제 39권 2호

2014 추계학술대회 연구논문 초록집

PROCEEDINGS

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한국고분자학회

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processible inorganic semiconductors such as high processing temperature and weak chemical resistance in precursor solution. In this study we designed and synthesized high thermal and chemical resistant pyridine containing polybenzoxazole as organic gate dielectric for solution processible inorganic semiconductor TFTs.

3PS-284 최수나

Synthesis and Characterization of Thieno[3,4-*b*]thiophene(TT)-based Conjugated Polymers

최수나, 박지은, 신지철, 조민주, 최동훈† 고려대학교

Donor-acceptor (D-A) alternating copolymers are the most promising and attractive materials for electronic and optoelectronic applications in recent years. As a molecular component, thieno[3,4-*b*]thiophene (TT) unit extends the backbone planarity and promotes the delocalized electron distribution along a polymer backbone. Also, anthracene (ANT) unit affects the chain-packing and alignment behavior. In this study, we demonstrate synthesis and characteristics of TT-ANT-based conjugated polymer. The effect of anchoring position of TT unit from the 2,6- to the 9,10-position in the anthracene ring was investigated on the semiconducting property. Therefore, we investigated their physical properties by thermal analysis, cyclic voltammetry and absorption spectroscopy. Eventually, we successfully fabricated field-effect transistor devices to study their charge transport properties.

3PS-285 최은수

Tuning the Graphene Oxide Properties of Organic Solar Cells via Metal Chloride Doping

최은수, 나석인† 전북대학교

Organic solar cells (OSCs) have emerged as a promising low-cost renewable energy source, due to their potential application in lightweight, easy solution-based fabrication, and large-area processability. Recently, graphene oxide (GO) is widely used as an efficient anode interfacial material in OSCs, due to its long-term stability and solution processability. However, GO has several undesired properties, such as a poor conductivity and unsuitable work function. In this study, we demonstrate highly efficient polymer solar cells obtained by GO interfacial doping via various solution-processed metal chloride treatments. We investigate the effects of metal chlorides as an interfacial modifier on the cell-performance of OSCs. Kelvin probe, 4-point probe, atomic force microscopy, and X-ray photoelectron spectroscopy studies will demonstrate that the metal chloride treatments modify the work function and sheet resistance of GO.

3PS-286 최종완

Photophysical Property of nanosized-graphene oxide containing electron acceptor moiety

최종완, 신창현[1], 오진우[2], 김선주[3], 김낙중† 한양대학교 화학과; [1]부산대학교 차세대기판학과; [2]부산대학교 나노소재공학과, 차세대기판학과; [3]중앙대학교 화학신소재공학부

Nanosized graphene and its derivatives have been receiving much attraction in various research fields due to their unique physical properties including intense photoluminescence. Several researchers have developed various strategies to control the band gap of nanosized graphene (or graphene oxide) and to tune the luminescence wavelength. Among the strategies are doping of the graphene derivatives with heteroatoms via solvothermal treatment in the presence of precursors and direct functionalization via organic synthesis. In this work, nanosized graphene oxides (NGO) containing electron acceptor moieties were synthesized. The structural characterization of functionalized NGO was performed through spectroscopic and microscopic studies. Band gap of the NGO was controlled by chemical functionalization, as the shift of the emission color from blue to green was observed with functionalization.

3PS-287 최종용

Low Band Gap Ultra Flat Polymers for High Performance Ambipolar Thin Film Transistors

최종용, 윤영운[1], 신나라[1], 옥주원[1], 정혜승[2], 조정호[3], 강영종[4], 김봉수[1,†] 한국과학기술연구원/한양대학교; [1]한국과학기술연구원; [2]이화여자대학교; [3]성균관대학교; [4]한양대학교

