Clean Energy Conversion Research Section

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(Daicel corporation)

1. Introduction

As a senior research scientist, the author is responsible for "improving technical capabilities" and "problem solving" in the field of organic synthesis in our company. In particular, he has focused on "developing high-performance catalysts" and "establishing organic synthesis technology using simple materials as raw materials" to improve the technology.

For example, as an example of a high-performance catalyst, a system that can use a safe oxidizing agent in an epoxidation reaction, and as an example of organic synthesis technology using simple raw materials as raw materials, consider the organic synthesis technology using molten sulfur that is a by-product in the factories.

Since 2017, as a senior research scientist, he has expanded his expertise from organic synthesis to forest science and has achieved some results. We will also introduce its contents. At the same time as signing a comprehensive collaboration agreement with Kyoto University in October 2021, Daicel established an industry-academia collaborative research laboratory in the Uji area as a base for the fusion of research fields and industry-government-academia collaboration. We believe that these efforts will lead to the realization of a sustainable society.

2. Efforts of the senior research scientist

The author, as a senior research scientist, is making efforts to "improve technical capabilities" and "solve problems" in the organic synthesis field of our company. In particular, he focused on "developing high-performance catalysts", "establishing organic synthesis technology using simple materials as raw materials", and "early acquisition and practical application of new technologies" as key points for technological improvement. In this paper, we will introduce related research such as epoxy compounds, which are organic synthesis products of our company, in relation to these points. In terms of "developing high-performance catalysts," we are working to develop high-performance catalysts for the production of epoxy compounds, which are our main products. Specifically, as a safe and environmentally friendly method, we have conducted the joint research with some university to construct an electrolytic epoxidation system. This is a system in which oxidation (epoxidation) is carried out on the positive electrode and reduction is carried out on the negative electrode. However, although it is oxidized on the positive electrode, we thought it would be difficult to oxidize the olefin to the epoxides directly on the electrode. We therefore decided to investigate the electrochemical generation of the oxidant. After studying various electrolytes, it was found that peroxides were produced when hydrogen carbonates or carbonates were used, and it was also confirmed that olefin epoxidation would proceed in the presence of a suitable catalyst[1].

In "Establishing organic synthesis technology using simple materials as raw materials", we are investigating organic synthesis technology using molten sulfur produced as a by-product in factories. As an ultimate goal, we expect to be able to develop functional materials such as thiirane. Finally, we have not yet succeeded in introducing elemental sulfur into organic compounds using elemental sulfur itself as a reaction reagent. This is also the subject of joint research with a university, but first, in order to get used to working with organic sulfur compounds, we started to develop a new organic synthesis method using thiols. We have been able to publish several joint results in papers[2], the most interesting of which is the catalytic addition reaction of thiols to alkynes. Using a nickel catalyst, a sulfur atom was introduced on the same carbon and the dithioacetal was synthesized in good yields with high regioselectivity.

In "Early acquisition and practical application of new technology" we are looking at the industrialization of new organic synthesis technology using microreactor or microwave processes. Many excellent research results have been published in these areas, but commercialization is not possible unless the reactor and process conditions are taken into account at the same time. We don't think it's possible to start the research on our own. That is why we are working closely with the leading scientist who can guide us in building together from the basics, while gathering information and conducting internal reviews.

As a part of our efforts to create a sustainable society, we have been working on the use of woody biomass. For example, we have tried to produce hydrogen by dehydrogenation from cellulose, a component of woody biomass[3], and to introduce functional groups into saccharides by substitution of hydroxyl groups with carbon groups[4].

We believe that this category includes the electrosynthesis and photochemical reactions mentioned above, and we are looking for good topics to propose.

3. Summary

Based on the author's experience in synthetic organic chemistry, which is his specialty, he talked about the importance of pursuing a doctoral degree based on his experience in leading product development (development of monomers for electronic materials) and leading to commercialization. This talk will encourage undergraduate students and master's students. I also hope that it will be explained in a way that is easy to understand for them with different fields of expertise.

Finally, I would like to take this opportunity to express my gratitude to all the mentors, superiors, subordinates, seniors, and juniors who participated in the research.

