

FABRICATION OF HIGH-SENSITIVITY SERS SUBSTRATES BASED ON Cu/GRAPHENE
NANOWIRES VIA LOW-TEMPERATURE CVD FOR THE DETECTION OF THIRAM PESTICIDETrần Văn Tân¹, Nguyễn Văn Chúc², Nguyễn Việt Tuyên^{1*}, Phạm Nguyên Hải¹, Ngọc An Bang¹, Trần Thị Hà³¹Khoa Vật lý, Trường Đại học Khoa học Tự nhiên, Đại học Quốc gia Hà Nội, 334 Nguyễn Trãi, Thanh Xuân, Hà Nội, Việt Nam²Viện Khoa học Vật liệu, Viện Hàn lâm Khoa học và Công nghệ Việt Nam, 18 Hoàng Quốc Việt, Hà Nội, Việt Nam.³Trường Đại học Mỏ - Địa chất Hà Nội, 18 Đường Viên, Phường Đức Thắng, Bắc Từ Liêm, Hà Nội.

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ABSTRACT

In this study, copper nanowires (Cu NWs) were fabricated via thermal oxidation to form CuO nanowires, followed by chemical reduction to obtain Cu NWs. A Cu/Graphene hybrid structure was then created by coating a thin graphene layer onto the Cu NWs through low-temperature chemical vapor deposition (CVD). The Cu/Graphene SERS substrate enabled the detection of methylene blue (MB) down to 10^{-9} M and the pesticide Thiram down to 10^{-7} M, meeting EU safety standards. These results demonstrate that Cu/Graphene offers high sensitivity, stability, and cost-effectiveness, highlighting its strong potential for applications in food safety monitoring, pesticide residue detection, and environmental pollutant tracking at trace levels.

2. INTRODUCTION

Raman spectroscopy provides molecule-specific information but suffers from weak signal intensity, limiting trace detection [1]. Surface-enhanced Raman scattering (SERS) overcomes this by amplifying signals via localized surface plasmon resonance, enabling rapid and sensitive detection of hazardous compounds. In food safety, SERS is promising for detecting toxic pesticides like Thiram, which is banned by the EU [2]. While noble metals (Au, Ag) offer strong enhancement, their high cost limits practical use. Copper (Cu) is a low-cost alternative with visible-range plasmon resonance [3,4], though prone to oxidation [5,6]. Graphene effectively protects Cu and stabilizes signal enhancement [7]. In this work, a Cu/Graphene nanowire SERS substrate fabricated by low-temperature CVD achieved high sensitivity and stability for Thiram detection, meeting EU standards and offering a cost-effective platform for food safety and environmental monitoring.

2. METHOD

High-purity copper foils (99.99%) were first cleaned in 10% HCl for 10 minutes, followed by sequential ultrasonic cleaning in acetone, ethanol, and deionized water for 10 minutes each. After drying with N₂ gas, the substrates were annealed in air at 500 °C for 2 hours to form CuO nanowires. Argon gas was then introduced for 5 minutes to create an inert atmosphere, and the CuO nanowires were reduced in an Ar/H₂ (300/30 sccm) environment for 15 minutes. Finally, a graphene layer was deposited onto the reduced Cu nanowires using chemical vapor deposition (CVD) at 500 °C for 30 minutes.