We investigated the performance of ambipolar thin film transistors (TFTs) based on low band gap ultra flat polymers. The polymers were co-polymerized by 3,6-bis(thieno[3,2-b]thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (TTDPP) units and benzo[c][1,2,5]thiadiazole (BT) units to synthesize pTTDPP-BT polymer or by TTDPP units and 5,6-difluorobenzo[c][1,2,5]thiadiazole (DFBT) units to yield pTTDPP-DFBT polymer. DFT calculations revealed that all the dihedral angles of the polymer backbones were zero. The HOMO level of pTTDPP-BT polymer is −5.34 eV and that of pTTDPP-DFBT polymer is −5.40 eV. pTTDPP-BT TFT devices showed an excellent ambipolar behavior with hole and electron mobilities of 0.14 and 0.52 cm^2 V−1 s−1, respectively, upon 200 oC-annealing. pTTDPP-DFBT TFT devices also exhibited a similar behavior with hole and electron mobility of 0.014 and 0.048 cm^2 V−1s−1, respectively. We attributed these lower mobilities to the lower molecular weight of pTTDPP-DFBT polymer.

3PS-288 최현지

수분산성이 향상된 코어셸 금속나노입자 제조 및 표면증강라만산란기반 센서로의 응용

최현지, 백연경[1,†], 김영국[1], 윤석영 부산대학교; [1]재료연구소

일반적인 라만 분광법은 감도가 낮아 미량의 신호 분석에 이용되기 어려우나, 표면 증강 라만 산란(Surface Enhanced Raman Scattering, SERS)분광법에 의해 다양한 물질의 검출이 가능하게 되었다. SERS는 분석물질이 금속표면에 근접할 때 표면 플라즈몬 공명효과에 의한 Hot-spot에 의해 유도된다. 또한 특정 분자에 의한 고유 진동에 의해 발생되는 신호로 다양한 분자를 감지하는 화학적 또는 바이오 물질을 분석하는 센서에 적용될 수 있다. 본 연구에서는 금속 코어셸 나노입자를 제조하여 라만 활성을 확인하고, Hot spot이 발생하는 최적의 외부 금속입자크기를 조절하여 라만 신호 증강을 확인하였다. 또한 바이오 물질을 분석하는 용액 타입 라만 센서에 적용시키기 위해, 수분산이 가능한 작용기를 코팅하여 수용액 내에서 금속 나노쉘 입자의 안정성을 확인하였다.

3PS-289 최현호

Conformation-Insensitive Ambipolar Charge Transport in a DPP-Based Copolymer Containing Acetylene Linkages

최현호, 윤희준[1], 권순기[1], 김윤희[1], 조길원† POSTECH; [1]경상대학교

A new organic semiconducting copolymer (PDPP-TAT) containing acetylene linkages based on diketopyrrolopyrrole (DPP) has been compared with a DPP-based copolymer (PDPP-TVT) containing vinylene linkages. The acetylene linkages result in favorable overlap of the electron wave-functions along main chain. Further, the π-conjugation of PDPP-TAT was found to be highly insensitive to the chain conformation. As a result, PDPP-TAT provides favorable charge transport for electrons as well as holes, and enables facile charge transport in tie-molecular regions connecting its crystalline domains. PDPP-TAT exhibits ambipolar characteristics with a high electron/hole mobility ratio (μ_e/μ_h) of ~0.3 in field-effect transistors, whereas PDPP-TVT exhibits unipolar characteristics with a value of μ_e/μ_h that is lower by a factor of 30. Our results demonstrate that the conformation sensitivity of charge transport is a vital factor in the electrical performances of actual organic transistor devices.

3PS-290 한승진

Solvent evaporation-assisted crystal growth of perovskite to achieve high performance organic-inorganic hybrid solar cells

배승환, 한승진, 조원호† 서울대학교 공과대학 재료공학과

Perovskite-based organic-inorganic hybrid solar cells have recently received great attention from both academia and industry. Methylammonium lead iodide (MAPbI3) for perovskite solar cells is one of the most-commonly used compounds as a photon absorber. In this study, we have demonstrated a novel method for formation of perovskite film on the PEDOT:PSS coated substrate using DMSO as a processing solvent, where the film is formed via the solvent evaporation- assisted crystal growth. When the MAPbI3 film is fabricated by the method using DMSO as a solvent, the film exhibits a flower-like morphology with good coverage and the crystals in the film are highly oriented along the (112) direction. As a result, the pervoskite solar cell fabricated from DMSO solution exhibits a PCE of 9.29% with a JSC of 16.13 mA/cm^2 while the cell fabricated from the conventional DMF solution shows a PCE of 4.52% with a JSC of 9.51 mA/cm^2.

3PS-291 한아름

Novel π-Spacer Linked Bis-Benzothiadiazole Blocks for Dominant Polarity Tuner in Organic Field-Effect Transistors

한아름, 김종기[1], 홍자연[2], 김경식[1], 이정훈[1], 신태주[2], 양창덕[1], 오준학[2,†] 포항공과대학교, 울산과학기술대학교; [1]울산과학기술대학교; [2]포항공과대학교

In general, steric hindrance of the polymer chains results in poor electrical performance in the semiconducting polymer-based organic field-effect transistors (OFETs). Recognizing the importance of the molecular co-planarity and with the aim of developing new, ideal strong acceptor building units in semiconducting polymers for high-performance organic electronics, herein we present a facile single-step synthesis of novel π-spacer linked monomers with enlarged planarity relative to a conventionally used acceptor, benzothiadiazole (BT). The novel π-spacer linked bis-benzothiadiazole units have been incorporated into centro-symmetric ketopyrrole cores to facilitate charge transport by enhancing the planarity of the polymer backbones with strong accepting properties. These polymers yield relatively well-balanced ambipolar OFET performances with tunability in the dominant polarity.

3PS-292 허정우

Solution-processed CIGS thin films and their application in solar cells

허정우, Bright Walker, 김진영† UNIST

We demonstrate solution-processed Copper Indium Gallium disulfide (CIGS) thin-film via spin-casting and thermal annealing using thermally cleavable metal thiolates. Ternary or quaternary semiconductor thin-films are achieved by solution-processing different metal thiolate solutions together. Energetic position of conduction band, valence band, and Fermi level of CIGS films can be easily tuned by varying the ratio of In to Ga thiolate solutions. All-solution processed solar cells with a structure of ITO/CIS/CdS/ZnO/Al exhibit 1.5% of power conversion efficiency.

3PS-293 홍한나

A Highly Sensitive Optical Sensor for Fe^{3+} and Cu^{2+} based on Diketopyrrolopyrrole: Synthesis and Spectral Investigation

홍한나, 이대희, 엄현아, 신지철, 조민주, Matinder Kaur, 최동훈† 고려대학교

Heavy and transition metal (HTM) ions have significant functions in many biological systems and environmental processes. The fluorescent probes for the recognition and the selective detection of HTM ions attract much interest in supramolecular chemistry because of the importance of these ions. Among the HTM ions, recognition of Iron (Fe^{3+}) and copper (Cu^{2+}) is particularly interesting because of their vital roles in biological systems. We have synthesized a series of new π-expanded diketopyrrolopyrrole (DPP)-based fluorescent probes for selective recognition of Fe^{3+}/Cu^{2+} over a wide range of metal ions. The probe exhibited pronounced on-off type fluoroionophoric properties with significant color change. Both UV-Vis and fluorescence spectroscopic studies demonstrated that probe was highly sensitive and selective towards Fe^{3+}/Cu^{2+}.

