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Crystal Growth of Coordination Polymers by Gel Diffusion.

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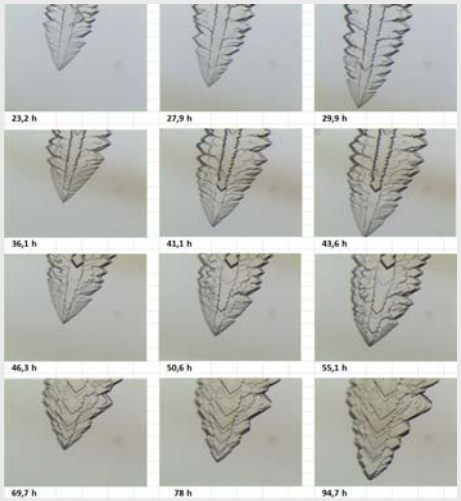
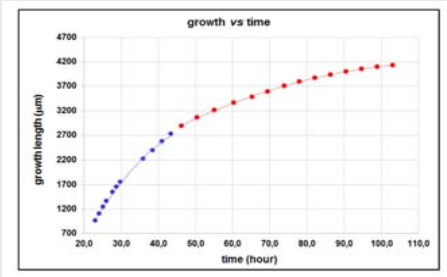
INTRODUCTION

Crystal growth in gels of coordination networks has been investigated to obtain proper protocols for reproducible synthetic procedures but also to develop gel technique as general method to obtain noteworthy effects on the physical properties and the functional performance of this materials opening up new possibilities for their characterization and their technological applications

RESULT 1: Kinetic Studies



By using gel technique we have performed a nucleation/growth kinetic study on the 1D polymeric $[Cd(bpp)_3Cl_2]\cdot 2H_2O$. The product was crystallized by layering, in optical, a water solution of the metal salt on a gelled aqueous solution of the ligand. The nucleation took place at the gel-sol interface and then the crystal has grown quickly and continuously in the gel up to several centimeters in length.
Thanks to the straightforward configuration of the growing system, we decided to follow the growth process by in-situ optical microscopy in order to determine the growth rate as function of the time and thus get some information on the kinetic behavior of the system.



An inverted kinetic roughening transition accomplished by a change in the growth mechanism reveled by the variation of the growth rate throughout the growth process
The initial portion of the curve (L vs t) is parabolic that is characteristic of a one dimensional diffusion control process. Instead, at the very late stage of growth, the interpolating function a surface-controlled mechanism.

RESULT 2: Gel Inclusion

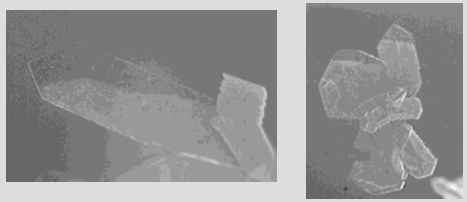
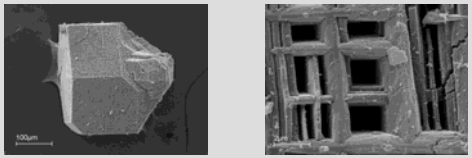


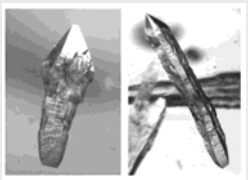
Figure. Agar gel grown crystals of the one dimensional coordination polymer $[Cd(bpp)_3Cl_2]\cdot 2H_2O$. The crystals appear cloudy and opaque to the inclusion of the gel matrix during growth. The mechanism of gel-incorporation is not entirely clear but the gel technique seems to be a promising methods to prepare single crystals composite systems and crystalline materials having a porous structure with a large internal surface area.[2, 3]

RESULT 3: Crystal Stabilization

The flexible porous 3D network $[Cu(bpy)_2(SO_3CF_3)_2]\cdot$*solvent* (bpy =4,4'-bipyridine),[4], crystallized in solution in form of small dark blue crystals that dehydrate quickly and lose part of their crystallinity upon removal from the mother liquor. In order to stabilize the samples, we carried out a series of crystallization trials by using a polysiloxane gel (TMS, tetramethoxysilane) as growth media. The really enhanced stability of these crystals, that show a characteristic micropattern reproducing the overall array of the crystal structure characterized by a channel system, has enabled an accurate determination of the dynamic behavior of the system during the desolvation process.



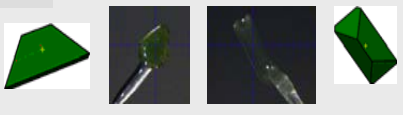
Crystals of porous diamantoid 3D network $[Cu(bpp)_2Cl_2]\cdot H_2O$ grown at the solution-gel interface. The upper part of the crystals, grown in solution, retains its pyramidal habit unaltered, while the bottom part, grown in gel, appeared clearly deformed with an elongated shape.



RESULT 4: Crystal morphology

On this topic, our research has provided us with some important results:
- as already reported in literature for other kind of compounds, morphological and habit evolution has been achieved essentially by changing the gel concentration. Increasing the gel density, the crystal morphology changes from specific, well formed, polyhedral habits, into deformed ones up to assume dendritic forms.
- differently from what previously observed for other kind of compounds (inorganic salts and small organic molecules), this behaviour has found to be independent of the type of gelling agent but dependent from the type of metal-ligand system.

We used gel technique as general method to produce controlled modifications of the crystal habit.



REFERENCES

(1) Garcia-Ruiz, J. M.; Moreno, A. *J. Cryst. Growth* **1997**, *178* (3), 393–401.
(2) (2) Li, H.; Estroff, L. A. *CrystEngComm*. **2007**, p 1153.
(3) Li, H.; Fujiki, Y.; Sada, K.; Estroff, L. A. *CrystEngComm*. **2011**, p 1060.
(4) Carlucci, L.; Ciani, G.; Garcia-Ruiz, J. M.; Moret, M.; Proserpio, D. M.; Rizzato, S. *Cryst. Growth Des.* **2009**, *9* (12), 5024–5034.

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