

# The 23<sup>rd</sup> Korean MEMS Conference

제23회 한국 MEMS 학술대회

2021.04.07(수) ~ 04.09(금), 부여 롯데리조트

| 논문원고접수 |

2020년 12월 14일(월) ~ 2021년 1월 13일(수)

| 논문심사결과 통보일 |

2021년 2월 17일(수)까지 홈페이지 (<http://www.micronanos.org>)에  
공지 및 책임저자에게 이메일로 통보

| 초록 및 논문접수처 |

<http://www.micronanos.org>

| 논문범위 |

1. Materials, Fabrication, Packaging and Simulation Technologies
2. Micro/Nanofluidics
3. Bio/Medical Micro/Nano Devices
4. Physical and Mechanical Micro/Nano Sensors and Systems
5. Chemical and Environmental Sensors
6. RF/Optical Devices
7. Micro/Nano Energy and Power Devices
8. Soft, Flexible and Printed Devices

주최 : (사)마이크로나노시스템학회 (E-mail : [master@micronanos.org](mailto:master@micronanos.org), 전화 : 02-749-6482)

# 2021, 제23회 한국 MEMS 학술대회

## 제23회 KMEMS 학술대회 ORAL SESSION

### Soft, Flexible and Printed Devices

4월 7일 수요일  
15:45~16:45

No.	Journal Title	First Author	Corresponding Author	Organization
WO-1-01	Fabrication of shape memory polymer based switchable dry adhesive and the adaptability	송현우	곽문규	경북대학교
WO-1-02	유전탄성체를 이용한 유연 플라즈모닉 디스플레이	기석호	박정열	서강대학교
WO-1-03	Development of Carbon Nanotube-Embedded Conductive Rubber Composite for Biaxial Strain Detection	이가연	최정욱	영남대학교

### Materials, Fabrication, Packaging and Simulation Technologies

4월 8일 목요일  
08:00~09:00

No.	Journal Title	First Author	Corresponding Author	Organization
TO-2-01	마이크로 히터의 국소가열을 통한 영역선택적 백금 원자층 증착	강윤성	김종백	연세대학교
TO-2-02	고투과도를 가지는 CuO/Cu(OH) <sub>2</sub> 나노와이어 초발수 표면 제작 및 특성에 관한 연구	김동환	고종수	부산대학교
TO-2-03	Triboelectric nanogenerator based on triple perovskites for self-powered Morse code Generator	Sugato Hajra	김회준	대구경북과학기술원
TO-2-04	Fabrication of highly sensitive microfluidic detector using liquid metal-based 3D electrodes	황혜수	김현수	광운대학교

### Bio/Medical Micro/Nano Devices

4월 8일 목요일  
11:00~12:00

No.	Journal Title	First Author	Corresponding Author	Organization
TO-3-01	A Disposable Microfluidic Platform with On-chip Integrated Flow Sensors	김진호	한기호	인제대학교
TO-3-02	Development of the cell delivery microrobot using droplet generation	노승민	최홍수	대구경북과학기술원
TO-3-03	이온 농도 분극 현상을 이용한 동시 농축과 용출로 신속한 박테리아 검출이 가능한 종이 기반 장치	김원석	김성재	서울대학교
TO-3-04	초음파 이미징을 위한 웨이퍼 접합된 정전용량형 미세가공 초음파 트랜스듀서	심신용	이병철	한국과학기술연구원

### RF/Optical Devices, Micro/Nano Energy and Power Devices

4월 8일 목요일  
15:55~16:55

No.	Journal Title	First Author	Corresponding Author	Organization
TO-4-01	Ultrathin Contact Imaging System Based on Microlens Arrays and Versatile Micropinhole Arrays	장경원	정기훈	한국과학기술원
TO-4-02	Simulation of Surface Plasmon Resonance Characteristics of DMMP according to Palladium Thickness	김지원	김정무	전북대학교
TO-4-03	기계적 혼합을 통한 식물 조류 세포로의 CNT 삽입 및 광합성 전자 추출 연구	권효진	류원형	연세대학교
TO-4-04	Wet chemical preparation of cobalt sulfide and iron oxide for asymmetric supercapacitor application	라홀	이동원	전남대학교

