Reduced Graphene Oxide Ink/Conductive Polymeric Composites for Enhanced Field Emission Devices



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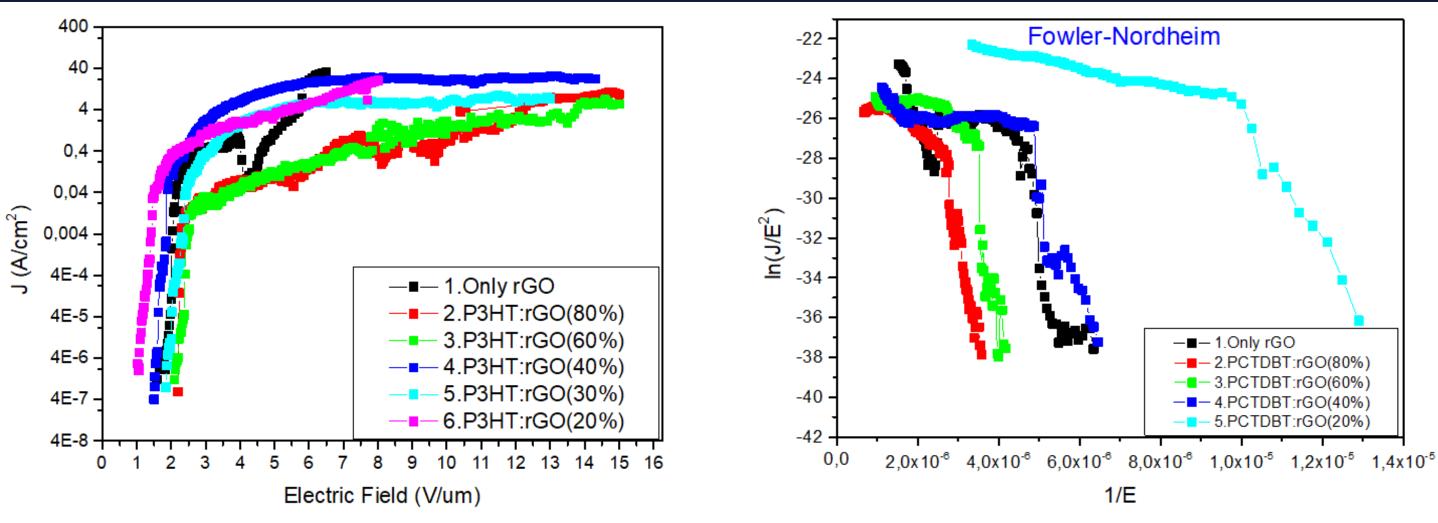
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Abstract

Hydroiodic acid (HI) treated - reduced graphene oxide (rGO) ink/conductive polymeric composites are considered as promising cold cathodes in terms of high geometrical aspect ratio and low field emission (FE) threshold devices [1-4]. In this study, four simple, cost-effective, solution-processed approaches for rGO-based field effect emitters were developed, optimized and compared; rGO layers were coated on a) n+ doped Si substrate, b) n+-Si/P3HT:rGO, c) n+-Si/PCDTBT:rGO and d) n+-Si/PCDTBT:PC₇₁BM:rGO composites, respectively. The fabricated emitters were optimized by tailoring the concentration ratios of their preparation and field emission characteristics. In a critical ratio, FE performance of the composite materials was remarkably improved compared to the pristine Si, as well as n+-Si/rGO field emitter. In this context, the impact of various materials, such as polymers, fullerene derivatives, as well as different solvents on rGO function reinforcement and consequently on FE performance, upon rGO-based composites preparation, was investigated. The field emitter consisted of n+-Si/PCDTBT:PC₇₁BM(80%):rGO(20%)/rGO displayed a field enhancement factor of ~2850, with remarkable stability over 20h and low turn-on field in 0.6V/µm. Highefficiency graphene-based FE devices realization paves the way towards low-cost, large-scale electron sources development. Finally, the contribution of this hierarchical, composite film morphology was evaluated and discussed.



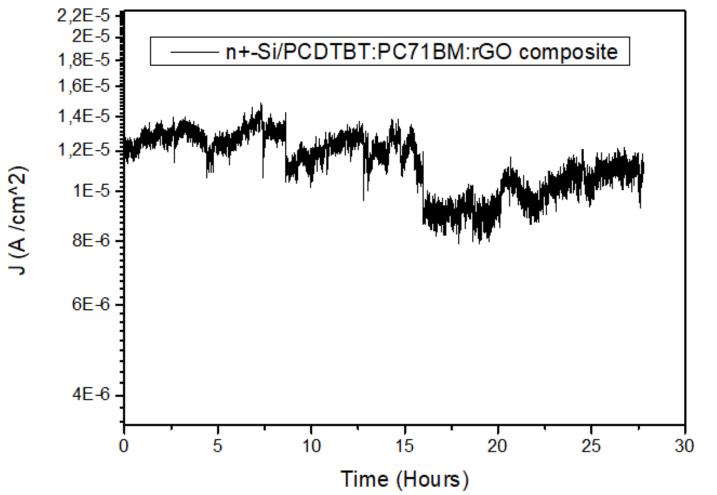
Field Emission Measurements

rGO ink preparation



Logarithmic plot of the current density J, measured as a function of the electric field E (J-E), obtained by different concentration ratios of rGO in composite n⁺-Si/P3HT:rGO field emitters

 \rightarrow Electrical field threshold Low in **P3HT:rGO(20%)**



The evolution of the emission current density at a constant bias voltage of 1500 volts over a long period of continuous operation for the best rGO cathodes measured.