Solvent evaporation-assisted crystal growth of perovskite to achieve high performance organic-inorganic hybrid solar cells

배승환, 한승진, 조원호*
서울대학교 재료공학부

Perovskite-based organic-inorganic hybrid solar cells have recently received great attention from both academia and industry. Methylammonium lead iodide ($MAPbI_3$) for perovskite solar cells is one of the most-commonly used compounds as a photon absorber. In this study, we have demonstrated a novel method for formation of perovskite film on the PEDOT:PSS coated substrate using DMSO as a processing solvent, where the film is formed *via* the solvent evaporation-assisted crystal growth. When the $MAPbI_3$ film is fabricated by the method using DMSO as a solvent, the film exhibits a flower-like morphology with good coverage and the crystals in the film are highly oriented along the (112) direction. As a result, the pervoskite solar cell fabricated from DMSO solution exhibits a PCE of 9.29% with a J_{SC} of 16.13 mA/cm^2 while the cell fabricated from the conventional DMF solution shows a PCE of 4.52% with a J_{SC} of 9.51 mA/cm^2.

Solvent evaporation-assisted crystal growth of perovskite to achieve high performance organic-inorganic hybrid solar cells

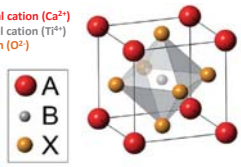
배승환, 한승진, 조원호*
서울대학교 재료공학부

Introduction

❖ Advantages of perovskite solar cells

ABX$_3$ Perovskite

A: Metal cation (Ca^{2+})
B: Metal cation (Ti^{4+})
X: Anion (O^{2-})



➢ Methylammonium lead triiodide ($CH_3NH_3PbI_3$) is the most popular material

✓ Easy and low-cost process

✓ Extremely long exciton diffusion length

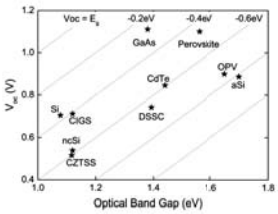
Perovskite	Species	D (cm^2 s^{-1})	L_D (nm)
$CH_3NH_3PbI_{3-x}Cl_x$	Electrons	0.042 ± 0.016	1069 ± 204
	Holes	0.054 ± 0.022	1213 ± 243
$CH_3NH_3PbI_3$	Electrons	0.017 ± 0.011	129 ± 41
	Holes	0.011 ± 0.007	105 ± 32

Science **2013**, *342*, 341.

✓ Easily tunable optoelectronic properties

Energy Environ. Sci. **2014**, *7*, 982.

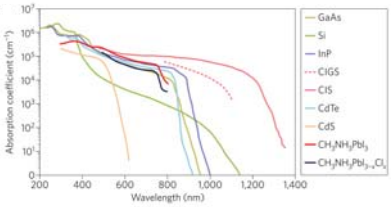
✓ High open-circuit voltage (V_{OC}) with wide optical band gap (E_g)



Open-circuit voltage (V_{OC}) versus optical band gap (E_g) for the best-in-class solar cells

J. Phys. Chem. Lett. **2013**, *4*, 3623.

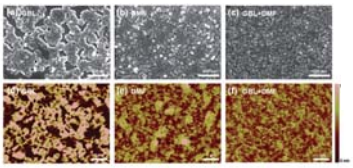
✓ Good absorption coefficients



Absorption coefficients

Nature Photon. **2014**, *8*, 506.

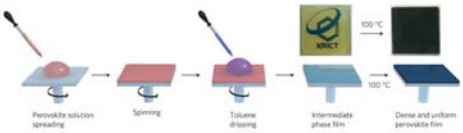
❖ Solvent engineering



Solvent	J_{SC} [mA cm^{-2}]	V_{OC} [V]	FF	PCE [%]	Cal. J_{SC} [mA cm^{-2}]
GBL	7.19	0.95	0.60	4.14	7.21
DMF	7.35	0.93	0.73	5.02	7.55
GBL + DMF	8.74	0.92	0.76	6.16	8.84

N,N-dimethylformamide (DMF)
γ-butyrolactone (GBL)

Nanoscale **2014**, *6*, 6679.



Devices	Scan direction	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	PCE (%)
Al/O mp-TiO_2	Forward	19.2	1.07	0.44	9.1
	Reverse	19.2	1.09	0.69	14.4
200-nm-thick mp-TiO_2	Forward	20.1	1.08	0.73	15.8
	Reverse	19.9	1.06	0.75	15.9

Nature Mater. **2014**, *13*, 897.