# 2021, 제23회 한국 MEMS 학술대회

## 제23회 KMEMS 학술대회 ORAL SESSION

### Micro/Nanofluidics

4월 9일 금요일  
08:00~09:00

No.	Journal Title	First Author	Corresponding Author	Organization
FO-5-01	기공성 나노채널 벽면을 통한 증발로 유도된 이류흐름을 이용한 나노유체역학적 분자 전달현상 제어	서상진	김태성	울산과학기술연구원
FO-5-02	Power generation through improved permeability and ion-selectivity in graphene oxide-based heterogeneous membranes	고영수	이충엽	경희대학교
FO-5-03	배양조건 제어를 위한 미세유체 챔버 구조상 원심가속도에 의한 마이크로 비드의 거동 분석	강동희	강현욱	전남대학교
FO-5-04	음파와 유전 영동 현상을 이용한 기포 제거	현영빈	정상국	명지대학교

### Physical and Mechanical Micro/Nano Sensors and Systems

4월 9일 금요일  
10:50~11:50

No.	Journal Title	First Author	Corresponding Author	Organization
FO-6-01	Dynamic inertial imaging of heater integrated microchannel dispensers for real-time monitoring of bubble jet monitoring	고주희	이정철	한국과학기술원
FO-6-02	나노입자의 크기분포와 밀도를 동시에 분석가능한 MEMS기반 나노입자 선량계	이승수	김용준	연세대학교
FO-6-03	스트레인과 온도 모니터링을 위한 이형 접합 구조의 합성물 기반 스트레처블 하이브리드 센서	Ashok Chhetry	박재영	광운대학교
FO-6-04	물방울 충격력 측정을 위한 PDMS 멤브레인 센서의 민감도에 관한 연구	강동관	이상민	동의대학교

### Chemical and Environmental Sensors

4월 9일 금요일  
14:10~14:55

No.	Journal Title	First Author	Corresponding Author	Organization
FO-7-01	딤러닝 기반 선택적 가스 감지가 가능한 반도체식 가스 센서 어레이	강민구	박인규	한국과학기술원
FO-7-02	팔라듐 캡핑 공정을 이용한 광섬유 기반 국소화 표면 플라즈몬 공명 수소 센서	김효준	이승기	단국대학교
FO-7-03	수생태계 내 프탈레이트 고감도 측정을 위한 골드 나노플라워 표면 개질 기반 전기 화학 압타 센서	이경연	정효일	연세대학교

# Wet chemical preparation of cobalt sulfide and iron oxide for asymmetric supercapacitor application

Rahul B Pujari, Munirathinam Karthikeyan, Dong-Weon Lee\*,  
MEMS and Nanotechnology Laboratory, School of Mechanical System Engineering, Chonnam National  
University, Gwangju, 61186, Republic of Korea.  
E-mail: [mems@jnu.ac.kr](mailto:mems@jnu.ac.kr)