It can be observed that the emission current lasts for over 25 hours

β

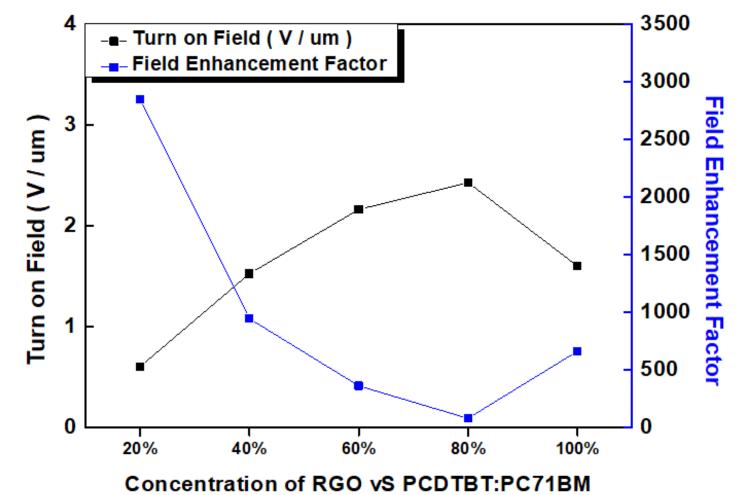
660±10

(/ 0)

Only rGO

Fowler-Nordheim curves of the J-E plots of field emitters with different concentration ratios of rGO in composites n⁺-Si/PCDTBT:rGO. →High Enhancement factor

in PCTDBT:rGO(20%)



Variation of the turn on field (black line) and the enhancement factor (blue line) in different concentrations of PCDTBT:PC71BM:rGO and P3HT:rGO

The higher aspect ratio ($\beta = h/d$) value is observed in 20% rGO, leading to amplified E_{loc}

β

 660 ± 10

80±10

 360 ± 10

950±10

2850±10

 F_{to} (V/µm)

 $1,60\pm0.1$

 $2,43\pm0.1$

 $2,16\pm0.1$

 $1,53\pm0.1$

 $0,60\pm0.1$

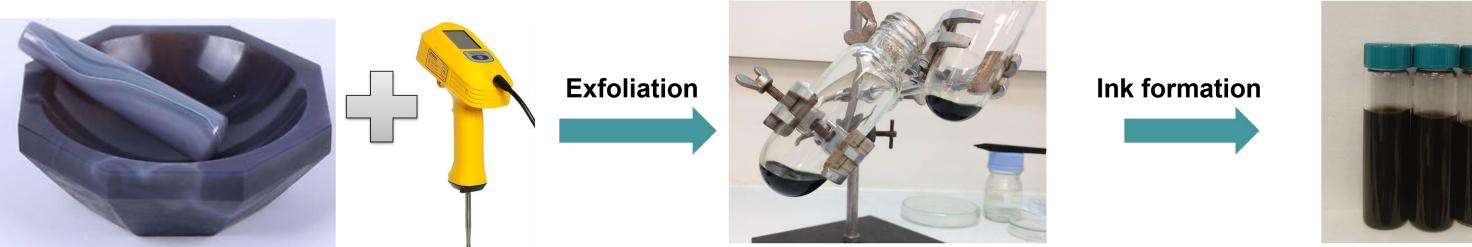
rGO	n ⁺ -Si/P3HT:rGO	n ⁺ -Si/PCDTBT:rGO	n ⁺ -Si/PCDTBT:PC ₇₁ BM:rGO
Ratio	Field Enhancement Turn-on Fiel	d Field Enhancement Turn-on Field	Field Enhancement Turn-on Field

