

Detection of Anticancer Drugs in Urine Samples Using an Electrochemical Sensor with a Modified Electrode

Sundaresan Ruspika¹, Saranvignesh Alagarsamy¹, Tse-Wei Chen¹, **Shen Ming Chen^{1*}**,
Ramachandran Balaji¹, Elayappan Tamilalagan¹, Chen-Chi Wang², Narendhar
Chandrasekar³, **Ming-Chin Yu^{4,5}**, **Heng-Yuan Hsu^{4,5}**

¹Department of Chemical Engineering and Biotechnology, National Taipei University of Technology, Taiwan; ²Department of Greenergy, National University of Tainan, Taiwan; ³Department of Electronics and Communication Engineering, Koneru Lakshmaiah Education Foundation, India; ⁴Department of Surgery, New Taipei Municipal Tucheng Hospital, Taiwan; ⁵Chang-Gung University, Taiwan.

Abstract

A novel and cost-effective electrochemical sensor was developed for the rapid and sensitive detection of mesalamine using a nanocomposite of rare earth tungstate incorporated with reduced graphene oxide (REW@rGO). The nanocomposite was synthesized and characterized through various analytical and spectroscopic techniques to confirm its successful formation. The synergetic effect between REW and rGO significantly enhanced the electrocatalytic performance, offering a broad linear detection range of 0.01–723 μM , a high sensitivity of $1.3406 \mu\text{A} \mu\text{M}^{-1} \text{cm}^{-2}$, and a low detection limit (LOD) of 0.0039 μM . These results demonstrated that the REW@rGO-based sensor is a highly efficient platform for the real-time analysis of mesalamine in pharmaceutical and clinical applications.

Introduction

Idiopathic ulcerative colitis is an inflammatory chronic disease requiring long-term medical treatment with oral mesalazine (5-aminosalicylic acid; MLM) formulations. Despite its efficacy, MLM can be detrimental to health if not accurately monitored at clinical levels. While several analytical techniques are available, electrochemical methods offer low costs, simplicity, and fast response times. Rare earth tungstate nanoparticles, specifically Ho_2WO_6 , are introduced to overcome poor electrical conductivity through the high surface area and conductivity of RGO, forming stable hybrid composites with synergistic effects for superior sensing performance.

Experimental

The nanocomposite $\text{Ho}_2\text{WO}_6/\text{RGO}$ was synthesized via a facile hydrothermal method. Stoichiometric ratios of $\text{Ho}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ were dissolved separately in DI H_2O . Subsequently, urea and graphene oxide (GO) were added, and the mixture was stirred for 30 minutes before being hydrothermally treated in a Teflon-lined autoclave at 180°C for 12 hours. After cooling to room temperature, the obtained precipitate was washed, centrifuged, and dried to acquire the purified catalyst. For electrode fabrication, the $\text{Ho}_2\text{WO}_6/\text{RGO}$ was dispersed (3 mg/mL) in DI water. A pre-cleaned glassy carbon electrode (GCE) was then modified by drop-casting 6 μL of the catalyst ink to reach an average loading of $0.254 \text{ mg} \cdot \text{cm}^{-2}$.

Results and Discussion

The structural characteristics of the synthesized $\text{Ho}_2\text{WO}_6/\text{RGO}$ were verified by XRD, confirming the diffraction peaks of crystalline Ho_2WO_6 with an average crystalline size of 8.76 nm. FE-SEM and HRTEM images displayed a nanoplate-like structure of Ho_2WO_6 successfully wrapped over the surface of wrinkled RGO sheets, which effectively prevented the agglomeration of nanoparticles and facilitated sensing capabilities.

