Photostable Single $KTiOPO_4$ Nanocrystals for Second-Harmonic Generation Microscopy

L. Le Xuan, C. Zhou, A. Slablab, D. Chauvat, N. Sandeau, S. Brasselet , J.-F. Roch
C. Tard*, S. Perruchas*, T. Gacoin*, P. Villeval**

Laboratoire de Photonique Quantique et Moléculaire, ENS Cachan, UMR CNRS 8537,

61, av. du Président Wilson, 94235 Cachan Cedex, France

**Laboratoire de Physique de la Matière Condensée, Ecole Polytechnique, UMR CNRS 7643,*
91128 Palaiseau Cedex, France
***Cristal Laser S.A, 32, rue Robert Schumann, F-54850 Messein, France*
Correspondent email: xuan-loc.le@m4x.org

Abstract

The finding of nonlinear nanometric-sized probes is of key importance for the development of nonlinear microscopy in nanosciences and biology. We isolate nonlinear $KTiOPO_4$ nanocrystals with remarkable photostability in second-harmonic generation under femtosecond infrared laser light excitation. Their size distribution is determined using dynamic light scattering and atomic force microscopy. With both polarization analysis and defocused imaging of the emitted second-harmonic field, we also extract the Euler angles of the crystalline axes of a single nanocrystal. These sub-wavelength particles can find application as near-field vectorial probes.

Keywords: nanocrystal, second harmonic generation, nonlinear microscopy

1 INTRODUCTION

The recent development of non-linear second-harmonic generation (SHG) microscopy has lead to the study of single nanoobjects like ZnO [1], GaAs [2], and CMONS [3]. Optical materials such as $KTiOPO_4$ (KTP) have been optimized for growing large efficient non-linear crystals with high damage threshold, and are widely used as frequency doublers or converters in laser systems. Here we isolate single KTP nanocrystals, and determine their complete properties in SHG microscopy.

2 SAMPLE PREPARATION AND MEASUREMENT

We obtain KTP nanocrystals by size-selection from a powder of KTP, which remains at the end of the flux-growth process for large crystal. For that selection, the powder is diluted in isopropanol and mixed with a polymer (polyvynilpyrolidone, PVP). The solution is then centrifuged resulting in a colloidal solution which contains dispersed and size-selected KTP nanoparticles. Dynamic light scattering (DLS) analysis of these solutions show size distributions with a mean size ranging from 150 nm to a few tens of nanometers depending on centrifugation time and speed (Figure 1).

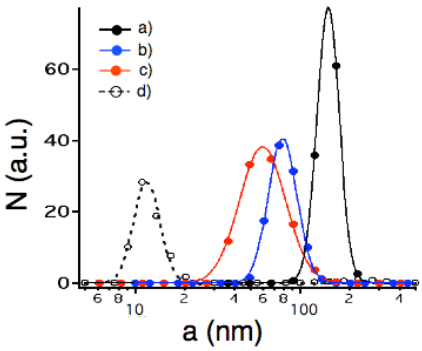

Figure 1. DLS spectra measured after successive centrifuged solutions. Mean size of (a) 150 nm, (b) 80 nm, (c) 60 nm are obtained. (d) is close to the detection sensitivity, the particle sizes being in fact (30±10) nm (cf. Figure 4).

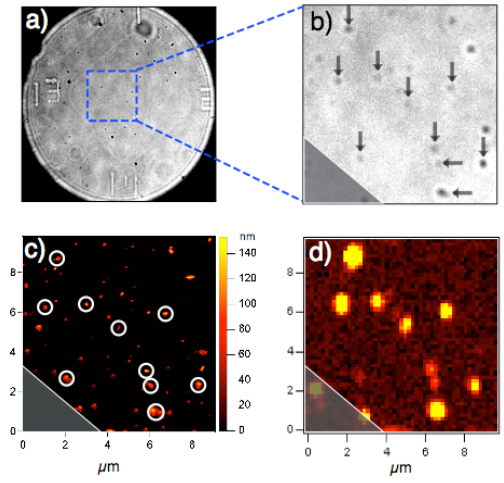

Figure 2. Observations of nanoparticles by different methods. a) Overview in white-light microscopy, b) 10×10 μm^2 zoom of a), c) corresponding AFM image, with circles pinpointing the SHG emitters, and d) corresponding SHG raster scan image.

The sample is then prepared so that a single nanoparticle can be unambiguously isolated. A chosen colloidal solution is spin-coated on a plasma-cleaned glass coverslip, which results in a uniform 100-nm thin polymer coating embedding the nanocrystals. A transmission electron microscope copper grid with 25 × 25 μm^2 empty squared holes is deposited onto the polymer film, and the sample is etched for 15 minutes under oxygen plasma. The polymer is thus removed from the empty squares, leaving the KTP nanocrystals uncovered on the glass surface. We measure their height with an atomic force microscope (AFM). An SHG image which reveals nonlinear nano-emitters is obtained using a inverted microscope with high numerical aperture objective (x100, NA =1.4) and femtosecond pulse illumination (100 fs, 987 nm, 1-15 mW). Nearly all these emitters can be unambiguously found in the AFM image (Figure 2). Some objects revealed in the AFM image do not correspond to an SHG emission spot. We attribute them to a polymer residue, or a KTP polycrystalline nanoparticle.

