Literature Research

Nanoparticles, analysis, printing and coating technologies, polymer nanoparticles and solar cells

THE USE OF NANOPARTICLES

- Application in:
  - Printed electronics
  - Solar cells

  - Electroluminescence devices
  - RFID tags

  - Microelectronic devices

REF.: Shlomo Magdassi , Michael Grouchko and Alexander Kamyshny; Copper Nanoparticles for Printed Electronics: Routes Towards Achieving Oxidation Stability; 2010

Copper nanoparticles

- Positive points:
  - Copper is much cheaper
  - Very high conductivity (6% less then Ag NPs)
  - It can be synthesized with essentially low-cost equipment and in large volume
- Negative points:
  - In oxygen and hydrogen atmosphere, the surface of the NPs undergoes oxidation
  - Consequences:
    - It increases the required sintering temperature
    - It reduces the electrical conductivity

REF.: Shlomo Magdassi , Michael Grouchko and Alexander Kamyshny; Copper Nanoparticles for Printed Electronics: Routes Towards Achieving Oxidation Stability; 2010

Copper nanoparticles

- Solution
  - Minimizing the exposure of the copper NPs to oxygen, by a protective layer at the surface of the particles of a second material
  - Materials groups:
    - Carbon-based materials (carbon and graphene)
    - Surfactants and polymers
    - Silica
    - Metal

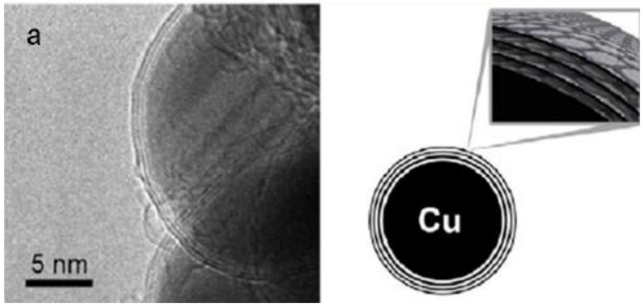
REF.: Shlomo Magdassi , Michael Grouchko and Alexander Kamyshny; Copper Nanoparticles for Printed Electronics: Routes Towards Achieving Oxidation Stability; 2010

Protective layer

- Carbon-based materials
  - $CuCO_3 \cdot Cu(OH)_2 \cdot xH_2O \xrightarrow{350^0 C} 2CuO + CO_2 + (x+1)H_2O$

    $C_6H_{12}O_6 \cdot H_2O \xrightarrow{350^0 C} 6C + 7H_2O$

    $CuO + C \xrightarrow{350^0 C} Cu + CO$
  - It can be realized on reducing flamea large scale
  - Synthesized by the technique
  - ~50 nm cooper NPs coated with ~3nm layer graphene
  - One step process



REF.: Shlomo Magdassi , Michael Grouchko and Alexander Kamyshny; Copper Nanoparticles for Printed Electronics: Routes Towards Achieving Oxidation Stability; 2010

Protective layer

- Surfactants and Polymers
  - Copper NPs with a dense layer of capping agents
  - Prevent aggregation and agglomeration in dispersions
  - Polymers as capping agents: poly(N-vinylpyrrolidone) (PVP)
  - Minimum thickness: ~1.6 nm → determines the electrical conductivity
  - Others: polypyrrole (PPY), polyethylene imine (PEI), Tetraethylenepentamine (TEPA)

REF.: Shlomo Magdassi , Michael Grouchko and Alexander Kamyshny; Copper Nanoparticles for Printed Electronics: Routes Towards Achieving Oxidation Stability; 2010

