure 7. The protein bands in human whole blood

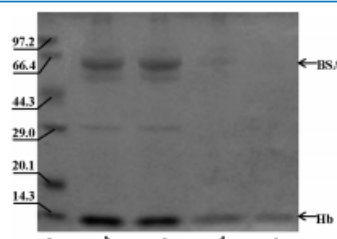


Figure 7. SDS-PAGE assay results. Lane a, molecular weight standards (Marker in kDa); Lane b, 100-fold diluted human whole blood; Lane c, 100-fold diluted human whole blood adsorbed by the SiW₁₁Ni/PANI hybrid; Lane d, collected Hb by eluting with BR buffer (0.04 mol L^{-1} , pH 9); Lane e, Hb standard ($100 \mu\text{g mL}^{-1}$).

(Lane b) mainly correspond to Hb (14.3 kDa) and HSA (66.4 kDa). After eluting adsorbed proteins from the hybrid, Lane 5 shows the protein profile in the supernatant where only a single band appears at 14.3 kDa (Lane d) consistent with Hb. Lane e shows the band of standard Hb ($100 \mu\text{g mL}^{-1}$) solution for comparison. The abovementioned result indicates that Hb in human whole blood could be effectively separated and purified using the SiW₁₁Ni/PANI hybrid as the adsorbent.

CONCLUSIONS

The organic-inorganic hybrid SiW₁₁Ni/PANI is synthesized using the liquid-phase method at room temperature. In the

experiment, the SiW₁₁Ni/PANI hybrid shows excellent adsorption selectivity toward Hb according to the affinity interactions and π - π interactions. Therefore, a new method for isolating Hb is established, and isolation of Hb in human whole blood is realized with high purity, which further broadens the application of POMs in sample pretreatment and provides a method for bio-macromolecules, especially proteins with highly selective isolation and purification from complex biological samples as an alternative to other nonmild processes.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.2c01997>.

Additional information as noted in the text, materials and reagents, and instruments (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Dan-Dan Zhang — Department of Public Health and Public Health Laboratory Centre, Shenyang Medical College, Shenyang 110034, China; Phone: +86 24 62215712; Email: 604859039@qq.com; Fax: +86 24 62215712

Authors

Qing Chen — Department of Pharmacy, Shenyang Medical College, Shenyang 110034, China; orcid.org/0000-0001-6251-8292

Meng-Meng Wang — Department of Pharmacy, Shenyang Medical College, Shenyang 110034, China; orcid.org/0000-0001-5517-2529

Yang Zhang — Department of Pharmacy, Shenyang Medical College, Shenyang 110034, China; orcid.org/0000-0001-9594-1695

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/acsomega.2c01997>

Author Contributions

Q.C. and M.-M.W. contributed equally to this work.

Notes

The authors declare no competing financial interest.

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