

ELECTROCHEMICAL SENSING OF HEAVY METAL CONTAMINANTS

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INDIAN INSTITUTE OF TECHNOLOGY DELHI
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by

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submitted

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ਜਿਉ ਅੰਧੇਰੈ ਦੀਪਕੁ ਬਾਲੀਐ ਤਿਉ ਗੁਰ ਗਿਆਨਿ
ਅਗਿਆਨੁ ਤਜਾਇ ॥੨॥

ਸਿਰੀਰਾਗੁ (ਮਃ੩) (੬੪) ੨:੪ - ਗੁਰੂ ਗ੍ਰੰਥ ਸਾਹਿਬ:
ਅੰਗ ੩੯ ਪੰ. ੧੦

Sri Raag Guru Amar Das

Jio Andhhaerai Dheepak Baaleeai Thio Gur Giaan

Agiaan Thajaae //2//

*Like a lamp lit in the darkness, the
spiritual wisdom of the Guru dispels
ignorance. //2//*

Dedicated to the Almighty and my Family

Certificate from Advisors

This is to certify that the thesis entitled **ELECTROCHEMICAL SENSING OF HEAVY METAL CONTAMINANTS**, being submitted by Priya Vinayak to IIT Delhi, is worthy of consideration for the award of the degree of Ph.D. and is a record of the original research work carried out by this student under our supervision. The results contained in this thesis, which may have been previously communicated in the form of manuscripts, conference presentations or patent filings, have not been submitted in part or full, to any other University or Institute for the award of any academic degree.

We certify that this student has pursued the prescribed course of research.

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Abstract

The World Health Organization recognizes heavy metal toxicity arising from contaminated water supplies as a significant challenge affecting millions of people worldwide, especially in rapidly developing economies of Asia. The maximum permissible limit for heavy metals has been identified as 3 ppb for Cd^{2+} , 10 ppb for Pb^{2+} , 2000 ppb for Cu^{2+} , 1 ppb for Hg^{2+} and 3000 ppb Zn^{2+} and the exposure above these limit can cause serious health hazards in humans. Henceforth, tracking the concentration of these heavy metal ions in water samples (drinking water and effluent discard) is of utmost importance. The conventional techniques for detecting heavy metal ions in water samples involve inductively coupled plasma mass spectroscopy (ICP-MS), atomic absorption spectroscopy, and chemiluminescence, which have been used in the lab for efficient sensing of heavy metal in the water and biological samples. However, these techniques require trained personnel, costly equipment, and a longer turnaround time. Further, these techniques cannot be currently used for onsite, real-time monitoring. On the other hand, electrochemical sensors have been used for the last two decades to sense heavy metal ions in water samples. The Environmental Protection Agency recommends tracing the amount of heavy metals in water. The electrochemical sensor consists of 2 important components: the sensing layer and the transducer. Oxide layers, polymers, 2D nanomaterials, carbon nanotubes, graphene, chalcogenide, and dichalcogenide are the most popular sensing layers for detecting heavy metal ions. Chalcogenides and dichalcogenide materials are known to stable in harsh chemical environments and, hence, were chosen for the detection application in this dissertation. The transducing structure should be stable in the chemical environment. The most commonly used are ion-selective electrodes, field effect transistors, colorimetric,

fluorescent, and surface-enhanced Raman scattering. This dissertation focuses on synthesizing, depositing, and fabricating different transducing devices using chalcogenide and dichalcogenide sensing films. Ion selective electrodes, electrolyte insulator semiconductor capacitors, and extended gate field effect transistor devices were fabricated using chalcogenide and dichalcogenide materials. Nanoheterostructures composed of chalcogenides to sense Cd^{2+} , Cu^{2+} , Hg^{2+} and Pb^{2+} ions in water samples in low ppb regime.