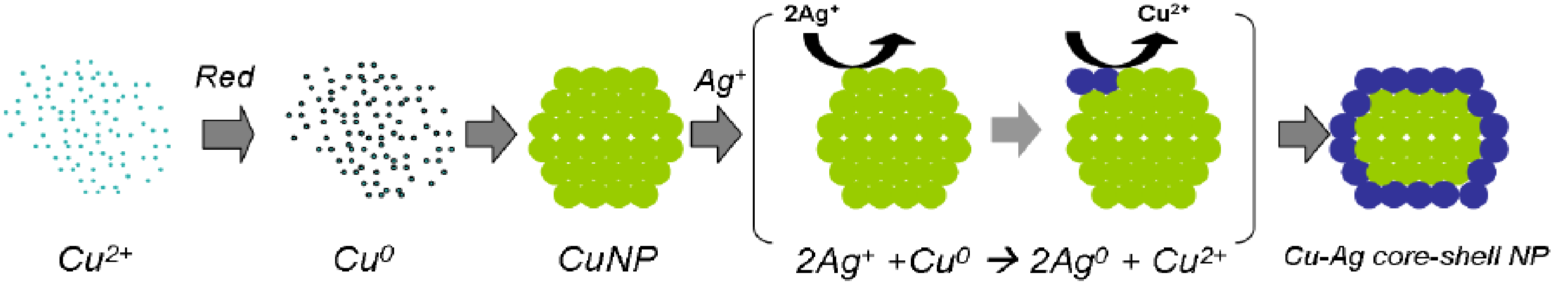
Protective layer

- Silica Coating
  - Inorganic protection layer
  - Thin layer of silica
  - The presence of silica, an insulating material with high melting point, is a major obstacle in obtaining a continuous conductive pattern

REF.: Shlomo Magdassi , Michael Grouchko and Alexander Kamyshny; Copper Nanoparticles for Printed Electronics: Routes Towards Achieving Oxidation Stability; 2010

Protective layer

- Metallic Coating
  - Bimetallic NPs → reduction of one metal over the nuclei of another
  - Formation of a thin metallic shell
  - It requires several steps
  - Size: 10 nm to 50 nm
  - Inkjet water-based formulation: 25 wt % Cu-Ag core-shell
  - After a sintering process: decrease of the resistance



REF.: Shlomo Magdassi , Michael Grouchko and Alexander Kamyshny; Copper Nanoparticles for Printed Electronics: Routes Towards Achieving Oxidation Stability; 2010

Preparation of copper nanoparticles

- The wet phase (polyol method)
- Thermal decomposition
- Chemical reduction
- Thermal plasma method

Preparation of copper nanoparticles

- The wet phase (polyol method)
  - Use of glycol-polyvinyl-pyrolidone (PVP) solution – protecting agent
  - Synthesis of noble metal
    - Can be produced in aqueous and non-aqueous solvents
    - Unique properties: electronic susceptibility and magnetic resonance relaxation
  - Preparation of the solution
    - PVP + solution (e.g. ethylene glycol) + solvent (e.g. $AgNO_3$)
  - Characterization (size, shape and metal presence)
    - Transmission electron microscopy – TEM (size and shape)
    - UV absorption spectroscopy techniques (size and shape)
    - Absorbance peak – presence of metal – height gives the metallic concentration in the medium (metal presence)

REF.: Pierre-Yves Silvert, Ronaldo Herrera-Urbinab and Kamar Tekaia-Elhsissena; Preparation of colloidal silver dispersions by the polyol process Part 2.— Mechanism of particle formation; 1997

Preparation of copper nanoparticles

- The wet phase (polyol method)
  - Results
    - Monodisperse colloids
    - 21 nm particles
    - Steps:
      - 1 – System unstable, heterogeneous distribution, small particles (10 nm)
      - 2 – Fast evolution, small particles quickly disappears, majority larger particles (~21 nm)
      - 3 – Monodisperse colloid stable with a mean size 21nm
  - Influence of PVP
    - Important role in the protection of the synthesized particles
    - In low concentration: not monodisperse colloid and evolution not regular
    - In hight concentration: monodisperse colloid

REF.: Pierre-Yves Silvert, Ronaldo Herrera-Urbinab and Kamar Tekaia-Elhsissena; Preparation of colloidal silver dispersions by the polyol process Part 2.— Mechanism of particle formation; 1997

Preparation of copper nanoparticles

- Chemical reduction
  - Relative large-scale
  - Chemical reduction of copper sulfate with sodium hypophosphite in ethylene glycol within the presence of PVP
  - Size between 30 and 65 nm by varying the reaction time, temperature and ratio of copper sulfate to the surfactant
  - Materials
    - Polyvinylpyrrolidone (PVP)
    - Sodium hypophosphite monohydrate ($NaH_2PO_2.H_2O$)
    - Copper sulfate pentahydrate ($CuSO_4.5H_2O$)
    - Ethylene glycol
    - Acetone
    - 2-(2-butoxyethoxy)ethanol

REF.: Youngil Lee, Jun-rak Choi, Kwi Jong Lee, Nathan E Stott and Donghoon Kim; Large-scale synthesis of copper nanoparticles by chemically controlled reduction for applications of inkjet-printed electronics; 2008

