

多晶向摻釷鐵酸鈹陶瓷之電極化調制光伏效應

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Polarization-modulated photovoltaic conversion in polycrystalline bismuth ferrite

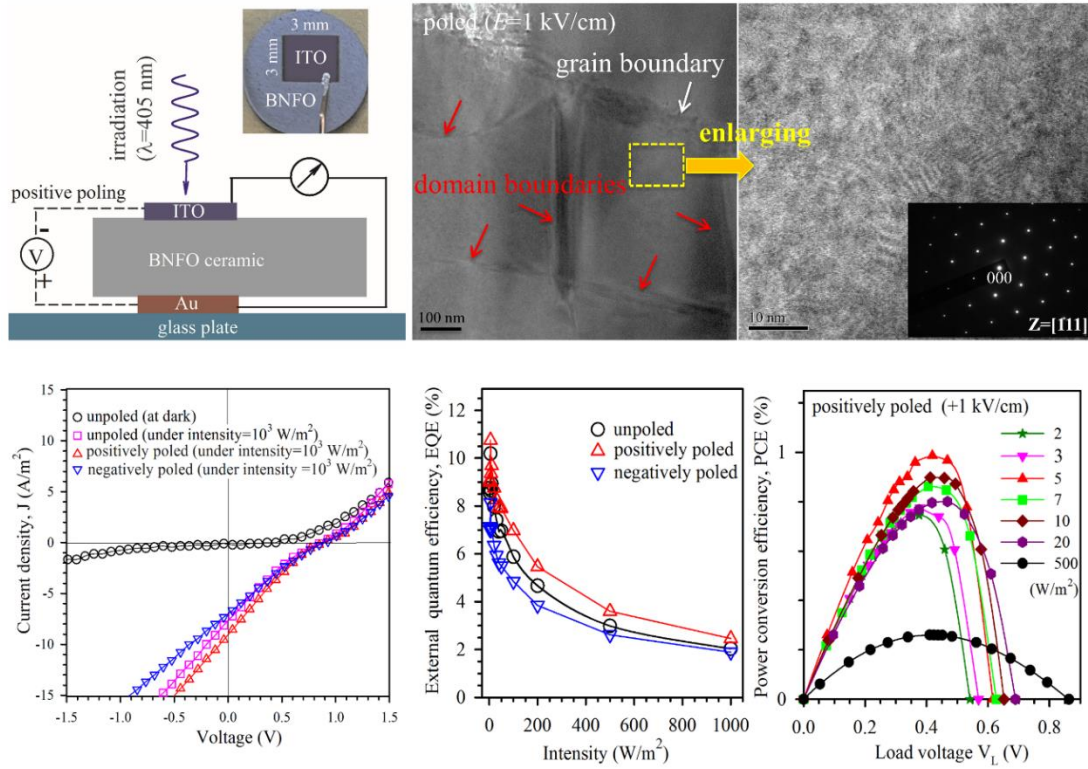
光能轉換電能(photovoltaic)相關應用是一日益重要能源課題。近年染料敏化太陽能電池(dye-sensitized solar cell; DSSC)由於低成本及光伏轉換效率可達到 20% 受到許多重視，不過 DSSC 最大問題是轉換效率隨時間快速衰減及封裝不易。另一個近年備受關注光伏應用材料是有機-無機鈣鈦礦太陽能電池(organic-inorganic perovskite based solar cell)，例如 $\text{CH}_3\text{NH}_3\text{PbX}_3$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}$)，這些含鉛鈣鈦礦鹵化物的光伏轉換效率雖已達到 21%，不過有機-無機鈣鈦礦太陽能電池最大問題是光伏轉換效率在大氣環境快速衰減及含鉛元素。另一方面，許多無中心對稱(non-centrosymmetric)無機鉛鈣鈦礦結構鐵電材料也具有光伏效應(photovoltaic effect)，例如 BaTiO_3 (BTO)及 $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ (PZT)，因為能隙(bandgap; E_g)過寬 (≥ 3.5 eV)導致光伏電流太小 ($\leq 10^9$ A/cm²)及轉換效率太小 ($< 0.01\%$)等問題，使此類材料在光伏效應的應用發展受到限制。近年因為多鐵性(multiferroic) BiFeO_3 (BFO)材料能隙($E_g \leq 2.8$ eV)明顯小於傳統鉛鈣鈦礦結構鐵電材料($E_g > 3.58$ eV)，BFO 比傳統鈣鈦礦氧化物具有更好光伏轉換效應的性質及具有光觸媒(photocatalytic)應用潛力，在光感測元件(optical sensor)、光觸媒元件(photocatalytic device)及光導元件具有相當的應用潛力。

