Sintesi di nanostrutture cristalline inorganiche con metodi colloidali e di chimica umida

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Ambito di ricerca

Green chemistry & wet chemistry

Green chemistry is based on "the utilization of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical products"
Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.

Anastas, P. T.; Warner, J. C. *Green Chemistry Theory and Practice, Paperback Ed.*; Oxford University Press: New York, 2000

Ambito di ricerca

Linee guida sintetiche

- low operative temperatures (< 150°C) and pressures
- resort to safe, common and cheap precursors chemicals and solvents
- replacement of solvents with water or other less hazardous solvents
- resort to not critical raw materials (CRM)
- easy processing (typically one batch/one step)
- economic and environmental sustainable processes
- simple separation/recovery of the products
- wet chemistry, solution chemistry
- high yield, high throughput
- high selectivity in terms of target stoichiometry and crystalline phases
- reduction of waste and of by-products, easy recyling

S. Diodati, P. Dolcet, M. Casarin and S. Gross*
Pursuing the Crystallization of Mono- and Polymetallic Nanosized Crystalline Inorganic Compounds by Low-Temperature Wet-Chemistry and Colloidal Routes
Chem. Rev., 2015, *115*, 11449–11502

Ambito di ricerca

Chimica umida e chimica colloidale

- Sintesi idrotermale subcritica
- Miniemulsione
- Nucleazione e crescita da soluzione
- Combinazione delle precedenti (miniemulsione/idrotermale)

Argomenti correlati:

- Studi di cristallizzazione *in situ*, risolti in temperatura e in tempo
- Strategie di funzionalizzazione di ossidi e solfuri

Ambito di ricerca

Open issues:

- Structure and structural evolution at different lenght scale as a function of T and atmosphere
- Understanding the material also at atomic level (for instance to understand OSC et al.)

lenght scale

Atomic, local order (< 1 nm)

Nanosize range order (~ 10 nm)

Long range order (>10 nm)

Macroscopic structure

XAS (bulk)

- ❑ Structural information (bond lenghts, coordination number & geometry, symmetry)
- ❑ Chemical information (neighbouring atoms, oxidation states)
- ❑ Atomic intermixing: M-O-M' bonds

XPS (only surface)

- ❑ Chemical information (neighbouring atoms, oxidation states)
- ❑ Atomic intermixing