Preparation of copper nanoparticles

- Chemical reduction
  - Synthesis
    - PVP + Sodium hypophosphite + Ethylene glycol - stirring
    - Heated to 90°C at a rate of 5°C/min
    - + Copper sulfate pentahydrate (90°C) – stirring
    - Reduction – color green to henna – formation of copper NPs
    - Washed with deionized water – remove PVP excess
    - Dried under vacuum at 40°C for 2-3h
  - Ink preparation
    - 30% weight of copper
    - Dispersible copper NPs + 2-(2-butoxyethoxy)ethanol – mixed 15 min
    - Resulting NPs inks were pressed through 0,4 μm syringe filters to eliminate any large particles, aggregates and agglomerates

REF.: Youngil Lee, Jun-rak Choi, Kwi Jong Lee, Nathan E Stott and Donghoon Kim; Large-scale synthesis of copper nanoparticles by chemically controlled reduction for applications of inkjet-printed electronics; 2008

Preparation of copper nanoparticles

- Chemical reduction
  - Synthesis of copper NPs
    - 3 stages
      - Stage 1 – blue copper sulfate solution becomes colorless

$$2\underset{\text{Blue}}{[Cu(H_2O)_6]^{2+}} + 4H_2PO_2^- \rightarrow \underset{\text{Colorless}}{[Cu_2(H_2O)_4\cdot(H_2PO_2)_4]^0}$$

      - Stage 2 – reduction of copper (II) to copper (I)

$$\underset{\text{Colorless}}{[Cu_2(H_2O)_4\cdot(H_2PO_2)_4]^0} + H_2O \rightarrow \underset{\text{Green}}{[Cu_2(H_2O)_4\cdot(H_2PO_2)_3\cdot(H_2PO_3)]^{2-}} + 2H^+$$

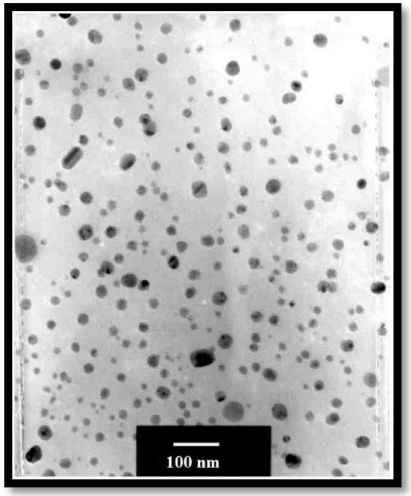
      - Stage 3

$$\underset{\text{Green}}{[Cu_2(H_2O)_4\cdot(H_2PO_2)_3\cdot(H_2PO_3)]^{2-}} + H_2O \rightarrow \underset{\text{Henna}}{2Cu^0} + 2H_2PO_2^- + 2H_2PO_3^- + 2H^+$$

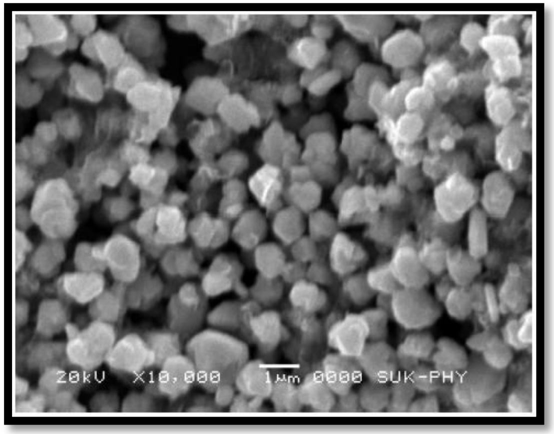
REF.: Youngil Lee, Jun-rak Choi, Kwi Jong Lee, Nathan E Stott and Donghoon Kim; Large-scale synthesis of copper nanoparticles by chemically controlled reduction for applications of inkjet-printed electronics; 2008

Analysis

- Evaluate the size and shape of the particle
  - Transmission electron microscopy – TEM
  - UV absorption spectroscopy techniques
  - Scanning electron microscope – SEM