3. RESULTS

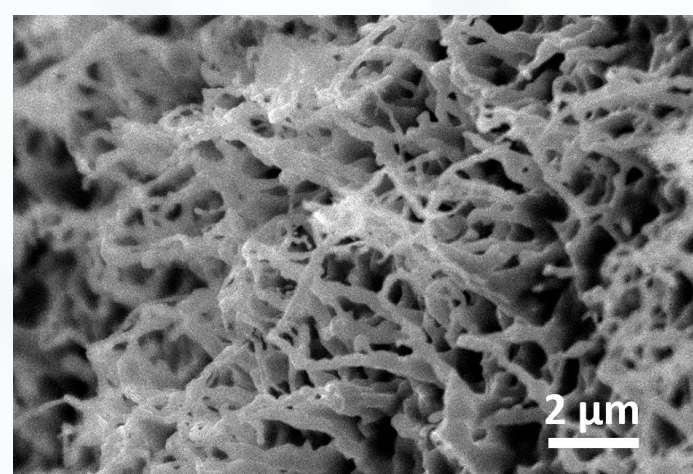


Fig 1. SEM image of Cu/G nanowires

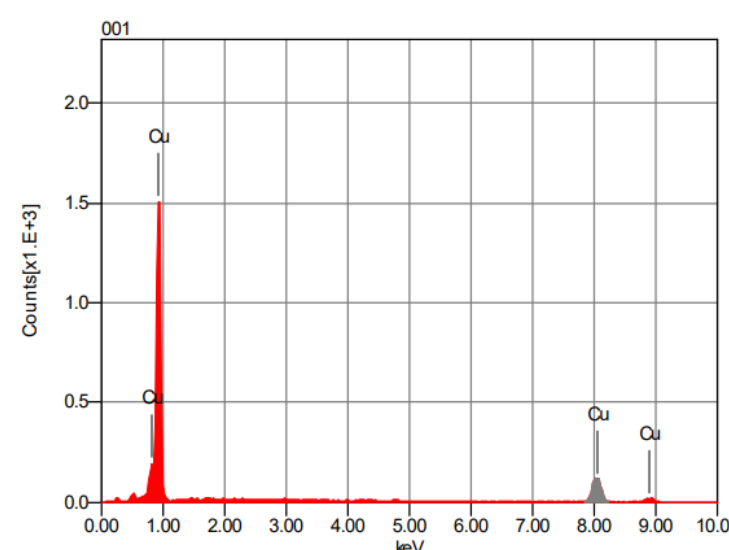


Fig 2. EDS spectrum of Cu/G nanowires

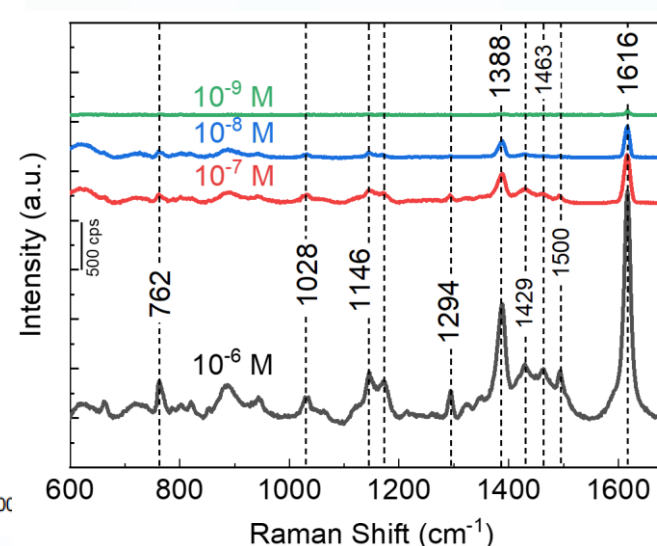
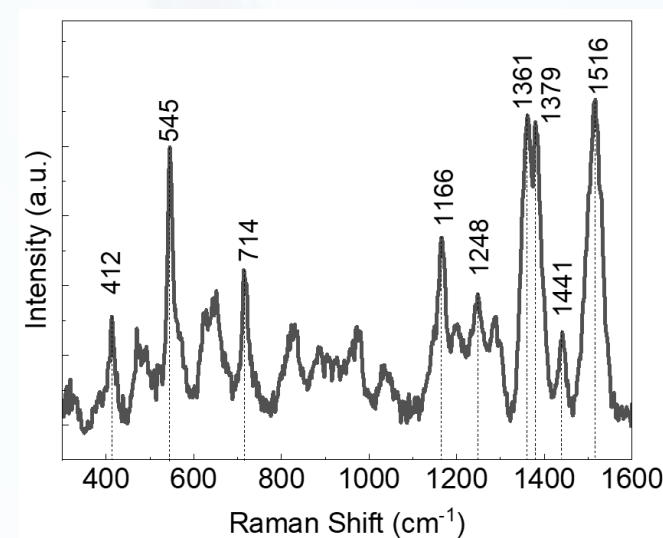