TEM/SAED/SAXS

- ❑ Structural information

XRD

- ❑ Structural information
- ❑ Phase stability
- ❑ Temperature dependence

Raman spectroscopy

- ❑ Structural information
- ❑ Symmetry

SEM

- ❑ Morphology

Perché condizioni idrotermali

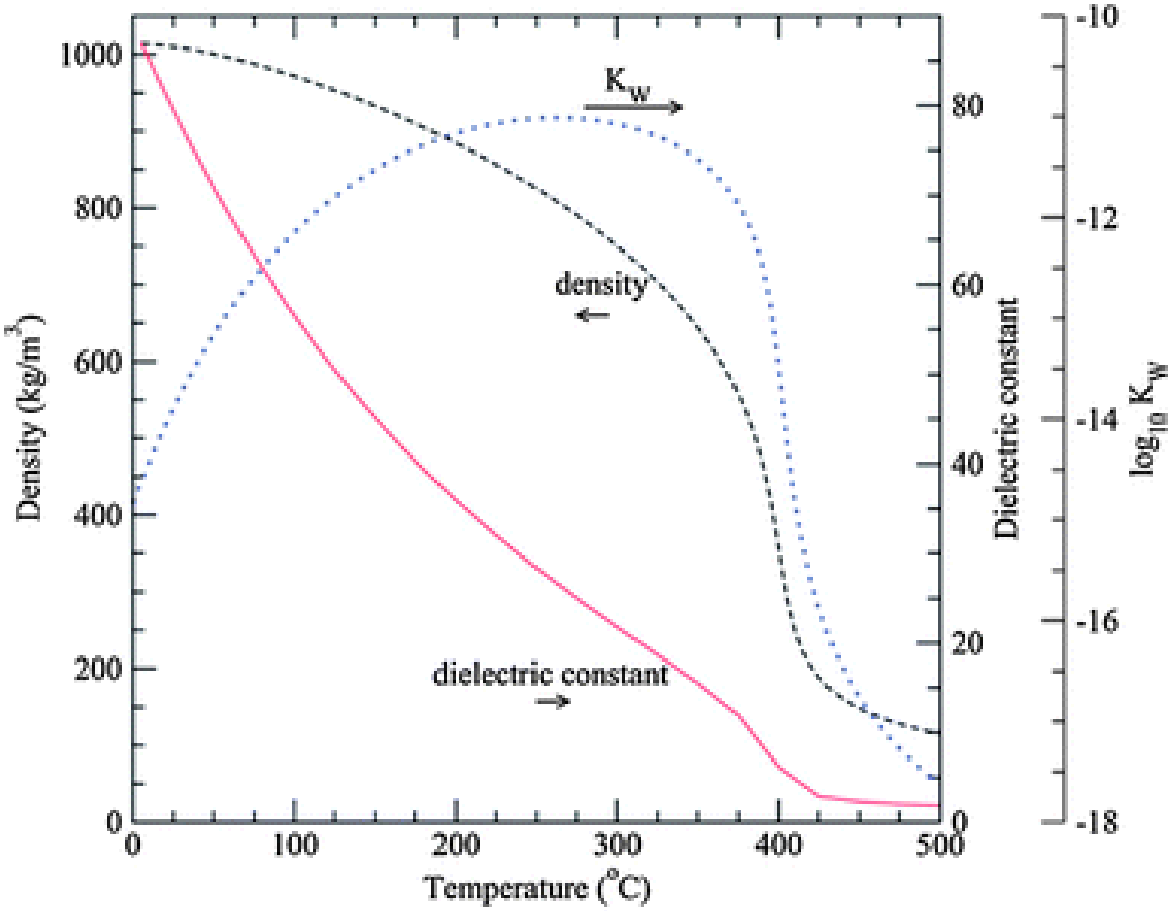
Definition of hydrothermal reaction

Heterogeneous chemical reaction in aqueous media above room temperature (normally above 100 °C) and at a pressure greater than 1 atm

- supercritical
- subcritical

Mari-Ann Einarsrud and Tor Grande, Chem. Soc. Rev., 2014, 43, 2187-2199
A. Rabenau, Angew. Chem., Int. Ed. Engl., 1985, 24, 1026–1040

Perché condizioni idrotermali



M.A. Einarsrud , T. Grande
Chem. Soc. Rev., 2014, 43, 2187-2199

Fig. 1 Density, dielectric constant and ionic product, K_W, of pure water at 30 MPa as a function of temperature.

Sistemi realizzati (idrotermale)

