

論文 / 著書情報  
Article / Book Information

題目(和文)	セルロースとリグニン由来2-ピロン-4,6-ジカルボン酸の非共有結合により形成される導電性有機ゲルおよびハイドロゲル
Title(English)	Conductive Organogels and Hydrogels Formed by the Non-covalent Interactions of Cellulose and Lignin-Derived 2-Pyrone-4,6-Dicarboxylic Acid
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Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

(博士課程)  
Doctoral Program

## 論文要旨

THESIS SUMMARY

系・コース： Department of, Graduate major in	材料 材料	系 コース	申請学位 (専攻分野)： Academic Degree Requested	博士 Doctor of	(理学)
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			指導教員 (副)： Academic Supervisor (sub)		

要旨 (英文 800 語程度)

Thesis Summary (approx.800 English Words)

In this thesis, in order to develop conductive gels for the next generation of flexible electronic devices with outstanding performance, a series of conductive hydrogels and organogels were fabricated by wooden biomass-derived cellulose and 2-pyrone-4,6-dicarboxylic acid (PDC). The fabricated gels were comprehensively investigated and successfully applied to the gel-based polyelectrolytes (GPE) for supercapacitors, electrical-responsive actuators, stretching/compressing sensors, and temperature detectors.

In Chapter 2, ionic conductive cellulose-PDC organogels were prepared by dissolving PDC in cellulose LiCl/DMAc solution. By structural characterization including FTIR,  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ , SANS, and DLS, the gelation mechanism was revealed. The addition of PDC interfered with the electrostatic balance in cellulose LiCl/DMAc solution, which further resulted in the formation of a polymer network connected by cellulose-PDC colloids. Attributed to free  $\text{Li}^+$  and  $\text{Cl}^-$  uniformly dispersed in DMAc, the resultant organogels showed high ionic conductivities. Additionally, the formation of strong hydrogen bonds between cellulose-PDC colloids endowed the organogels with reparability. The organogels were further applied to the GPEs for supercapacitors. The polarity of PDC effectively increased the ion transfer efficiency and therefore improved the supercapacitor performance. Besides, the organogels were also successfully utilized as electrical responsive actuators in LiCl/DMAc-based electrolytes. The electrostatic repelling between negatively charged carboxylic groups in the polymer network and the mobile  $\text{Cl}^-$  anions aggregating on the anode side initiated the swelling on the anode and shrinking on the cathode side, which eventually results in the actuator bending toward the cathodes side. Due to its high ionic conductivity and facile fabrication method, the cellulose-PDC organogels showed a significant potential for applications in the fabrication of environmentally-friendly supercapacitors and actuators. This study also provides a new strategy to utilize naturally derived materials for the development of green energy and flexible electronics.

In Chapter 3, a series of PVA/PEDOT:PSS/PDC organogels were fabricated. As previously demonstrated in Chapter 2, PDC showed significant potential for the fabrication of conductive gels assigned to its carboxyl groups which can form hydrogen bonds with hydroxyl groups in cellulose. As a unique lignin-derived substance, it is also noteworthy that PDC owns an electron-deficient pyrone ring and strong acidity. Hence, PDC may be employed as a potential p-dopant additive for conductive materials. To verify this hypothesis, PDC was introduced into poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS), which is one of the most frequently used conductive polymers due to its flexibility, excellent conductivity, and the possibility of secondary doping. Attributed to the strong acidity of carboxyl groups, PDC could induce the crosslinking of PEDOT:PSS, which eventually forms a conductive polymer network of the organogel. The characterization of ESR and UV-vis-NIR spectra suggested the secondary doping PEDOT:PSS by PDC, which could significantly improve the charge transfer efficiency and conductivity of PEDOT:PSS. By forming a PVA polymer network in the PEDOT:PSS/PDC polymer network via solvent exchange with ethylene glycol, the resultant PVA/PEDOT:PSS/PDC organogels were prepared. The obtained physically crosslinking organogels showed outstanding mechanical performance and significantly improved conductivity. Based on this simple fabrication method, conductive organogel fibers were also produced. The obtained conductive organogel and its fibers were successfully applied to stretching/compressing sensors and temperature detectors.

In Chapter 4, a PVA/TEMPO-cellulose/carbonized  $\text{C}_{60}$ -based nanosphere hydrogel was introduced. Fullerene  $\text{C}_{60}$  is a well-known molecule with the ability to form various morphologies, including nanospheres via self-assembly. Attributed to the rich  $\pi$ -electrons, controllable morphology, and high specific surface area,  $\text{C}_{60}$ -based carbonized spheres (CS) are applicable to carbon electrode materials in energy storage devices. However, there are few reports about the effects of porous carbon nanospheres on solid electrolytes due to the hydrophobicity of carbonized nanospheres. Therefore, in this chapter, CS was introduced into PVA/TEMPO-cellulose-based hydrogels via electrostatic interactions with the carboxyl groups of the TEMPO-cellulose to investigate the effect of highly mesoporous channels on the supercapacitor device performance. The performance of the supercapacitor was improved due to the enhanced ionic diffusion of electrolytes through the nanospace. Moreover, the mechanical properties of the prepared hydrogel were also greatly improved due to the deformability of CS, which effectively suppressed stress concentration and crack growth.

In summary, the unique effects of wooden biomass-derived cellulose and PDC on the fabrication of non-covalently

crosslinked conductive organogels and hydrogels were comprehensively investigated in this thesis. However, in order to produce practical, low-cost, and environmentally-friendly electronics using biomass-derived materials, the following challenges must be overcome. First, operation under extreme conditions limits the use of conductive gels because of the inevitable loss of solvents. Hence, improving the stability of the gels by enhancing the solvent-retention and anti-freezing abilities would be of great significance for future applications of conductive gels based on biomass-derived materials. Second, to fabricate conductive gels with excellent mechanical properties, petrol-derived polymers must be used. Therefore, it is of great significance to develop environmentally-friendly alternatives to petrol-derived materials for the fabrication of future conductive gels. Last but not least, it is still a challenge to develop new green solvents for cellulose to achieve the production of environmentally-friendly cellulose-based conductive gels. By combining the green solvent concept with environmentally-friendly crosslinking methods, a new generation of green conductive gels based on biomass-derived materials will be developed.

備考：論文要旨は、和文 2000 字と英文 300 語を 1 部ずつ提出するか、もしくは英文 800 語を 1 部提出してください。

Note : Thesis Summary should be submitted in either a copy of 2000 Japanese Characters and 300 Words (English) or 1copy of 800 Words (English).

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