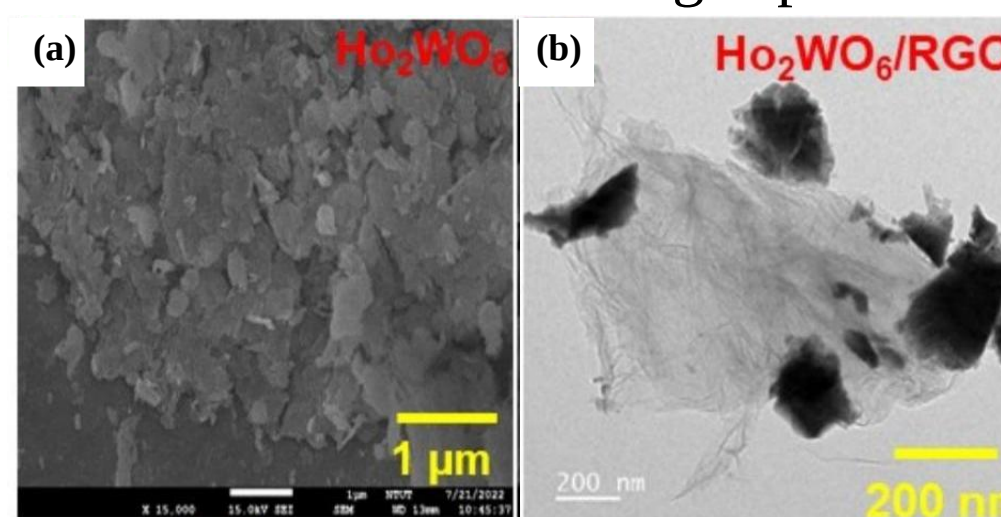


Fig. 1. (a) FESEM image of Ho_2WO_6 , and (b) HRTEM image of the final $\text{Ho}_2\text{WO}_6/\text{RGO}$ nanocomposite.

EIS demonstrated a remarkably small charge transfer resistance ($R_{ct} = 74.93 \Omega$) for $\text{Ho}_2\text{WO}_6/\text{RGO}/\text{GCE}$. DPV measurements showed an outstanding sensitivity of $1.3406 \mu\text{A} \mu\text{M}^{-1} \text{cm}^{-2}$, an ultra-low LOD of 0.0039 μM , and a broad linear range (0.01–723 μM).

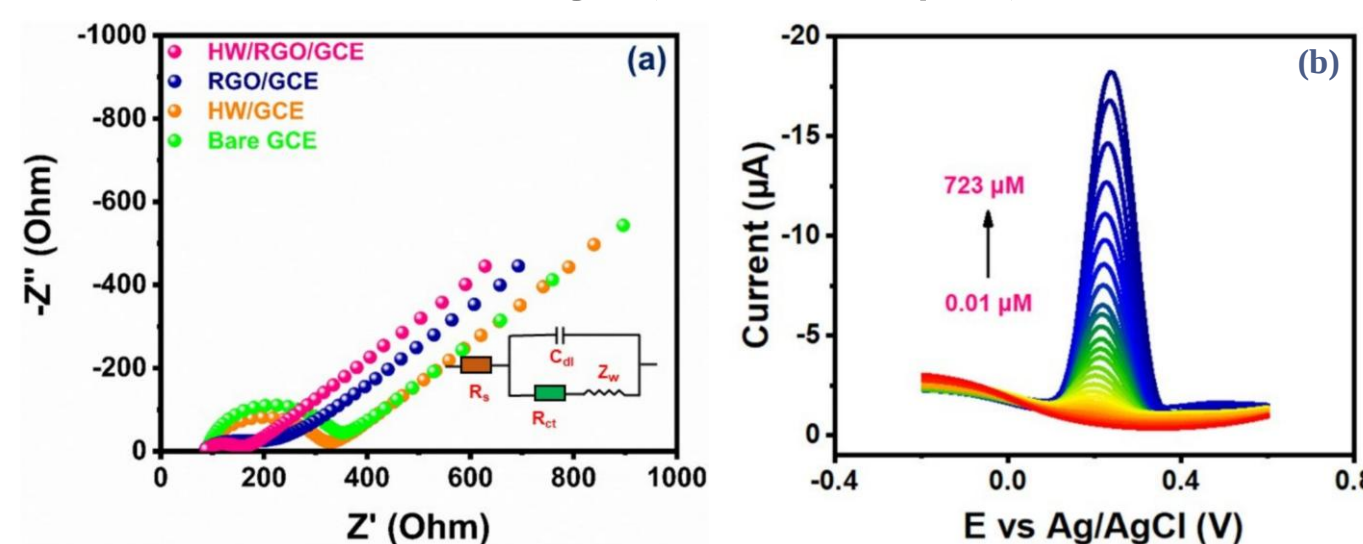


Fig. 2. (a) EIS Nyquist plot, and (b) DPV response for MLM detection.