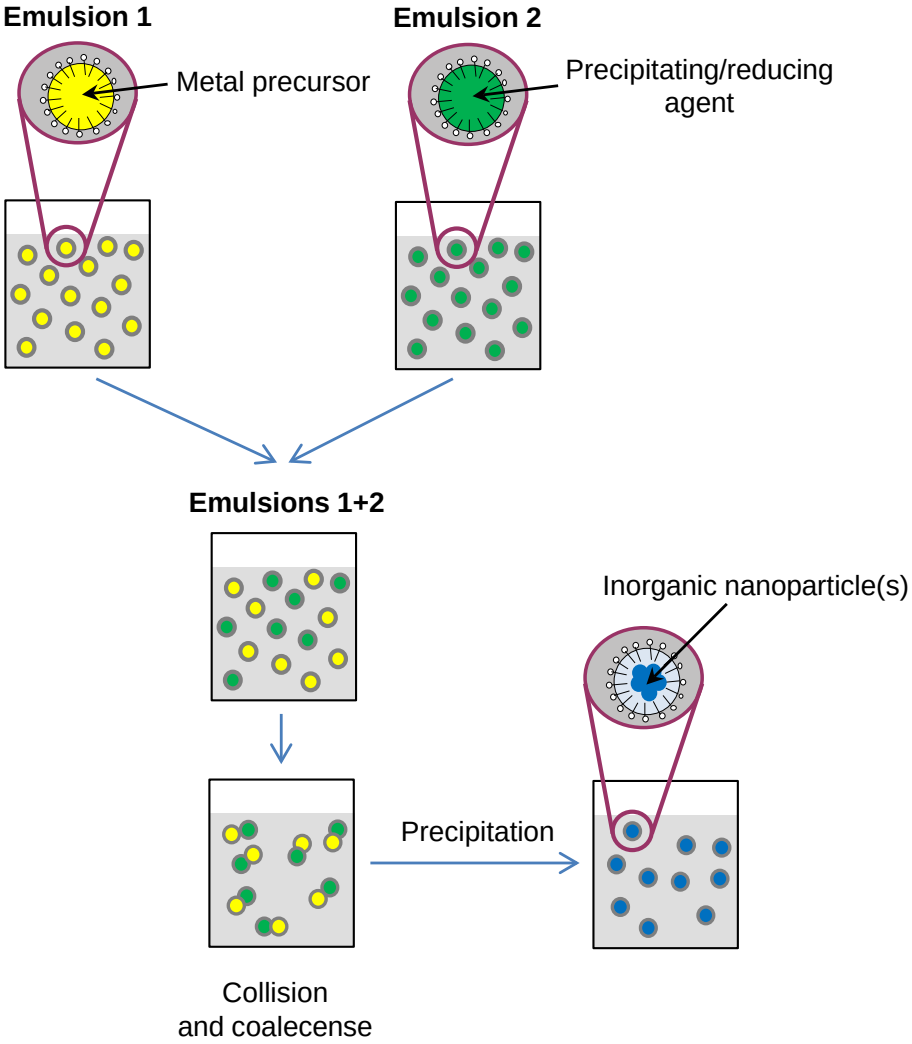
Synthesis of nanocrystalline $CoFe_2O_4$, $MnFe_2O_4$, $NiFe_2O_4$, $ZnFe_2O_4$, $ZnMn_2O_4$, $ZnMnO_3$, $CuMnO_2$, ZnO, ZnS, Ag_2S, CuO, CuS

combining coprecipitation of oxalates and hydrothermal treatment

- At very low temperature (100-150°C)
- Using water as solvent: greenest solvent!
- Very easy and reproducible procedure
- Very common, cheap and safe precursors
- Effective control over the products stoichiometry
- Compounds obtained in highly crysyalline form
- Small crystallite size (15-40 nm, depending on conditions)
- High yields (60-90%)
- Very pure compounds (clean decomposition of oxalates)
- Magnetic properties assessed

S. Diodati, L. Pandolfo, S. Gialanella, A. Caneschi and S. Gross
Green and low temperature synthesis of nanocrystalline transition metal ferrites by simple wet chemistry routes
Nano Res., 2014, 7, 1027-1042
A. Minelli, P. Dolcet, S. Diodati, A. Caneschi and S. Gross et al. submitted

Miniemulsione: chimica in nanoreattore



Two mini/microemulsion approach

Miniemulsion

- heterogeneous systems
- dispersing phase: direct/inverse ME
- reaction confinement in the droplet

Size and size distribution control

Munoz-Espi R.; Weiss C.K.; Landfester K. Current Opin. Coll. Interface Sci. 2012 (7) 212–224

R. Muñoz-Espí, Y. Mastai, S. Gross, K. Landfester CrystEngComm 15 (2013) 2175-2191

Sistemi realizzati (miniemulsione)

Synthesis of nanocrystalline ZnO, ZnS, CuO, CuS, Ag_2S, CaF_2, $Ca(OH)_2$, $Mg(OH)_2$, (all pure or doped with Ln^{3+}), Au/TiO_2

- Crystallisation at room temperature
- Very easy and reproducible procedure
- Very common, cheap and safe precursors
- Effective control over the products stoichiometry
- Nanoreactor concept works

R. Muñoz-Espí, Y. Mastai, S. Gross and K. Landfester, *Colloidal systems for crystallization processes from liquid phase* (Invited highlight), CrystEngComm, 2013, 15, 2175-2191