此研究主要突破是 ITO 透明導電薄膜/Nd-doped BiFeO_3 陶瓷/Au 薄膜之異質結構在紫藍光($\lambda=405$ nm)照射下的光電轉換效率，最大功率轉換效率(power conversion efficiency, PCE)及外部量子效率(external quantum efficiency; EQE)分別達到 1% 及 11%，在 10^2 mW/cm² 光強度的開路電壓(open-circuit voltage)及短路電流(short-circuit current density)分別達到 0.9 V 及 8.0 A/m²，這些光伏參數是目前多晶向(polycrystalline)鐵電/壓電材料中最大的光伏效應實驗值。另外依據光學穿透與光致發(photoluminescence)光譜，Nd-doped BiFeO_3 陶瓷的光學能隙(optical bandgap, E_g) 約在~2.12-2.24 eV。學理創新方面，我們發展 p-n-junction model 理論及 polarization-induced Schottky-barrier 模型解釋電場極化增強光伏效應及能量轉換效率的物理機制。

主要以 $(\text{Bi}_{0.93}\text{Nd}_{0.07})\text{FeO}_3$ 為基本材料架構，在 B-site 摻雜過渡金屬(transition metal)元素多鐵性材料。材料製備方面，將使用固態反應法(solid state reaction)製備陶瓷塊材及薄片，同時進行一系列分析實驗，有系統性探討材料微觀結構及物理性質，例如使用 synchrotron soft X-ray absorption spectroscopy (新竹國家同步輻射中心 BL20A1)、high-resolution TEM、micro-Raman spectroscopy 等高解析分析實驗，探討極化電場對 Nd-doped BiFeO_3 陶瓷晶粒內部 microstructure (例如 grain & domain boundaries)、microdomains、orbital hybridizations ($\text{O } 2p\text{-Fe } 3d$ & $\text{O } 2p\text{-Bi } 6sp$)及 vibrational modes 等微觀物理性質的影響，提供多鐵性 BiFeO_3 材料在光電能量轉換及光觸媒(photocatalyst)重要學術及應用參數。

光伏效應實驗的激發光源是使用紫藍光($\lambda=405$ nm)及綠光($\lambda=532$ nm)，針對沒有極化及 dc 電壓極化過的異質結構試片進行下列光照強度的光伏相關實驗；(1) 光伏開路電壓(photovoltaic open-circuit voltage)、(2) 光伏短路電流(photovoltaic short-circuit current)、(3) 電流 vs 電壓特徵曲線(I-V characteristic curve)、(4) 光電阻(photoresistivity)、(5) 功率轉換效率(light-to-

electric power-conversion efficiency; PCE)、(6)外部量子效率(photon-to-electron external quantum efficiency; EQE)。探討在紫藍光($\lambda=405\text{ nm}$)、綠光($\lambda=532\text{ nm}$)及標準太陽光譜照射下。



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Above-bandgap photovoltages in lead-free perovskite BiFeO₃ have been substantially studied for energy harvesting and photocatalytic applications. However, most reported photocurrents and conversion efficiencies are still too small due to wide bandgaps. Remarkably large and durable field-modulated external quantum efficiency (EQE) ~11% and power conversion efficiency (PCE) ~1% have been achieved under 405 nm irradiation in polycrystalline Nd-doped BiFeO₃ (BNFO) ceramic with a bandgap $E_g \sim 2.12\text{-}2.24$ eV. The photovoltaic voltage and current density can reach ~0.9 V and ~8.0 A/m² after poling ($E=1$ kV/cm) at irradiation intensity 10² mW/cm². The p-n-junction layer between indium tin oxide (ITO) thin film and BNFO ceramic is the primary mechanism for the field-modulated photovoltaic responses in conjunction with the polarization-induced Schottky-barrier modulation. The field-induced domain nucleation within the grains and nanodomains play important roles for the enhanced photocurrent and conversion efficiencies.