Objectives

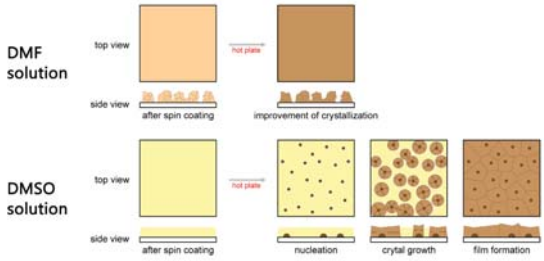
➢ To fabricate perovskite film for the enhancement of power conversion efficiency in $MAPbI_3$ perovskite photovoltaic cells

➢ To investigate the photovoltaic properties and crystallinity of perovskite relying on a solvent used for active layer (DMF, DMSO)

Results

❖ Schematic plot

✓ Growth of $MAPbI_3$

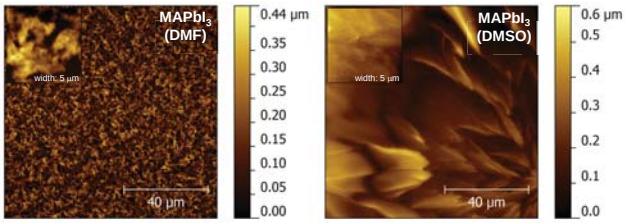


Dimethyl sulfoxide (DMSO)

- DMF solution: crystallization during the spin-coating process
- DMSO solution: crystallization during the thermal treatment

❖ Film morphology

✓ AFM images

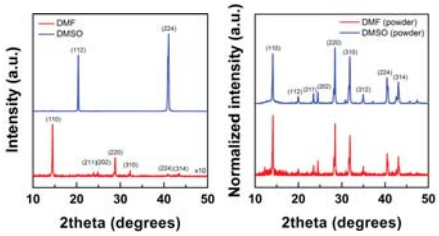


Film thickness: 140.6 nm (DMF), 146.2 nm (DMSO)

- DMF: poor film coverage
- DMSO solution: good film coverage

❖ Crystallinity

✓ XRD



<March-Dollase coefficient P_{MD}>

✓ Range from 0 to 1

✓ P_{MD}=0: 100% preferentially oriented crystallites

✓ P_{MD}=1: completely random orientation of its crystallites

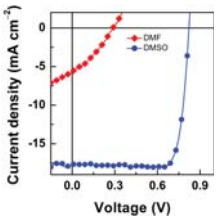
	March-Dollase coefficient
DMF	0.572, (110) direction
DMSO	0.071, (112) direction

Physica C **1997**, *277*, 82.

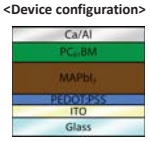
- DMSO: highly oriented perovskite film, higher crystallinity than films from DMF

❖ Photovoltaic properties

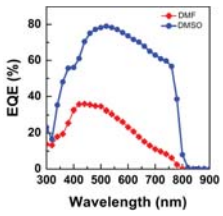
✓ J–V curves



<Device configuration>



✓ EQE spectra



Film thickness: 140.6 nm (DMF), 146.2 nm (DMSO)

	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)	Cal. J_{SC} (mA cm^{-2})
DMF	0.29	5.68	32.0	0.53	5.73
DMSO	0.82	17.80	82.8	12.08	17.94

Conclusions

➢ The usage of DMSO as a solvent for a perovskite film contributes to the good coverage and the crystallinity of perovskite.

➢ The perovskite film fabricated by DMSO solvent provides the enhancement of J_{SC} (17.80 mA cm^{-2}) with PCE (12.08%) in a perovskite photovoltaic cell compared to a cell with DMF (J_{SC}: 5.68 mA cm^{-2}, PCE: 0.53%).