N. A. Heutz, P. Dolcet, S. Gross et al., *Inorganic chemistry in a nanoreactor: Au/TiO2 nanocomposites by photolysis of a single-source precursor in miniemulsion,* Nanoscale, 2013, 5, 10534-10541

P. Dolcet, S. Diodati, M. Casarin and S. Gross, *Very low temperature wet-chemistry colloidal routes for mono- and polymetallic nanosized crystalline inorganic compounds*, Journal of Sol-Gel Science and Technology, 2015, *73*, 591-604

P. Dolcet, S. Gross et al. *Room temperature crystallization of highly luminescent lanthanide-doped CaF_2 in nanosized droplets: first example of the synthesis of metal halogenide in miniemulsion with effective doping and size control* RSC Advances, 2015, *5*, 16302-16310

P. Dolcet, S. Gross et al., *An Effective Two-Emulsion Approach to the Synthesis of Doped ZnS Crystalline Nanostructures* European Journal of Inorganic Chemistry, 2015, 2015, *4*, 706–714

P. Dolcet, S. Gross et al. , *Simple, Common but Functional: Biocompatible and Luminescent Rare-Earth Doped Magnesium and Calcium Hydroxides from Miniemulsion*, J. Mater. Chem. B, 2014, *2*, 6639-6651

Combinazione di condizioni non standard: miniemulsione e idrotermale

Obtain complex inorganic nanostructures in miniemulsion under non-standard conditions: better dispersibility/processability and higher crystallinity

Complex Inorganic Systems in Confined Droplets: Miniemulsionsunder Hydrothermal Conditions

Ph.D. Project A. Antonello
Max Planck Institut Polymerforschung
Supervisors: K. Landfester, S. Gross

Hydrothermal / solvothermal route ⇒ non-standard conditions

+

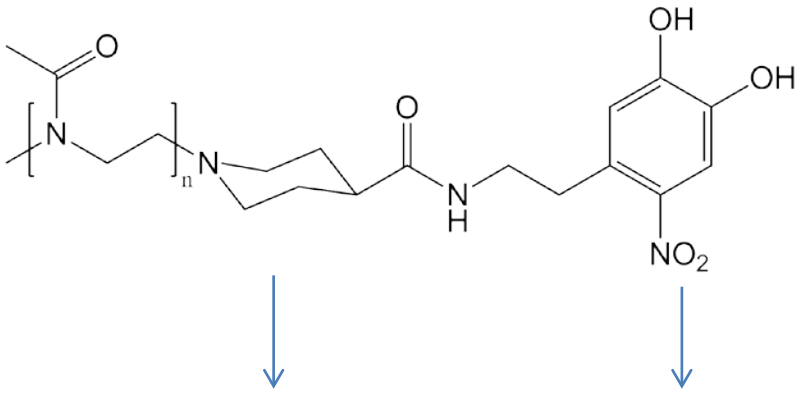
Miniemulsion synthesis ⇒ confinement

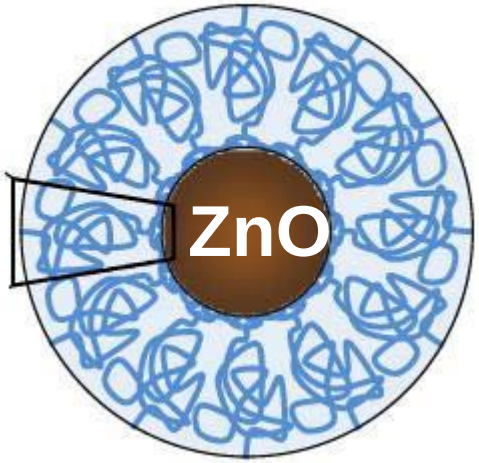
Addressed systems

- Single metal oxides (ZnO, CeO_2, MoO_3, WO_3, Fe_3O_4)
- Mixed oxides ⇒ ferrites (MFe_2O_4 M= Mn, Fe, Co, Ni, Cu, Zn)