## 비대칭 슈퍼 커패시터 적용을 위한 황화 코발트 및 산화철의 습식 화학적 준비

라훌 비 푸자리, 카르틱, 이동원\*,  
전남대학교 기계공학과

### Abstract

The current state of art for improvement of energy density of aqueous supercapacitors is preparation of nanostructured electrodes that are operated in wide operating potential window. In this work, nanostructured cobalt sulfide ( $\text{Co}_x\text{S}_y$ ) (nanosheets and nanoparticles) and iron oxide ( $\text{Fe}_3\text{O}_4$ ) (nanorods) electrodes are prepared by hydrothermal method. The nanostructured cobalt sulfide and iron oxide electrodes show higher charge storage properties in  $-0.1$  to  $+0.45$  V/SCE and  $-1.0$  to  $-0.5$  V/SCE operating potential windows, respectively in aqueous 1 M KOH electrolyte. The  $\text{Co}_x\text{S}_y$ /PVA-KOH/ $\text{Fe}_3\text{O}_4$  asymmetric supercapacitor is assembled using polyvinyl alcohol (PVA)/KOH gel electrolyte that shows outstanding energy density of  $8.85 \text{ Whkg}^{-1}$  and power density of  $208 \text{ Wkg}^{-1}$ . The obtained high energy density of supercapacitor is associated with nanostructured surface and low internal resistance of the electrodes as well as different potential windows of cobalt sulfide and iron oxide electrodes in same electrolyte beneficial for enhancing operating voltage of supercapacitor.

Keywords: Cobalt sulfide (코발트 황화물), Energy density (에너지 밀도), Iron oxide (산화철), Power density (출력 밀도) Supercapacitor (슈퍼 커패시터).

### 1. Introduction

Among the all electrochemical capacitors (or supercapacitors), pseudocapacitors show better energy density than electrochemical double layer capacitors. Still, energy density of pseudocapacitors is hindered by low specific capacitance values of electrodes owing to sluggish charge transfer kinetics, poor ionic diffusion, and low electronic conductivity of electrode material. Smaller operating potential window of metal oxide electrodes such as cobalt nickel oxide and cobalt oxide ( $\sim 0.4$  V) is another reason for low energy density of pseudocapacitor [1].

Iron oxide and cobalt sulfide electrodes show large theoretical specific capacitance values because of multiple valence states of iron and cobalt atoms. However, low electronic conductivity of iron oxide ( $\sim 10\text{-}14 \text{ Scm}^{-1}$ ) and low operating potential window of cobalt oxide ( $\sim 0.4$  V) in aqueous electrolytes restricts their use for enhancement of energy density of supercapacitors [2].

It is well known that preparation of nanostructures of electrochemically active materials enhances the specific capacitance and specifically, nanorods like structure of material favors fast electron transfer useful for improving electrochemical charge kinetics of the electrode material. Therefore, in this work cobalt sulfide is prepared with nanosheets and nanoparticle like structure and iron oxide is prepared with nanorods surface morphology for improvement of charge storage properties of supercapacitor. Furthermore, energy density of supercapacitor is improved by utilizing negative ( $-1.0$  to  $-0.5$  V/SCE) and positive ( $-0.1$  to  $0.45$  V/SCE) potential windows of iron oxide and cobalt sulfide electrodes in aqueous 1 M KOH, respectively.

### 2. Experimental section

#### 2.1 Cobalt sulfide ( $\text{Co}_x\text{S}_y$ ) preparation

Cobalt sulfide was prepared using wet chemical ion exchange method. Initially, manganese sulfide thin film was prepared with method reported elsewhere [3]. Then, manganese sulfide was treated with aqueous cobalt chloride solution at  $100^\circ\text{C}$  in the hydrothermal autoclave using laboratory oven. The black cobalt sulfide thin film was formed after hydrothermal treatment, which was cleaned with de-ionised water and ethanol repeatedly for exclusion of impurities.

#### 2.2 Iron oxide ( $\text{Fe}_3\text{O}_4$ ) preparation

Iron oxide was prepared by single step hydrothermal method. Briefly, aqueous solutions of iron chloride ( $\text{FeCl}_3$ ), sodium sulfate ( $\text{Na}_2\text{SO}_4$ ), and urea ( $\text{CH}_4\text{N}_2\text{O}$ ) were mixed together in Teflon container. Then, container was sealed in stainless steel autoclave and heated in oven at  $100^\circ\text{C}$ . The brown iron oxide ( $\text{Fe}_3\text{O}_4$ ) thin film was formed after hydrothermal treatment. Thin film was cleaned with DI water and ethanol repeatedly.