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1. Introduction

Terahertz (THz) radiation sources have attracted considerable interests because of their potential applications in fields such as material science, medical imaging, and high-speed communication. The coherent THz radiation having polarization control ability can be used for various types of scientific investigation and applications. Vibrational circular dichroism (VCD) measurements in the THz region are extremely sensitive to conformational changes in proteins. THz source capable of switching left and right circular polarizations with high speed is very useful for biological analysis and is in great demand. As described above, THz waves is traditionally used as probes for characterization, or spectroscopic means for “observation”. Furthermore, high-field THz waves from the short electron bunches allow "control" of the molecular arrangement.

We are developing an accelerator-based THz radiation sources using the test accelerator (t-ACTS) [1] at Tohoku University and the THz-CUR of KU-FEL facility [2] at Kyoto University. In particular, the research is being conducted on the generation mechanism and polarization/amplitude control of a coherent undulator radiation (CUR) from extremely short electron beams.

2. THz coherent undulator radiation

The relativistic and short electron bunches passing through an undulator is capable of generating high intensity, coherent, and narrowband radiation in THz wavelength region. The radiation spectrum from the electron bunch can be written as

$$\left.\frac{d^2I}{d\omega d\Omega}\right|_N = \{N + N(N-1)|F_{3D}(\boldsymbol{k})|^2\} \cdot \left.\frac{d^2I}{d\omega d\Omega}\right|_1 \quad (1)$$

where N is the number of electrons in the bunch, I radiation intensity, ω radiation frequency, Ω solid angle of the radiation. The three-dimensional form factor is defined by

$$F_{3D}(\boldsymbol{k}) = \int S_{3D}(\boldsymbol{r})\, e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} d\boldsymbol{r}. \quad (2)$$

$\boldsymbol{k}$ and $S_{3D}(\boldsymbol{r})$ are the wave vector towards the observation point and the three-dimensional charge distribution of the electron bunch, respectively. If the form factor is sufficiently large, the radiation intensity from the electron bunch is proportional to the square of the electron number N.

As a relativistic electron beam propagates through

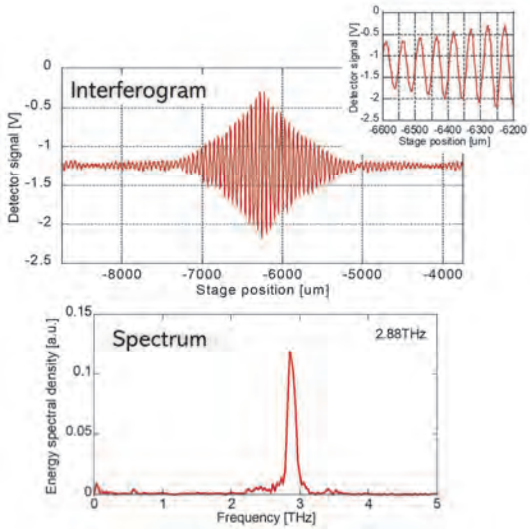

Fig.1: (Up) Measured interferogram of CUR; (Down) derived frequency spectrum from interferogram with K=3.6 [3].

an undulator, under the condition that the pulse length of the electron beam is sufficiently shorter than the resonance wavelength of the undulator radiation, the radiation will have temporal coherence. The temporal profile of the electric field of the undulator radiation shows an almost sinusoidal wave with a cycle of the number of undulator periods. The frequency spectrum of the CUR were measured by the Michelson interferometer with pyro-electric detector at t-ACTS. In this experiment, electron beam energy was 30 MeV and the pulse length of electron beam was approximately 80 fs. A 2.5 m long undulator with 25 periods and a peak magnetic field of 0.41 T was utilized to generate the CUR [3].

3. Variable polarized coherent THz source

We have demonstrated to produce arbitrary polarization states from the linearly polarized CUR with a frequency of 1.9 THz at the t-ACTS at Tohoku University. Figure 2 shows a variable polarization manipulator (VPM) using a Martin–Puplett interferometer [4,5]. The VPM consists of a beam-splitter wire-grid and two rooftop mirrors, with one rooftop mirror mounted on a movable stage. The CUR from a planar undulator is linearly polarized. An incident beam of the CUR is split into two orthogonal linear polarizations by the beam-splitter wire-grid, and the reflected and transmitted beams travel to the rooftop mirrors. The two beams rotated by 90° using the rooftop mirrors are polarized and superimposed at

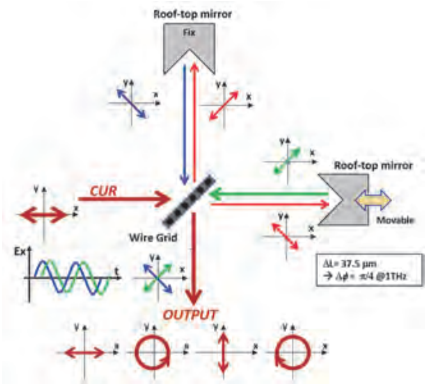

Fig.2: Variable polarization manipulator (VPM) using a Martin–Puplett interferometer.

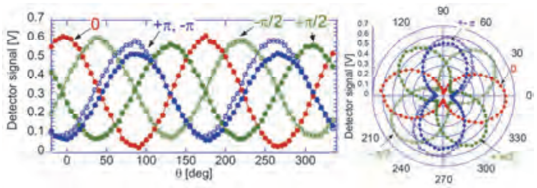

Fig.3: Measured intensity of the CUR as a function of rotating angle of the polarizer wire-grid. The phase difference (δ) between two orthogonal linear polarizations are 0, $\pm\pi$, $\pm\pi/2$, respectively.

the splitter wire-grid. The relative phase (δ) between the two orthogonal linearly polarized beams is adjusted using the movable stage. By using the VPM, it is possible to produce various polarization states by simply adjusting the relative phase. All polarization states of linearly polarized, elliptically polarized, and left and right circularly polarized states can be realized by moving the interferometer stage. In other words, the left and right circular polarization can be switched by simply shifting the movable stage by half a wavelength of the CUR. The VPM can realize high-speed switching the left and right circular polarization at several-hundred-Hz using a piezoelectric actuator stage. In addition, the VPM has the advantage of high transmission efficiency in the interferometer. The results of the polarization measurement using the wire-grid polarizer and quarter-waveplate clearly showed that variable polarized states were created from the CUR (Fig.3). Stokes parameters were measured using a polarizer to derive the degree of polarization.

5. CUR stacking using optical cavity

To generate intense terahertz pulses, we are conducting research on the superposition of CUR pulses using an optical resonator as shown in Fig.4. The THz CUR pulse stacked in an optical cavity are extracted using plasma mirror. Test experiments were carried out using the THz-CUR source at Kyoto University (Fig.5). It was confirmed that the transmittance was almost 100% when the Si-plate was placed at Brewster's angle to the CUR pulse. Using an Si-plate and a nanosecond time duration of Nd:YAG

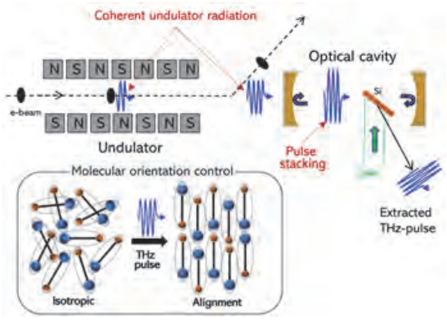

Fig.4: Generation of a high field THz CUR pulse using optical resonator and plasma mirror.

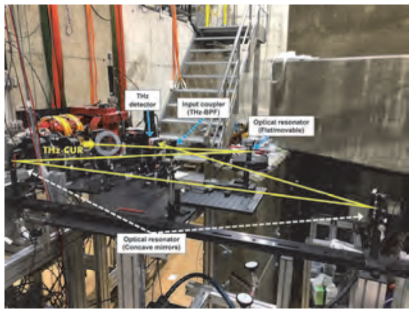

Fig.5: Optical resonator at THz-CUR source.

laser, we were able to reflect THz CUR pulses by a plasma mirror. In the experiment, the electric field superposition in the optical resonator was confirmed by changing the resonator length and measuring the interference pattern, however it was not sufficient enhancement. As next step, it will be necessary to improve the injection optics of the CUR into the optical resonator.

5. Summary

High-intensity THz sources based on CUR are being developed at Tohoku University and Kyoto University. We were able to establish a variable polarization THz source using VPM. For further THz pulse enhancement, we continue basic research on pulse stacking of CURs using optical resonators and plasma mirrors. This research is supported by the Joint Usage/Research Program on Zero-Emission Energy Research, IAE, Kyoto University (ZE30C-08, ZE31C-12, ZE2020A-30, ZE2021A-33, ZE2022A-19).

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