TEM

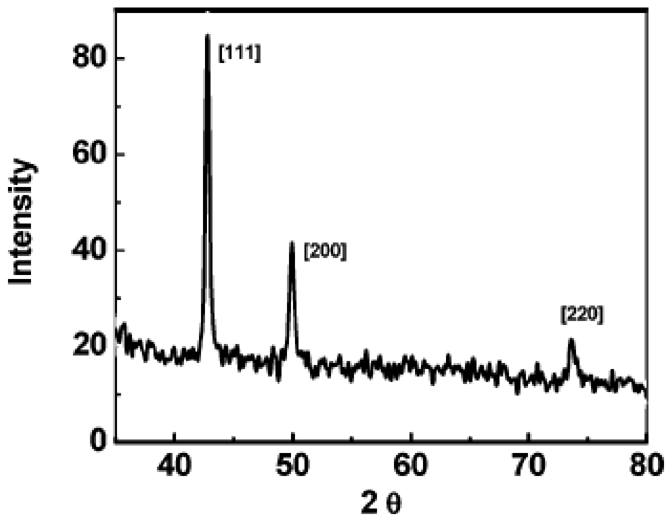


SEM

REF.: A. Sarkar, T. Mukherjee, and S. Kapoor; PVP-Stabilized Copper Nanoparticles: A Reusable Catalyst for "Click" Reaction between Terminal Alkynes and Azides in Nonaqueous Solvents; 2008

Analysis

- Metal presence
  - X-ray diffractogram



- Resistance
  - Sheet resistance – the four-point probe technique (Ω/□)

REF.: A. Sarkar, T. Mukherjee, and S. Kapoor; PVP-Stabilized Copper Nanoparticles: A Reusable Catalyst for "Click" Reaction between Terminal Alkynes and Azides in Nonaqueous Solvents; 2008

Steven K. Hau, Hin-Lap Yip, Kirsty Leong, Alex K.-Y. Jen; Spraycoating of silver nanoparticle electrodes for inverted polymer solar cells; 2009

PRINTING AND COATING TECHNOLOGIES

- Printing
  - It is used to describe a method by which a layer of ink is transferred from a stamp to a substrate by a reversing action.
  - Techniques:
    - Screen printing
    - Pad printing
    - Gravure printing
    - Flexographic printing
    - Offset printing
- Coating
  - It is used to describe a process by which a layer of ink is transferred to the substrate by essentially pouring, painting, spraying, casting or smearing it over the surface.
  - Techniques:
    - Spin coating
    - Doctor blading
    - Casting
    - Spray coating
    - Slot-die coating

REF.: Frederik C. Krebs; Fabrication and processing of polymer solar cells: A review of printing and coating technique; 2009

Printing and coating technologies

- Spin coating
  - Most reliable and reproducible deposition method
  - Produces smooth and uniform layers
  - It is not suitable for roll-to-roll fabrication
- Alternative deposition methods
  - Ink jet printing
  - Screen printing
  - Doctor blading
  - Spray coating
- It reduces production costs

REF.: Claudio Girotto, BarryP.Rand, JanGenoe, PaulHeremans; Exploring spray coating as a deposition technique for the fabrication of solution-processed solar cells; 2009

PRINTING AND COATING TECHNOLOGIES

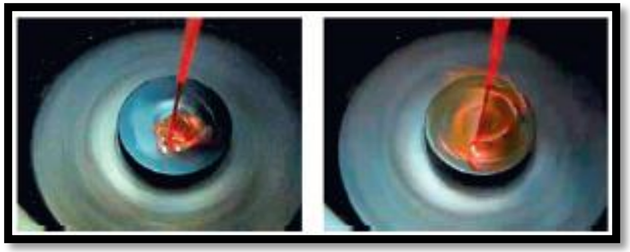
- Substrate
  - Glass
  - Silicon
  - Plastic
  - ITO (indium tin oxide) covered glass
- Substrate pre-cleaning
  - Detergent
  - De-ionized water
  - Acetone
  - Isopropanol

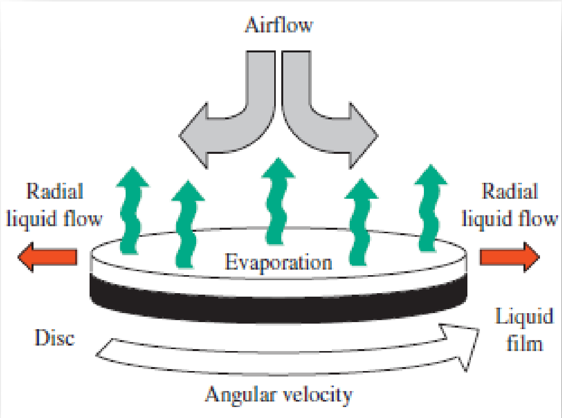
  - In a ultrasonic bath (~10 min)