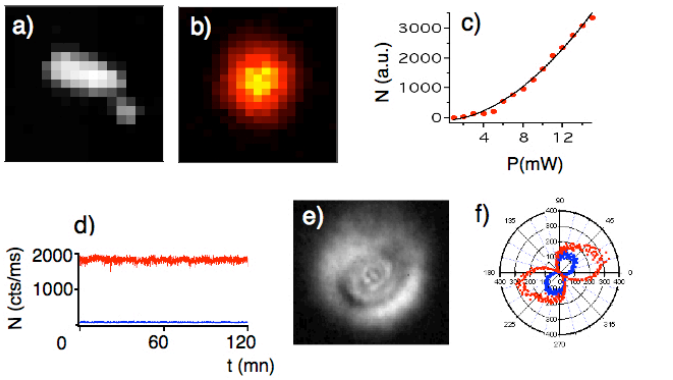

Figure 3. Investigation of a single KTP nanocrystal. a) AFM image of a nanocrystal: height = 59 nm, b) SHG scanning image (FWHM = 350 nm), (c) check of second-order nonlinearity, quadratic data fit, d) photostability of the x- and y-polarized emitted field components, (e) SHG defocused image and (f) polar graph of x- and y-polarized emitted field components, as a function of the excitation polarization angle.

We can now fully investigate a single nanocrystal. Figure 3a) shows a zoomed AFM image on one particle selected among those observed in figure 2, which measured height is 59 nm. The corresponding SHG image is well contrasted, with a signal-to-background ratio of 120. The number of photons emitted is proportional to the square of excitation power as expected (Figure 3c). Most remarkably, figure 3d) shows the very high photostability of the emitter, since perfectly constant signals are detected for both polarizations for more than 120 minutes, at a mean excitation power of 15 mW focused on a 350 nm diameter surface. We attribute this feature to the non-resonant character of the SHG emission in our experimental conditions. Finally, the emission pattern of this sub-wavelength emitter is accessed by a defocused imaging method [4] adapted to the nonlinear situation (Figure 3e). Combined with a polarization analysis technique [5] (Figure 3f), this method allows us to determine the three Euler angles that describe the nanocrystals orientation, (θ,φ,ψ) = (85°±5° , 35°±5° , 70°±15°) for the described example. The absolute direction of the non centro-symmetric emitter could also be obtained using a phase-sensitive detection scheme that we have recently developed [6].

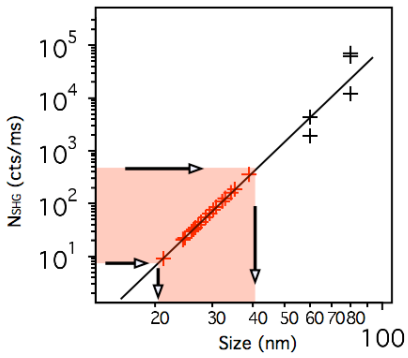

Figure 4. Size estimation of smallest KTP nanocrystals. Black crosses: signal levels of nanocrystals from solutions (b) and (c), line slope equal to 6, red crosses: signal level of smallest KTP nanocrystals in solution (d), which correspond to a size of (30±10) nm

The solution labeled (d) in figure 1 contains the smallest KTP nanoparticles. However, their sizes are not satisfactorily estimated by DLS due to a very weak light scattering signal. For size estimation, we measured the emitted SHG signal in the same conditions as for solutions labeled (b) and (c) for which the average sizes are known. Since the SHG process is coherent, the intensity emitted by a nanocrystal is proportional to the nanocrystal mean size to the power of six. Using this dependency, we can deduce the mean size of particles in solution (d), which is (30±10) nm. (Figure 4)

3 CONCLUSION

In summary, we have isolated photostable KTP nanocrystals. A full investigation of a single KTP nanocrystal is performed leading to its size, its orientation and its SHG efficiency. Nanoparticle sizes as small as 30 nm are obtained. We plan to use these nanocrystals as vectorial probes of optical near-fields, in association with an AFM tip.

We thank F. Treussart for helpful discussions. We are grateful to J. Lautru and A. Brosseau for samples preparations and AFM measurements.

REFERENCES

[1] J. C. Johnson *et al*, *Nano Lett*. **2**, 279 (2002).
[2] J. P. Long *et al*, *Nano Lett.* **7**, 831 (2007).
[3] F. Treussart *et al, ChemPhysChem*. **4**, 757 (2003).
[4] M. Böhmer *et al, J. Opt. Soc. Am. B* **20**, 554 (2003).
[5] S. Brasselet *et al, Phys. Rev. Lett.* **92**, 207401 (2004).
[6] L. Le Xuan *et al, Appl. Phys. Lett.* **89**, 121118 (2006).