Properties:
- ✓ Optical
- ✓ Thermal
- ✓ Electronic
- ✓ Mechanical
- ✓ Magnetic

Funzionalizzazione di ossidi





Hydrophilic moiety

Grafting moiety

G. Morgese, V. Causin, M. Maggini, S. Corrà, S. Gross and E. M. Benetti
Ultra-stable Suspensions of Polyoxazoline-Functionalized ZnO Single Nanocrystals
Chem. Mater., 2015, 27, 2957-2964

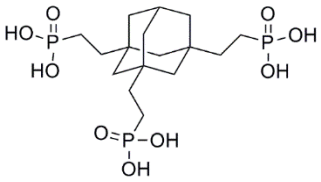
F. Klitsche, J. Ramcke, J. Migenda, A. Hensel, T. Vossmeyer, H. Weller, S. Gross and W. Maison
Synthesis of tripodal catecholates and their immobilization on zinc oxide nanoparticles
Beilstein J. Org. Chem., 2015, *11*, 678–686

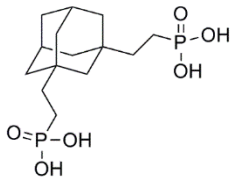
Funzionalizzazione di solfuri

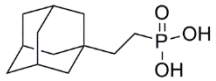
Nicola Dengo POSTER P37
Tesi Magistrale in Chimica
Università di Padova, 2015

Collaborazione con:
Dr. A. Vittadini, M. Natile, IENI-CNR
Prof. W. Maison and F. Klitsche
Università Hamburg

Sviluppo di strategie di funzionalizzazione







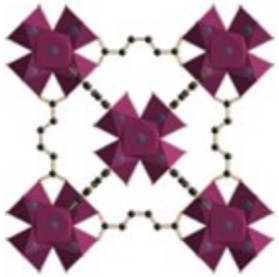
Implementazione di un modello

Analisi e modelling superficie

Scelta e sintesi del legante

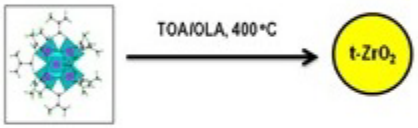
- Stable dispersion
- Not cytoxic, biocompatible
- Molecular recognition

Attività 2: materiali ibridi

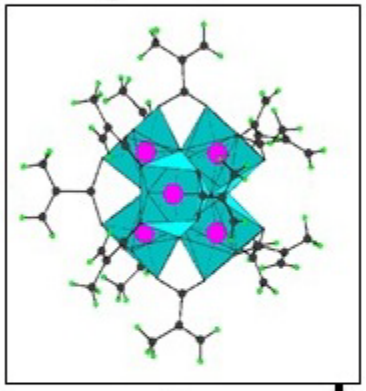


building blocks for MOF

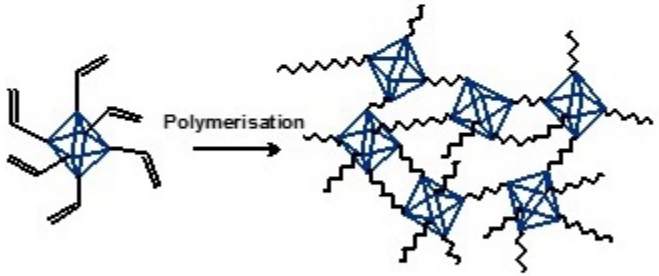
adduct with POM for enhanced functional properties (magnetic, catalytic, optical)