REF.: Claudio Girotto, BarryP.Rand, JanGenoe, PaulHeremans; Exploring spray coating as a deposition technique for the fabrication of solution-processed solar cells; 2009

SPIN COATING

- Formation of very homogenous films
- Large area (Diameter max 30 cm)
- Requires a substrate spinning (rotational speed)
- Ejection of most of the applied liquid
- Requires that substrates are handled individually
- Important for the development of polymer solar cells
- Not roll-to-roll compatible
- Thin film





REF.: Frederik C. Krebs; Fabrication and processing of polymer solar cells: A review of printing and coating technique; 2009

Spin coating

- The film thickness, d, can be expressed by:

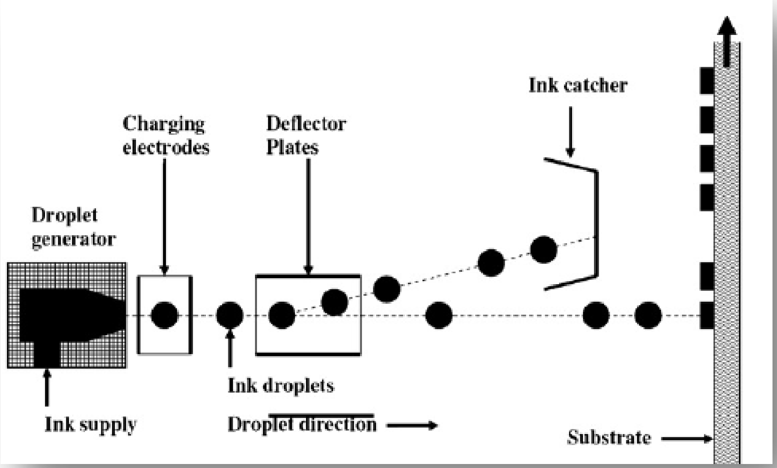
$$d = k\ \omega^\alpha$$

  - ω is the angular velocity
  - k contains many parameters such as the initial viscosity of the solution (empirical constant)
  - α has a value of around -0.5 (empirical constant)

REF.: Frederik C. Krebs; Fabrication and processing of polymer solar cells: A review of printing and coating technique; 2009

Ink jet printing

- Quite high resolution
- Limitation in printing speed
- It requires a ink with low viscosity (4-30 cP) and high volatility
- It requires to be electrostatically charged



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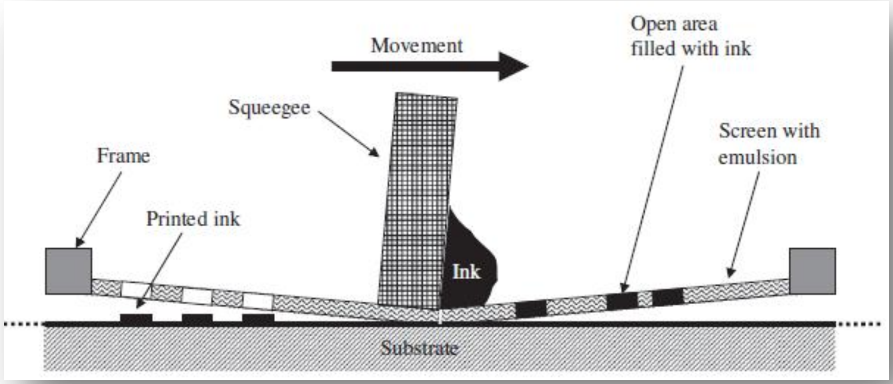
SCREEN PRINTING

- No loss of coating solution
- It requires a high viscosity and a low volatility
- Screen of woven materials (synthetic fiber or steel mesh)
- It can be adapted to a roll-to-roll process



REF.: Frederik C. Krebs; Fabrication and processing of polymer solar cells: A review of printing and coating technique; 2009