#### 2.3 Materials characterization

X-ray diffraction (XRD) study was performed for identification of phase and crystal structure of material. Field-emission scanning electron microscopy (FE-SEM) technique was employed for visualization of nanostructure of materials thin films. Electrochemical charge storage of materials thin film electrodes was evaluated using three electrode setup with cobalt sulfide, iron oxide thin film as working electrode, platinum plate as counter electrode and  $\text{Ag}/\text{AgCl}$  as reference electrode.

### 3. Results and discussion

Fig. 1 (a) shows XRD patterns of cobalt sulfide, and iron oxide thin films. It shows that multiple phases of cobalt sulfide are present in the material such as  $\text{Co}_9\text{S}_8$ ,  $\text{Co}_3\text{S}_4$ ,  $\text{Co}_4\text{S}_3$ , and  $\text{CoS}_2$ . However, in case of iron oxide, single phase of  $\text{Fe}_3\text{O}_4$  is observed from XRD pattern, which is identified from JCPDS no. 19-0629. FE-SEM study of thin films show that cobalt sulfide (Fig. 1 (b, c)) surface morphology is composed of nanosheets and nanoparticles and iron oxide (Fig. 1 (d, e)) surface exhibits nanorods like structure. Such a nanostructured electrode materials are beneficial for enhancing charge storage kinetics of supercapacitor.

For the electrochemical charge storage analysis, cobalt sulfide, and iron oxide thin films were used without further treatment as a working electrodes in 1 M KOH. Fig. 2 (a) and (b) show cyclic voltammetry curves of cobalt sulfide (in -0.1 to 0.45 V/SCE potential window), and iron oxide (in -1.0 to -0.5 V/SCE), respectively for different scan rates. The cathodic and anodic curves of both the electrodes follow capacitive trend and CV shapes show semi rectangular nature, which are useful properties for higher charge storage in the electrode. The galvanostatic charge-discharge (GCD) curves (Fig. 2 (c) and (d)) of cobalt sulfide and iron oxide, respectively show very small internal resistance of material at the beginning of discharge profile of each GCD curve. This is associated with highly nanostructured and easily accessible electrode surface feature of cobalt sulfide and iron oxide for electrolyte ions. Therefore, high specific capacitances are obtained for both iron oxide ( $306 \text{ mFcm}^{-2}$ ) and cobalt sulfide ( $88 \text{ mFcm}^{-2}$ ) electrodes as seen in Fig. 2 (e). The electrochemical impedance curve in Fig. 2 (f) of both the electrodes show pseudocapacitive feature useful for higher charge storage kinetics.

The asymmetric supercapacitor  $\text{Co}_x\text{S}_y/\text{PVA-KOH}/\text{Fe}_3\text{O}_4$  was assembled using polyvinyl alcohol (PVA)/KOH gel electrolyte and electrochemical charge storage evaluation was done via CV and GCD studies as shown in Fig. 3 (a-e). The highest energy density of  $8.85 \text{ Whkg}^{-1}$  and power density of  $208 \text{ Wkg}^{-1}$  are achieved for the supercapacitor (Fig. 3 (d)). The practical application of charge storage properties of supercapacitor is shown in Fig. 3 (f) by glowing white LED for 10 s.

### 4. Conclusions

The nanostructured cobalt sulfide and iron oxide electrodes are prepared by wet chemical method. The  $\text{Co}_x\text{S}_y/\text{PVA-KOH}/\text{Fe}_3\text{O}_4$  asymmetric supercapacitor is successfully assembled using polyvinyl alcohol (PVA)/KOH gel electrolyte with better energy density and power density features. The practical application of supercapacitor is demonstrated by white LED glow.

### 5. Acknowledgments

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (No. 2020R1A5A8018367).