Though high photovoltaic (PV) conversion efficiencies (> 20%) have been achieved in recent studies of textured perovskite/silicon tandem solar cells, the short-lifetime device stability, small active area, and lead toxicity of organic-inorganic metal halide perovskite materials remain a concern and can be drawbacks for applications. Lead-free multiferroic and ferroelectric (FE) materials as practical absorbing media for solar energy harvesting have increasingly attracted interest due to exceeding the Shockley-Queisser limit (i.e. photovoltage < bandgap E_g) and because of their polarization-switchable PV responses. The bulk PV effect (BPVE) in non-centrosymmetric perovskite FE/multiferroic materials has demonstrated anomalous above-bandgap photovoltages, but the power conversion efficiencies are still too small due to weak current densities (in order of $\mu\text{A}/\text{cm}^2$) or photocurrents (in order of nA-pA). Enhanced PV responses have been reported in recent years by tailoring polarization direction, thickness, bandgap and buffer layer in the FE/electrode interface. For instance, power conversion efficiencies (PCEs) of ~0.28% and ~0.57% were respectively reported in (La_{0.7}Sr_{0.3})MnO₃/(Pb_{0.97}La_{0.03})(Zr_{0.52}Ti_{0.48})O₃/Nb-SrTiO₃ under 354 nm irradiation and ITO/PZT/Cu₂O/Pt under AM1.5G solar spectral irradiance.

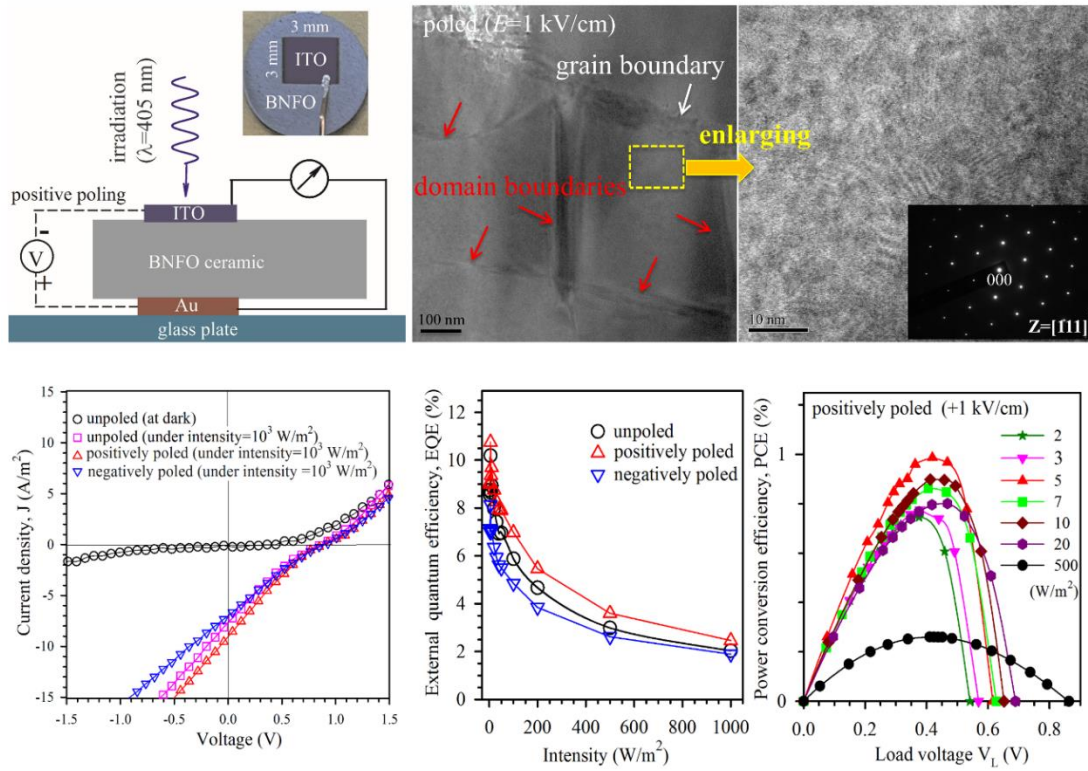
Two driving mechanisms are responsible for the BPVE in non-centrosymmetric materials, including ballistic and shift mechanisms associated with the asymmetric momentum distribution of non-thermalized carriers and the non-diagonal elements of the density

