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Author(s)	Chau, Yuen Ting Rachel
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## 学 位 論 文 内 容 の 要 旨

博士の専攻分野の名称    博士（工学）    氏名    Yuen Ting Rachel Chau

## 学 位 論 文 題 名

Synthesis and Femtosecond Laser Excited-Terahertz Wave Emission of Cu-based and ZnTe  
Nano/Micro Materials

(Cu 系と ZnTe ナノ・マイクロ材料の合成およびフェムト秒レーザーを用いたテラヘルツ波の発生)

Cu-based and ZnTe nano/micro materials are of interest due to their availability in tremendous applications such as broadband pulses emission in terahertz (THz) regime under femtosecond laser irradiation. Firstly, syntheses of these materials based on bottom-up and top-down approaches are discussed. In particular, Cu-based nanoparticles dispersion can be synthesized via sputter deposition, but the understandings to the sputtered nanoparticles are limited. ZnTe microstructures can be obtained via thermal decomposition, yet their formation mechanism remains unclear due to the unobservable characteristic of the solvothermal method. Secondly, with the development of ultrafast laser pulse technologies, the emission of X-ray and THz radiation as optical responses of materials to the laser excitation is concerned. Cu-based and ZnTe nano/micro materials are potential THz radiation sources as a semiconductor for Cu-based materials and as a nonlinear crystal for ZnTe. This dissertation focuses on the optical responses of Cu-based and ZnTe nano/micro materials to the ultrafast laser pulse excitation while elucidating their properties, structures, and formation mechanisms obtaining via different synthetic routes. The above research background and the objectives are given in chapter 1.

Chapter 2 presents the properties and structural characterization of Cu and Cu-Pd nanoparticles synthesized via sputter deposition onto a polymer matrix. Size of all nanoparticles obtained were less than 5 nm. Growth in size and the oxidation of monometallic Cu nanoparticles were monitored after synthesis. Cu-Pd alloy nanoparticles were synthesized by co-sputtering of each metal target. Compositions of Cu-Pd alloy nanoparticles obtained through alternating the sputtering currents were diversely characterized using UV-vis, TEM, STEM-EDS, XRD and XPS. The findings revealed that co-sputter deposition is a facile method of having composition-tunable bimetallic alloy nanoparticles dispersion. Low crystallinity and degradation during storage of these nanoparticles were discussed. This chapter provided detail information of Cu and Cu-Pd alloy nanoparticles synthesized via sputter deposition.

Chapter 3 studies the stability of  $Au - Cu_2O$  core-shell nanoparticles synthesized via wet-chemical route and stored in water/ethanol mixed solvents. Thickness-tunable  $Cu_2O$  shells (2 to 40 nm) grew epitaxially on 16 nm-sized Au nanoparticles to give metal/semiconductor heterostructure. Shell thickness altered the absorption peak in UV-Vis region of the nanoparticles. The stability of  $Au - Cu_2O$  core-shell nanoparticles was poor in the solvents that contain > 50 vol % water content. This study showed the  $Au - Cu_2O$  core-shell nanoparticles dispersed in aqueous solvents was not an

appropriate candidate for THz wave emission test due to their instability.

Chapter 4 presents THz wave emission from semiconductor/metal interface using aqueous free Cu and Cu/Au thin film (80nm-thick Cu, 55nm-thick Au) samples. Cu oxides as the semiconductor layer were obtained through oxidative annealing (80 to 300 °C, 2.5 h). Samples were irradiated by femtosecond laser (35 fs, 800 nm). THz wave emission intensity with respect to the oxidation temperature for annealing Cu layer was discussed. Results showed that  $Cu_2O/Cu$  interface was the key feature of THz wave emission. The further THz wave emission enhancement can be achieved by underneath Au film as a reflector of laser light and THz wave. This chapter explained the THz wave emitting mechanism from Cu oxides and the function of Au film in the heterostructure.

Chapter 5 performs syntheses of ZnTe microspheres in a PVP contained polyol system via a hot injection method, with the investigation of their possibility as a THz wave emitting source. A retrospective study was conducted to evaluate the formation process of ZnTe microspheres from 0.2 to 48 h. It was found that the initially formed Te rods in the reaction system were sacrificial templates for the growth of ZnTe. Amount of PVP controlled dimensions of Te rods formed at the initial stage as well as the sizes of ZnTe microspheres by influencing the nucleation and growth rate of ZnTe. Although the ZnTe microspheres were polycrystalline, they emitted THz wave under ultrafast laser pulse irradiation. The larger ZnTe microspheres ( $> 1.0 \mu m$ ) were prone to generate THz wave in higher intensity, which was originated from the nonlinear effect by ZnTe. This chapter discussed the formation of ZnTe microspheres and gave a preliminary report on THz wave emission from polycrystalline ZnTe microspheres.

Chapter 6 gives the general conclusion of the research topics covered by the dissertation, including the understanding on the properties of Cu-based and ZnTe nano/materials synthesized via different approaches, and the THz wave emission from these materials under ultrafast laser pulse excitation. The findings are significant to widen the availability of nano/micro materials for broadband THz pulse technologies.