molecular precursor for the nucleation of oxide colloids



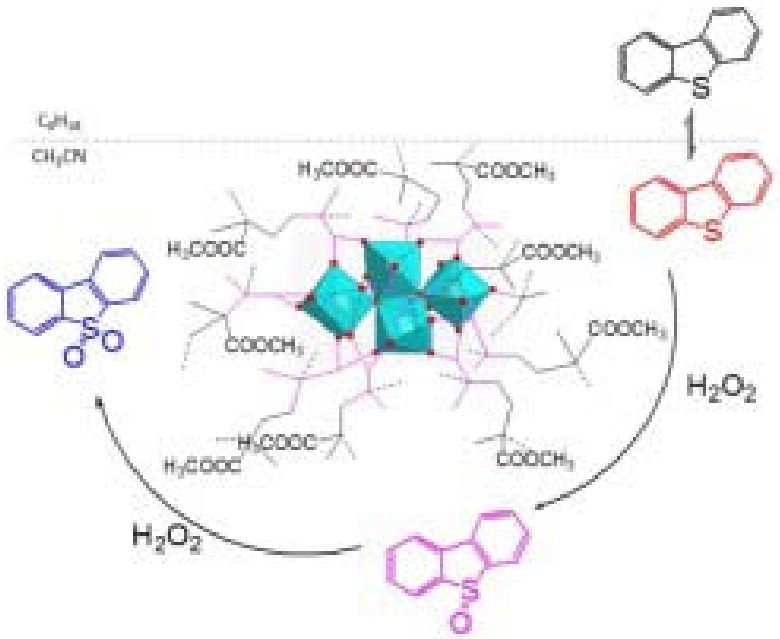
building blocks for I/O hybrids



catalysis in oxidation reactions

exploration of early TM chemistry

Materiali ibridi come catalizzatori



M. Vigolo, S. Borsacchi, A. Sorarù, M. Geppi, B. Smarsly, P. Dolcet, S. Rizzato, M. Carraro and S. Gross, *Engineering of oxoclusters-reinforced polymeric materials with application as heterogeneous oxydesulfurization catalysts*
Appl. Cat. B, 2016, *182*, 636-644

F. Faccioli, D. Pedron, A. Sorarù, M. Carraro and S. Gross, *Hydrolytic Stability and Hydrogen Peroxide Activation of Zirconium-Based Oxoclusters*, Eur. J. Inorg. Chem., 2015, *2*, 210-225

C. Benedetti, K. Landfester, S. Gross et al. submitted (cooperazione Max Planck, Mainz, DE)

Gruppo di ricerca

- Silvia Gross, Primo Ricercatore CNR
- Paolo Dolcet, Assegnista UniPd, Associato IENI-CNR
- Nicola Dengo, Borsista CNR
- Cesare Benedetti, dottorando in co-supervisione con Max-Planck Mainz, Germania
- Alice Antonello, dottoranda in co-supervisione con Max-Planck Mainz, Germania
- Jessica Munaro, laureanda UniPd
- Serena Busatto, laureanda UniPd
- Martina Marchioro, laureanda UniPd
- Flavio Massignan, laureando UniPd
- Tobia Cavalli, laureando UniPd
- Massimiliano Prior, laureando UniPd
- Federico Spolaore, laureando UniPd

Strumentazione
(in rosso: condivisa)

- 2 laboratori attrezzati per sintesi inorganica e in linea di Schlenk
- XRD, Bruker D8 Advance diffractometer
- XPS, Perkin, Elmer PHI 5600ci Spectrometer
- UV-Vis, Cary 5E Spectrophotometer with diffuse reflectance accessory
- FT- IR, Nicolet Nexus with ATR accessory
- Dynamic contact angle (T fino a 115°C)
- Micro-Raman ThermoFisher (laser 780, 532 nm), con mappature
- SEM (Zeiss Supra) equipped with EDX
- Mulino a palle Retsch MM200
- Durometro
- Spray-coater
- Dip-coater
- Turbidimetro
- Sonicatore per miniemulsione
- Forni e muffole (fino a 1300°C)
- Forno a microonde
- Strumentazione per sintesi idrotermale (10 reattori)
- Lampade UV a 100 W e 400 W per polimerizzazione fotoattivate

Collaborazioni

- Dr. Andrea Vittadini, Dr. Marta Natile, Dr. Luca Nodari, Dr. Daniel Forrer, Dr. A. Venzo, IENI-CNR
- Prof. Mauro Carraro, Prof. Paolo Pastore, Dr. D. Badocco, Prof. M. Casarin, Dip. Scienze Chimiche
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- Prof. F. Nestola, Dr. F. Zorzi Dipartimento di Geoscienze, Università degli Studi di Padova, Italy
- Prof. A. Lorenzetti, Prof. Michele Modesti, Prof. Al. Martucci, Dipartimento Ing. Industriale, UniPd