matrix, respectively. According to the BPVE model, the open-circuit photovoltage (V_{oc}) and photovoltaic field (E_{pv}) can be respectively described by $V_{oc} = j_{pv}d / (\sigma_d + \sigma_{pv})$ and $E_{pv} = j_{pv} / \sigma_{pv}$, where j_{pv} , d , σ_d , and σ_{pv} are respectively

photocurrent density, sample thickness, dark conductivity and photo-conductivity. The photo-conductivity can be further expressed as $\sigma_{pv} = eI_o \alpha \phi (\hbar\omega)^{-1} (\mu\tau)_{pv}$, where I_o , α , ϕ , $\hbar\omega$, μ and τ are respectively light intensity, absorption coefficient, quantum yield, incident photon energy, mobility and lifetime of carriers responsible for photoconductivity. The linear photocurrent density can be described by $j_{pv}^i = \alpha g_{ijl} e_j e_l I_o$, where g_{ijl} , e_j , and e_l are the third-rank piezoelectric tensor and components of light polarization.

Multiferroic BiFeO₃ (BFO) materials have shown smaller bandgaps of ~2.0-2.8 eV than typical perovskite FE materials (bandgap > 3.3 eV). It has been found that the bandgaps of BiFeO₃ materials are sensitive to particle (or grain) size, dopant, and particle morphology. Thus, PV properties have been extensively explored in various heterostructures of electrode/BFO materials/electrode and correlated to the BPVE or the p-n-junction effects. An external quantum efficiency (EQE)~10% was reported in ITO/BFO/SrTiO₃ films under 325 nm irradiation. PCE~0.8% and EQE~9% were reported in the heterostructure of ITO/(Bi_{1-x}Nd_x)FeO₃ ceramics/Au under 405 nm irradiation. The direct bandgaps of (Bi_{1-x}R_x)FeO₃ (R=Sm, Nd) ceramics appear in the range of ~2.1-2.2 eV, which correlate to hybridizations between O 2p and cation orbitals. A junction layer was reported at the interface of ITO-BFO thin films with a depletion layer thickness of ~300 nm and was considered as the primary mechanism for the PV effect. A theoretical junction model was developed based on optically excited charge carriers at the interface between n-type ITO film and p-type doped BFO ceramic and can quantitatively describe PV open-circuit voltage (V_{oc}) and short-circuit current density (J_{sc}) as functions of irradiation intensity. Synchrotron X-ray absorption spectra revealed a minor Fe⁴⁺ valence in the Fe³⁺ predominant matrix in (Bi_{1-x}Nd_x)FeO₃ ceramics, suggesting suppression of Fe²⁺ formation and oxygen vacancies by the A-site rare-earth substitution.

Local domain structures and polarization order are essential for the electric (E)-field-modulated PV phenomena. However, the nanoscale origins of field-modified PV responses still remain unclear, especially in polycrystalline BFO ceramics. In this study, we report record field-modulated PCE~1% and EQE~11% in the heterostructure of ITO film/(Bi_{0.93}Nd_{0.07})FeO₃ ceramic/Au film under 405 nm irradiation. These remarkable field-modulated PV effects are attributed to a combination of the p-n-junction-like effect and the polarization-modulated Schottky barrier. This study highlights that nanoscale field-modulated domain structures, polar nano-regions, and orbital hybridizations play important roles in the field-modulated PV responses.



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