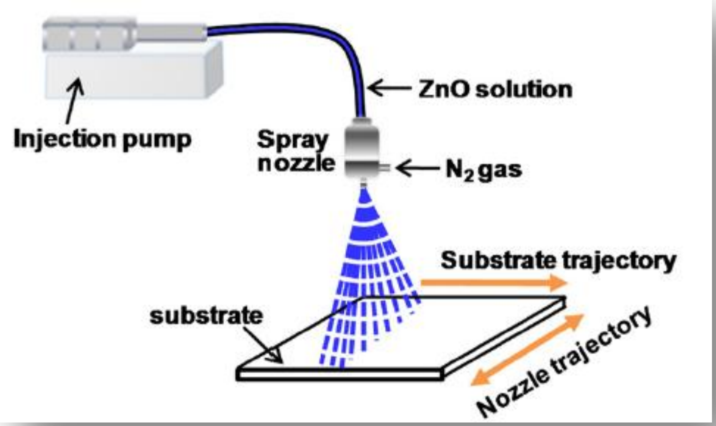
DOCTOR BLADING

- Films with a well-defined thickness
- Small lost of coating solution (~5%)
- The wet film formation is slow
- If the material has propensity to aggregate or crystallize at high concentration, this often happens during doctor blading
- Spin coating is preferred

REF.: Frederik C. Krebs; Fabrication and processing of polymer solar cells: A review of printing and coating technique; 2009

Spray coating

- It is a well established technique in graphic art, industrial and painting
- The ink is atomized at the nozzle by pressure or ultrasounds
- The ink is directed to the substrate by a gas flow
- It can cover relatively large area
- Fast drying time



REF.: Claudio Girotto, BarryP.Rand, JanGenoe, PaulHeremans; Exploring spray coating as a deposition technique for the fabrication of solution-processed solar cells; 2009

Spray coating

- Spray coating variables
  - Viscosity
  - Spray pressure
  - The distance between the nozzle and the sample
  - Spray time
  - Number of spray coats

- This variables can affect the formation of the final coating of the film

REF.: Steven K. Hau, Hin-Lap Yip, Kirsty Leong, Alex K.-Y. Jen; Spraycoating of silver nanoparticle electrodes for inverted polymer solar cells; 2009

Spray coating

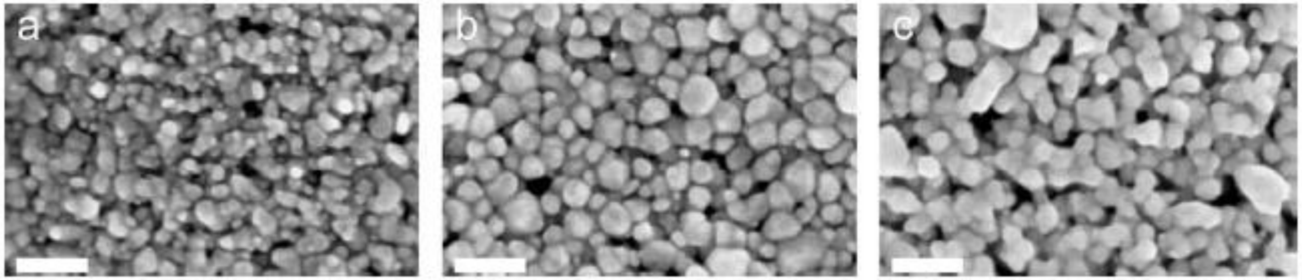
- Simple pass technique
  - Single and uniform wet layer
  - The airbrush moves in parallel lines
  - Flow rate of ~0,8 ml/min
  - Distance ~3 cm
  - Thin layer
- Multiple pass technique
  - Superposition of several ultra-thin sublayers
  - Several passes over the sample are required
  - Flow rate minimum: ~20μl/min
  - Distance 10 cm

REF.: Claudio Girotto, BarryP.Rand, JanGenoe, PaulHeremans; Exploring spray coating as a deposition technique for the fabrication of solution-processed solar cells; 2009

Spray coating

- Annealing treatments
  - Temperature in range of 130-150°C
  - Time intervals in range of 5-10 min
  - N_2 glovebox

- The increase of the sintering temperature is concomitant with an increase of agglomerate size
  - 100°C 140°C 180°C



REF.: Claudio Girotto, Barry P. Rand, Soeren Steudel, Jan Genoe, Paul Heremans; Nanoparticle-based, spray-coated silver top contacts for efficient polymer solar cells; 2009

Polymer nanoparticles

- Highly efficient organic solar cells have been made from thin layers containing a blend of an electron-donating and an electron-accepting polymer
- Resulting morphology strongly depends on various parameters:
  - The individual solubility of the polymers in the solvent used
  - The interaction with the substrate surface
  - The layer tickness
  - The method of deposition, drying and annealing