Fig 3. Raman spectra of methylene blue at different concentrations investigated on Cu/G nanowires

Fig 4. Raman spectrum of Thiram at concentration of 10^{-7} M investigated on Cu/G nanowires

SEM images (Fig. 1) confirm the dense Cu nanowire coated with Graphene, forming numerous “hot spots” and ensuring surface stability. EDS analysis (Fig. 2) verifies the high purity of the Cu/G nanowires structure. Raman spectra (Fig. 3) demonstrate that MB can be detected down to 10^{-9} M, while Thiram spectra (Fig. 4) show clear peaks at 10^{-7} M, proving the strong enhancement and high sensitivity of the Cu/G nanowires SERS substrate.

4. CONCLUSIONS

In this study, Cu/Graphene nanowire substrates were successfully fabricated using a low-temperature CVD method. The results show that the Cu nanowires possess a high-density structure uniformly covered by a graphene layer, which increases the effective surface area while simultaneously preventing the oxidation of Cu. Characterization results demonstrate that the Cu/Graphene-based SERS substrate can clearly detect Raman signals at concentrations as low as 10^{-9} M. Furthermore, its ability to detect the pesticide Thiram at concentrations down to 10^{-7} M meets the residue detection standards required by the European Union. Therefore, the Cu/Graphene nanowire-based SERS substrate represents a promising, low-cost, and stable platform suitable for practical applications in environmental monitoring, food safety, and biomedical diagnostics.

5. REFERENCE

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CHƯƠNG TRÌNH VÀ BÁO CÁO TÓM TẮT HỘI NGHỊ VẬT LÝ CHẤT RẮN VÀ KHOA HỌC VẬT LIỆU TOÀN QUỐC LẦN THỨ XIV

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Abstract: This study presents an effective method for fabricating porous ZnO/Ag nanostructures by combining sputtering technique with thermal oxidation based on the Joule-Lenz heating effect. The method is simple, energy-efficient, and environmentally friendly. After fabrication, the resulting substrate consists of porous ZnO nanostructures with a large surface area and uniform size distribution. These structures are subsequently coated with silver nanoparticles via sputtering to form a ZnO/Ag SERS substrate with good Raman enhancement capability. This SERS substrate enables the effective detection of Methylene Blue at concentrations as low as 10^{-11} M and Thiram at 10^{-7} M. The results suggest that the material holds great potential for applications in pollutant detection, contributing to environmental protection and human health.

Keywords: ZnO/Ag nanoporous, Joule-Lenz heating, Sputtering, SERS.

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FABRICATION OF HIGH-SENSITIVITY SERS SUBSTRATES BASED ON Cu/Graphene NANOWIRES VIA LOW-TEMPERATURE CVD FOR THE DETECTION OF THIRAM PESTICIDE

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Abstract: Surface-enhanced Raman scattering (SERS) is a powerful analytical technique that enables the detection of toxic substances at extremely low concentrations, making it highly valuable in biomedical and environmental applications. In this study, we successfully fabricated copper nanowires (Cu) by chemically reducing copper oxide nanowires (CuO), which were initially prepared via a thermal oxidation method. Simultaneously, a thin graphene (G) layer was directly synthesized on the Cu nanowires through low-temperature chemical vapor deposition (CVD), forming a Cu/G nanowire structure. The resulting Cu/G nanowire-based SERS substrates exhibit high sensitivity, enabling the detection of methylene blue down to 10^{-10} M and the pesticide thiram down to 10^{-9} M, while maintaining excellent chemical and optical stability under standard storage conditions. These findings highlight the potential of Cu/G nanowire-based SERS platforms as cost-effective, sensitive, and stable tools for applications in environmental monitoring, food safety, and biomedical diagnostics.

Keywords: SERS, Cu/G nanowires, Low-temperature CVD.