सार

विश्व स्वास्थ्य संगठन दूषित जल आपूर्त से उत्पन्न होने वाली भारी धातु विषाक्तता को दुनिया भर में लाखों लोगों को प्रभावित करने वाली एक महत्वपूर्ण चुनौती के रूप में मानता है, खासकर एशिया की तेजी से विकसित हो रही अर्थव्यवस्थाओं में। भारी धातुओं के लिए अधिकतम अनुमेय सीमा को Cd^{2+} के लिए 3 ppb, Pb^{2+} के लिए 10 ppb के रूप में पहचाना गया है।, 2000 ppb के लिए Cu^{2+} , 1 ppb के लिए Hg^{2+} और 3000 ppb Zn^{2+} और इन सीमा से ऊपर का जोखिम मनुष्यों में गंभीर स्वास्थ्य खतरे पैदा कर सकता है। अब से, पानी के नमूनों (पीने के पानी और अपशष्ट जल) में इन भारी धातु आयनों की सांद्रता पर नज़र रखना अत्यंत महत्वपूर्ण है। पानी के नमूनों में भारी धातु आयनों का पता लगाने के लिए पारंपरिक तकनीकों में प्रेरक रूप से युग्मित प्लाज्मा मास स्पेक्ट्रोस्कोपी (आईसीपी-एमएस), परमाणु अवशोषण स्पेक्ट्रोस्कोपी और केमिलुमिनसेंस का उपयोग पानी और जैविक नमूनों में भारी धातु के कुशल संवेदन के लिए प्रयोगशाला में किया गया है। हालाँकि, इन तकनीकों के लिए प्रशिक्षित कर्मियों, महंगे उपकरण और लंबे समय तक काम करने की आवश्यकता होती है। इसके अलावा, इन तकनीकों का उपयोग वर्तमान में ऑनसाइट, वास्तविक समय की निगरानी के लिए नहीं किया जा सकता है। दूसरी ओर, पानी के नमूनों में भारी धातु आयनों को समझने के लिए पिछले दो दशकों से इलेक्ट्रोकेमिकल सेंसर का उपयोग किया जा रहा है। पर्यावरण संरक्षण एजेंसी पानी में भारी धातुओं की मात्रा का पता लगाने की सिफारिश करती है। इलेक्ट्रोकेमिकल सेंसर में 2 महत्वपूर्ण घटक होते हैं, सेंसिंग परत और ट्रांसड्यूसर। भारी धातु धातु आयनों का पता लगाने के लिए ऑक्साइड परतें, पॉलिमर, 2डी नैनोमेटेरियल्स, कार्बन नैनोट्यूब, ग्राफीन, चाल्कोजेनाइड और डाइक्लोजेनाइड सबसे लोकप्रिय रूप से उपयोग की जाने वाली सेंसिंग परतें हैं। चाल्कोग्रेडीज़ और डाइक्लोग्रेडीज़ सामग्री कठोर रासायनिक वातावरण को बनाए रखने के लिए जानी जाती है और इसलिए उन्हें इस शोध प्रबंध में पता लगाने के अनुप्रयोग के लिए चुना गया था। रासायनिक को पठनीय सिग्नल में स्थानांतरित करने के लिए ट्रांसड्यूसिंग संरचना के लिए परिष्कृत डजाइन की आवश्यकता होती है और इसे रासायनिक वातावरण को भी बनाए रखना चाहिए। सबसे अधिक इस्तेमाल किया जाने वाला आयन चयनात्मक इलेक्ट्रोड, क्षेत्र प्रभाव ट्रांजिस्टर, वर्णमित, फ्लोरोसेंट और सतह-संवधत रमन बिखराव। यह शोध प्रबंध चाल्कोजेनाइड और डाइक्लोजेनाइड सेंसिंग फिल्मों का उपयोग करके विभिन्न ट्रांसड्यूसिंग उपकरणों को संश्लेषित करने, जमा करने और निर्माण करने पर केंद्रित है। आयन चयनात्मक इलेक्ट्रोड, इलेक्ट्रोलाइट इंसुलेटर सेमीकंडक्टर कैपेसिटोसर, और विस्तारित गेट फील्ड प्रभाव ट्रांजिस्टर उपकरणों को चाल्कोजेनाइड और डाइक्लोजेनाइड सामग्रियों का उपयोग करके निर्मित किया गया था, और चाकोजेनाइड्स से बने नैनोहेटेरोस्ट्रक्चर को Cd^{2+} , Cu^{2+} को समझने के लिए बनाया गया था। कम पीपीबी शासन में पानी के नमूनों में, Hg^{2+} और Pb^{2+} आयन।