### 6. References

1. P. Simon, Y. Gogotsi, Materials for Electrochemical Capacitors, *Nat. Mater.* 7, 845-854 (2008).
2. S. Sun, T. Zhai, C. Liang, S. V. Savilov, H. Xia, Boosted crystalline/amorphous  $\text{Fe}_2\text{O}_{3-\delta}$  core/shell heterostructure for

flexible solid-state pseudocapacitors in large scale, *Nano Energy* 45, 390–397 (2018).

3. R. B. Pujari, G. S. Gund, S. J. Patil, H. S. Park, D. W. Lee, Anion-exchange phase control of manganese sulfide for oxygen evolution reaction, *J. Mater. Chem. A*, 8, 3901-3909 (2020).

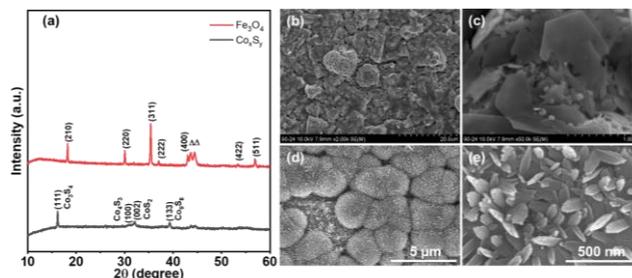


Fig. 1. (a) XRD patterns, and FE-SEM images of (b, c) cobalt sulfide, and (d, e) iron oxide thin films.

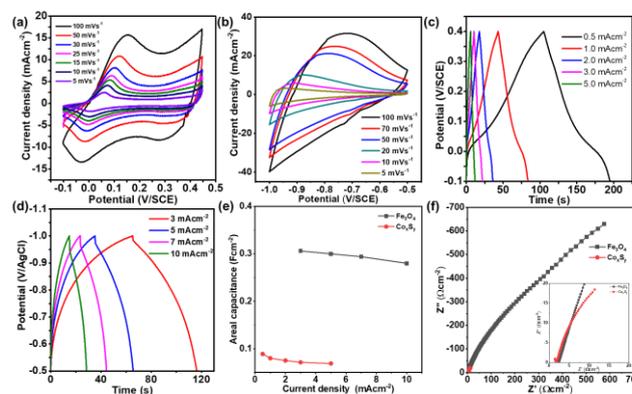


Fig. 2. Cyclic voltammetry (CV) curves of (a) cobalt sulfide, and (b) iron oxide, galvanostatic charge-discharge (GCD) curves of (c) cobalt sulfide, and (d) iron oxide, comparative (e) specific capacitance versus current density curve, and (f) impedance spectra of cobalt sulfide, and iron oxide.

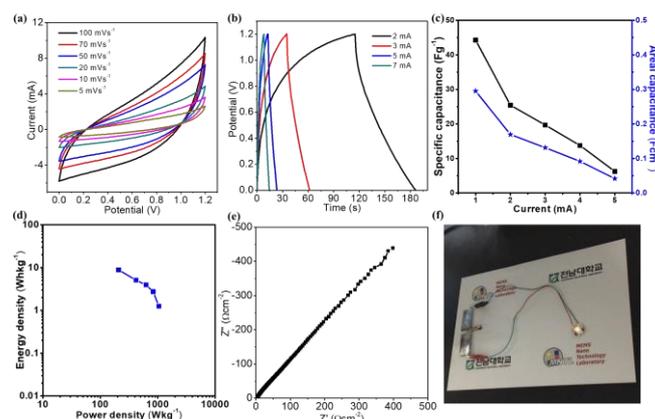


Fig. 3. (a) CV curves, (b) GCD curves, (c) specific and areal capacitances versus current density curve, (d) energy density versus power density plot, and (e) impedance spectrum of  $\text{Co}_x\text{S}_y/\text{PVA-KOH}/\text{Fe}_3\text{O}_4$  asymmetric supercapacitor. (f) The photograph of white LED glow using two asymmetric supercapacitor.