ß

660±10

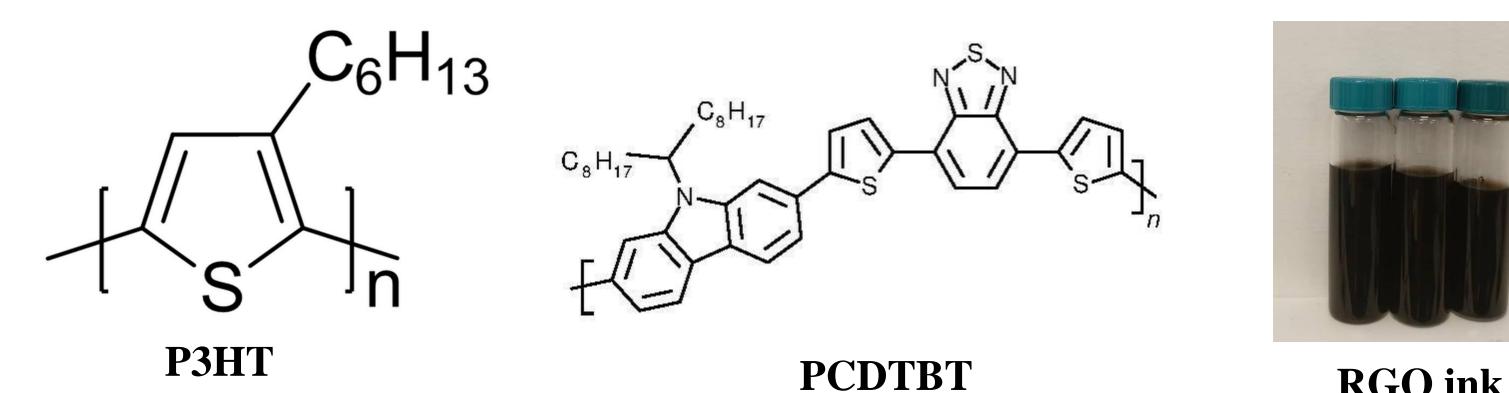
 F_{to} (V/µm)

 $1,60\pm0.1$



- GO prepared by Hummers' method
- RGO preparation by HI/AcOH reduction method
- **RGO** pulverization with mortar & pestle
- Inks preparation through ultrasonication probe
- High viscous rGO inks realization in THF, o-DCB and o-DCB:CB

rGO:Polymers Composites preparation



 F_{to} (V/µm)

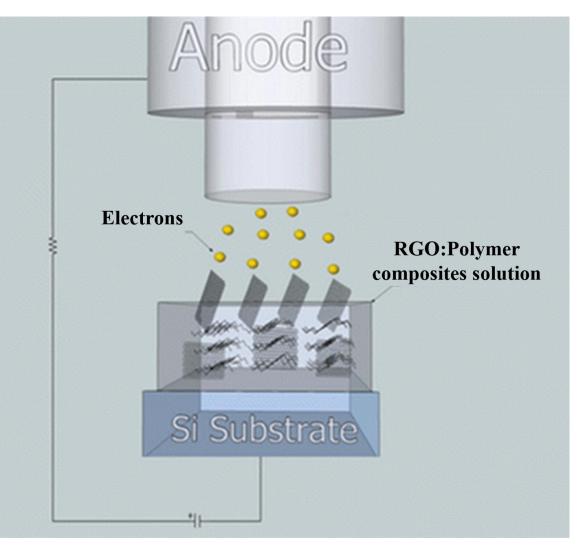
 $1,60\pm0.1$

npared. rGO layers prepared b) n+-Si/P3HT:rGO, c) n+-Si/PCDTBT:rGO and d) n+-Si/PCDTBT:PC₇₁BM:rGO composites, respectively. We investigate the FE properties of different concentrations of polymer composite solutions to control the structural end electrical properties of the substrate. It is found that the cathodes based on PCDTBT:PC71BM:rGO displayed a field enhancement factor of ~2850, with remarkable stability over 25 h and low turn-on field in $0.6V/\mu m$.

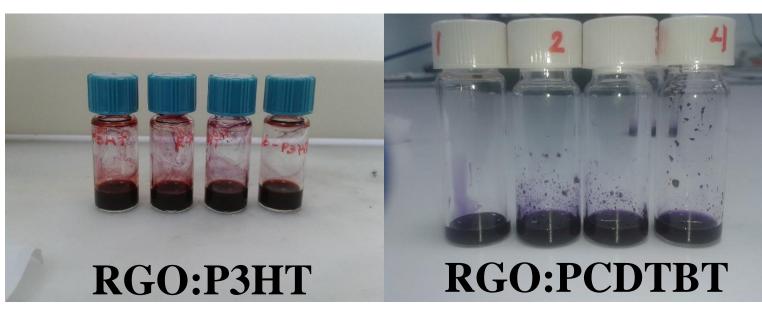
The threshold field, enhancement factor and the remarkable Stability of FE current was remarkably improved compared to the pristine Si demonstrating that is a promising FE cathode with potential applications in vacuum microelectronics and FEDs.

References

RGO ink



Field Emitter setup



- **THF and o-DCB to prepare P3HT and PCDTBT solutions** •
- **RGO** inks addition to the P3HT and PCDTBT solutions in controlled volume ratios equal to 20:80, 40:60, 60:40, 80:20 and 100%
- **RGO:**Polymer composites realization
- **PCDTBT:PC**₇₁**BM:rGO composites fabrication**

[1] G. Viskadouros, et al. Applied Physics Letters 105, 203104 (2014)

[2] G. Viskadouros, et al. ACS applied materials & interfaces 6, 388-393 (2013)

[3] L. Sygellou, et al. RSC Advances 5, 53604-53610 (2015)

[4] G. Viskadouros, et al. RSC Advances 6, 2768-2773 (2016)

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