ਸਾਰ

ਵਿਸ਼ਵ ਸਿਹਤ ਸੰਗਠਨ ਦੁਸ਼ਿਤ ਪਾਣੀ ਦੀ ਸਪਲਾਈ ਤੋਂ ਪੈਦਾ ਹੋਣ ਵਾਲੀ ਭਾਰੀ ਧਾਤੂ ਦੇ ਜ਼ਹਿਰੀਲੇਪਣ ਨੂੰ ਵਿਸ਼ਵ ਭਰ ਦੇ ਲੱਖਾਂ ਲੋਕਾਂ ਨੂੰ ਪ੍ਰਭਾਵਿਤ ਕਰਨ ਵਾਲੀ ਇੱਕ ਮਹੱਤਵਪੂਰਨ ਚੁਣੌਤੀ ਵਜੋਂ ਮਾਨਤਾ ਦਿੰਦਾ ਹੈ, ਖਾਸ ਕਰਕੇ ਏਸ਼ੀਆ ਦੀਆਂ ਤੇਜ਼ੀ ਨਾਲ ਵਿਕਾਸਸ਼ੀਲ ਅਰਥਵਿਵਸਥਾਵਾਂ ਵਿੱਚ। ਭਾਰੀ ਧਾਤਾਂ ਲਈ ਅਧਿਕਤਮ ਅਨੁਮਤੀਯੋਗ ਸੀਮਾ ਦੀ ਪਛਾਣ Cd^{2+} ਲਈ 3 ppb, Pb^{2+} ਲਈ 10 ppb ਵਜੋਂ ਕੀਤੀ ਗਈ ਹੈ। Cu^{2+} ਲਈ 2000 ppb, Hg^{2+} ਅਤੇ 3000 ppb ਲਈ 1 ppb, Zn^{2+} ਅਤੇ ਇਹਨਾਂ ਸੀਮਾ ਤੋਂ ਵੱਧ ਐਕਸਪੋਜ਼ਰ ਮਨੁੱਖਾਂ ਵਿੱਚ ਗੰਭੀਰ ਸਿਹਤ ਖਤਰੇ ਦਾ ਕਾਰਨ ਬਣ ਸਕਦੇ ਹਨ। ਇਸ ਤੋਂ ਬਾਅਦ, ਪਾਣੀ ਦੇ ਨਮੂਨਿਆਂ (ਪੀਣ ਵਾਲੇ ਪਾਣੀ ਅਤੇ ਗੰਦੇ ਪਾਣੀ ਨੂੰ ਛੱਡਣਾ) ਵਿੱਚ ਇਹਨਾਂ ਭਾਰੀ ਧਾਤੂ ਆਇਨਾਂ ਦੀ ਗਾੜ੍ਹਾਪਣ ਨੂੰ ਟਰੈਕ ਕਰਨਾ ਬਹੁਤ ਮਹੱਤਵਪੂਰਨ ਹੈ। ਪਾਣੀ ਦੇ ਨਮੂਨਿਆਂ ਵਿੱਚ ਭਾਰੀ ਧਾਤੂ ਆਇਨਾਂ ਦੀ ਖੋਜ ਲਈ ਰਵਾਇਤੀ ਤਕਨੀਕਾਂ ਵਿੱਚ ਪ੍ਰੋਰਕ ਤੌਰ 'ਤੇ ਜੋੜੀ ਗਈ ਪਲਾਜ਼ਮਾ ਮਾਸ ਸਪੈਕਟ੍ਰੋਸਕੋਪੀ (ICP-MS), ਪ੍ਰਮਾਣੂ ਸਮਾਈ ਸਪੈਕਟ੍ਰੋਸਕੋਪੀ ਅਤੇ ਕੈਮਿਲਿਊਮਿਨਸੈਂਸ ਦੀ ਵਰਤੋਂ ਪਾਣੀ ਅਤੇ ਜੈਵਿਕ ਨਮੂਨਿਆਂ ਵਿੱਚ ਭਾਰੀ ਧਾਤੂ ਦੀ ਕੁਸ਼ਲ ਸੰਵੇਦਨਾ ਲਈ ਲੈਬ ਵਿੱਚ ਕੀਤੀ ਗਈ ਹੈ। ਹਾਲਾਂਕਿ, ਇਹਨਾਂ ਤਕਨੀਕਾਂ ਲਈ ਸਿਖਿਅਤ ਕਰਮਚਾਰੀਆਂ, ਮਹਿੰਗੇ ਸਾਜ਼ੋ-ਸਾਮਾਨ ਅਤੇ ਲੰਬੇ ਸਮੇਂ ਦੀ ਲੋੜ ਹੁੰਦੀ ਹੈ। ਇਸ ਤੋਂ ਇਲਾਵਾ, ਇਹਨਾਂ ਤਕਨੀਕਾਂ ਨੂੰ ਵਰਤਮਾਨ ਵਿੱਚ ਆਨਸਾਈਟ, ਰੀਅਲ-ਟਾਈਮ ਨਿਗਰਾਨੀ ਲਈ ਨਹੀਂ ਵਰਤਿਆ ਜਾ ਸਕਦਾ ਹੈ। ਦੂਜੇ ਪਾਸੇ, ਪਾਣੀ ਦੇ ਨਮੂਨਿਆਂ ਵਿੱਚ ਭਾਰੀ ਧਾਤੂ ਆਇਨਾਂ ਨੂੰ ਸਮਝਣ ਲਈ ਪਿਛਲੇ ਦੋ ਦਹਾਕਿਆਂ ਤੋਂ ਇਲੈਕਟ੍ਰੋਕੈਮੀਕਲ ਸੈਂਸਰਾਂ ਦੀ ਵਰਤੋਂ ਕੀਤੀ ਜਾ ਰਹੀ ਹੈ। ਵਾਤਾਵਰਣ ਸੁਰੱਖਿਆ ਏਜੰਸੀ ਪਾਣੀ ਵਿੱਚ ਭਾਰੀ ਧਾਤਾਂ ਦੀ ਮਾਤਰਾ ਨੂੰ ਟਰੇਸ ਕਰਨ ਦੀ ਸਿਫਾਰਸ਼ ਕਰਦੀ ਹੈ। ਇਲੈਕਟ੍ਰੋਕੈਮੀਕਲ ਸੈਂਸਰ ਵਿੱਚ 2 ਮਹੱਤਵਪੂਰਨ ਭਾਗ, ਸੈਂਸਿੰਗ ਲੇਅਰ ਅਤੇ ਟ੍ਰਾਂਸਡਿਊਸਰ ਹੁੰਦੇ ਹਨ। ਆਕਸਾਈਡ ਪਰਤਾਂ, ਪੌਲੀਮਰ, 2D ਨੈਨੋਮੈਟਰੀਅਲ, ਕਾਰਬਨ ਨੈਨੋਟਿਊਬ, ਗ੍ਰਾਫੀਨ, ਚੈਲਕੋਜੀਨਾਈਡ ਅਤੇ ਡਾਇਕਲਕੋਜੀਨਾਈਡ ਭਾਰੀ ਧਾਤੂ ਧਾਤੂ ਆਇਨਾਂ ਦੀ ਖੋਜ ਲਈ ਸਭ ਤੋਂ ਵੱਧ ਵਰਤੀਆਂ ਜਾਣ ਵਾਲੀਆਂ ਸੈਂਸਿੰਗ ਪਰਤਾਂ ਹਨ। ਚੈਲਕੋਜੀਨਾਈਡ ਅਤੇ ਡਾਇਕਲਕੋਜੀਨਾਈਡ ਸਮੱਗਰੀ ਕਠੋਰ ਰਸਾਇਣਕ ਵਾਤਾਵਰਣ ਨੂੰ ਕਾਇਮ ਰੱਖਣ ਲਈ ਜਾਣੀਆਂ ਜਾਂਦੀਆਂ ਹਨ ਅਤੇ ਇਸ ਲਈ ਇਸ ਖੋਜ ਨਿਬੰਧ ਵਿੱਚ ਖੋਜ ਐਪਲੀਕੇਸ਼ਨ ਲਈ ਚੁਣਿਆ ਗਿਆ ਸੀ। ਰਸਾਇਣਕ ਨੂੰ ਪੜ੍ਹਨਯੋਗ ਸਿਗਨਲ ਵਿੱਚ ਟਰਾਂਸਡਕਸ਼ਨ ਲਈ ਟਰਾਂਸਡਿਊਸਿੰਗ ਢਾਂਚੇ ਨੂੰ ਵਧੀਆ ਡਿਜ਼ਾਈਨ ਦੀ ਲੋੜ ਹੁੰਦੀ ਹੈ ਅਤੇ ਰਸਾਇਣਕ ਵਾਤਾਵਰਣ ਨੂੰ ਵੀ ਕਾਇਮ ਰੱਖਣਾ ਚਾਹੀਦਾ ਹੈ। ਸਭ ਤੋਂ ਵੱਧ ਵਰਤੇ ਜਾਣ ਵਾਲੇ ਆਇਨ ਚੋਣਵੇਂ ਇਲੈਕਟ੍ਰੋਡਸ, ਫੀਲਡ ਇਫੈਕਟ ਟਰਾਂਜਿਸਟਰ, ਕਲੋਰੀਮੈਟ੍ਰਿਕ, ਫਲੋਰੋਮੈਟ ਅਤੇ ਸਤਹ-ਵਧੇ ਹੋਏ ਰਮਨ ਸਕੈਟਰਿੰਗ। ਇਹ ਖੋਜ ਨਿਬੰਧ ਚੈਲਕੋਜੀਨਾਈਡ ਅਤੇ ਡਾਇਕਲਕੋਜੀਨਾਈਡ ਸੈਂਸਿੰਗ ਫਿਲਮਾਂ ਦੀ ਵਰਤੋਂ ਕਰਦੇ ਹੋਏ ਵੱਖ-ਵੱਖ ਟ੍ਰਾਂਸਡਿਊਸਿੰਗ ਯੰਤਰਾਂ ਨੂੰ ਸਿੰਥੇਸਾਈਜ਼ ਕਰਨ, ਜਮ੍ਹਾਂ ਕਰਨ ਅਤੇ ਬਣਾਉਣ 'ਤੇ ਕੇਂਦਰਿਤ ਹੈ। ਆਇਨ ਸਿਲੈਕਟਿਵ ਇਲੈਕਟ੍ਰੋਡਸ, ਇਲੈਕਟ੍ਰੋਲਾਈਟ ਇੰਸੂਲੇਟਰ ਸੈਮੀਕੰਡਕਟਰ ਕੈਪੇਸੀਟੋਰ, ਅਤੇ ਐਕਸਟੈਂਡਡ ਗੇਟ ਫੀਲਡ ਇਫੈਕਟ ਟਰਾਂਜਿਸਟਰ ਯੰਤਰਾਂ ਨੂੰ ਚੈਲਕੋਜੀਨਾਈਡ ਅਤੇ ਡਾਇਕਲਕੋਜੀਨਾਈਡ ਸਮੱਗਰੀ ਦੀ ਵਰਤੋਂ ਕਰਕੇ ਬਣਾਇਆ ਗਿਆ ਸੀ, ਅਤੇ Cd^{2+} , Cu^{2+} ਨੂੰ ਸਮਝਣ ਲਈ ਚੈਲਕੋਜੀਨਾਈਡਾਂ ਨਾਲ ਬਣੇ ਨੈਨੋਹੋਟਰੋਸਚਰਜ਼, ਘੱਟ ppb ਪ੍ਰਣਾਲੀ ਵਿੱਚ ਪਾਣੀ ਦੇ ਨਮੂਨਿਆਂ ਵਿੱਚ Hg^{2+} ਅਤੇ Pb^{2+} ਆਇਨ।

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