REF.: THOMAS KIETZKE, DIETER NEHER, KATHARINA LANDFESTER, RIVELINO MONTENEGRO, ROLAND GÜNTNER AND ULLRICH SCHERF; Novel approaches to polymer blends based on polymer nanoparticles; 2003

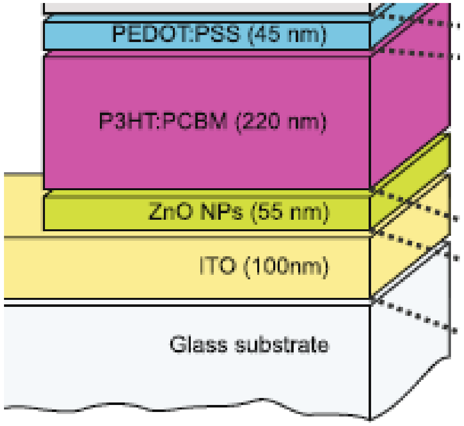
Polymer nanoparticles

- Experimental
  - The polymer is dissolved in a suitable solvent (not miscible with water)
  - Then it is added to an aqueous solution containing an appropriate surfactant
  - A high shear is applied to obtain a stable miniemulsion containing small droplets of polymer solution
  - Evaporation of the solvent
  - Result: a stable dispersion of solid polymer nanoparticles in water

REF.: THOMAS KIETZKE, DIETER NEHER, KATHARINA LANDFESTER, RIVELINO MONTENEGRO, ROLAND GÜNTNER AND ULLRICH SCHERF; Novel approaches to polymer blends based on polymer nanoparticles; 2003

SOLAR CELLS

- Polymer solar cells as alternative energy source
- Limited by the short operation life time
- Difficult to scale to large production
- Layers:
  - Poly(3-hexyl thiophene) – P3HT
  - (6,6)-phenyl C_{61}-butyric acid methyl ester – PCBM
  - Poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) – PEDOT:PSS
  - ZnO NPs
  - Indium-tin-oxide (ITO)



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Solar cells

- Organic photovoltaic (OPVs) – generating electricity directly from sunlight
- Fabricated from mixture of donor and acceptor materials dissolved in organic solvents
- Optimum size: 20-50 nm
- First OPV:
  - Nanoparticles of 50-250 nm
  - Poly(9,9-dioctyfluorene-co-benzothiadiazole) – F8BT
  - Poly(9,9-dioctyfluorene-co-N,N-bis(4-butylphenyl)-N,Ndiphenyl-1,4-phenylenediamine) – PFB
  - Power conversion efficiency (PCE) was extremely low
  - Use of chloroform (after evaporate)
  - Stable for 3 months

REF.: Andrew Stapleton, Bem Vaughan, Bofei Xue, Elisa Sesa, Kerry Burke, Xiaojing Zhou, Glenn Bryant, Oliver Werzer, Andrew Nelson, A. L. David Kilcoyne, Lars Thomsen, Erica Wanless, Warwick Belcher, Paul Dastoor; A multilayered approach to polyfluorene water-based organic photovoltaics; 2012

SOLAR CELLS

- Experimental
  - F8BT e PFB ratio 1:1 by weight
  - Dissolved in chloroform
  - Introduced to an aqueous sodium dodecylsuphane (SDS)
  - Stirring at 1200 rpm for 1 hour – macroemulsion
  - Sonicated 2 min at 60% amplitude with micro tip
  - Heated at 60°C for 3 hours
  - Stirring at 120 rpm – evaporate off chloroform

REF.: Andrew Stapleton, Bem Vaughan, Bofei Xue, Elisa Sesa, Kerry Burke, Xiaojing Zhou, Glenn Bryant, Oliver Werzer, Andrew Nelson, A. L. David Kilcoyne, Lars Thomsen, Erica Wanless, Warwick Belcher, Paul Dastoor; A multilayered approach to polyfluorene water-based organic photovoltaics; 2012

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- Thue T. Larsen-Olsen, Birgitta Andreasen,Thomas R. Andersen, Arvid P. L. Böttiger, Eva Bundgaard, Kion Norrman, Jens W. Andreasen, Mikkel Jørgensen, Frederik C. Krebs; Simultaneous multilayer formation of the polymer solar cell stack using roll-to-roll double slot-die coating from water; 2012
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Thank you!