Table 1. MLM determination in real samples.

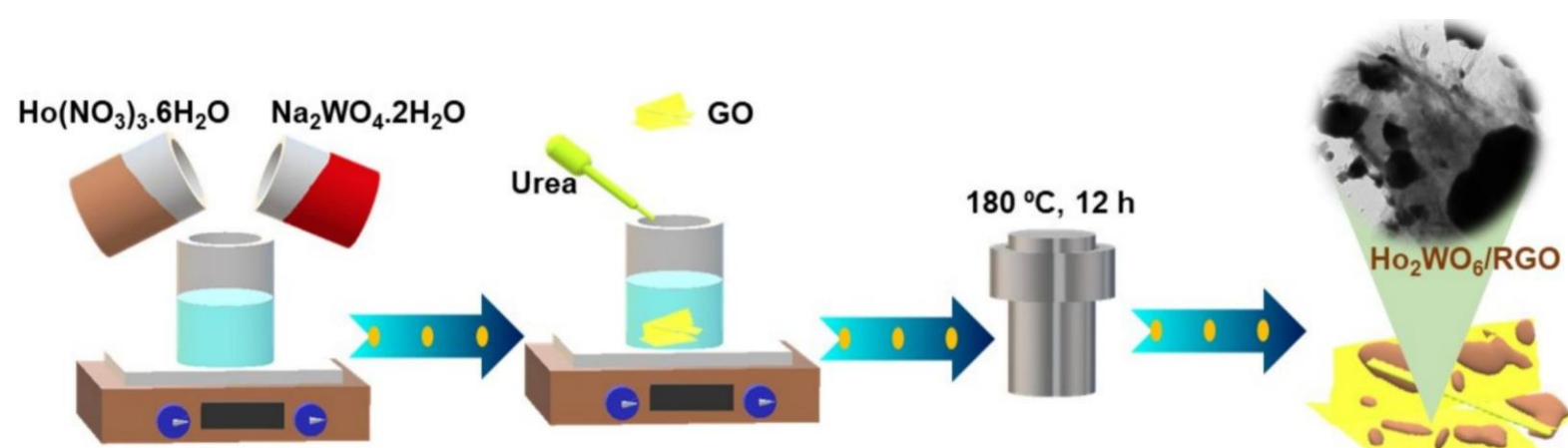
Sample	Added (μM)	Found (μM)	Recovery (%)
Blood serum	5	4.90	98.0
	15	14.99	99.9
Human urine	5	4.99	99.8
	15	14.99	99.9

CONCLUSION

In summary, a novel $\text{Ho}_2\text{WO}_6/\text{RGO}$ nanocomposite was successfully synthesized and applied for the electrochemical detection of mesalamine. The developed sensor exhibited an outstanding sensitivity of $1.3406 \mu\text{A} \mu\text{M}^{-1} \text{cm}^{-2}$ and an ultra-low LOD of 0.0039 μM with a broad linear range. Furthermore, tremendous recovery results (98.0%–99.9%) in real human blood serum and urine samples demonstrate its highly reliable and practical potential for biomedical sensing applications.

REFERENCES

[1] S.B. Hanauer, N. Engl. J. Med. 334 (1996) 841. [2] K. Hwa, et al., Mater. Today Chem. 23 (2022) 100739.



Scheme 1. Graphical representation of the synthesis procedure of $\text{Ho}_2\text{WO}_6/\text{RGO}$.