Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C

Electronic Supplementary Information (ESI)

THz nanocrystal acoustic vibrations from ZrO_2 3D supercrystals

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1 XRD

The particle size has been calculated according to Scherrer equation. The results are summarized in Tab. 1.

Sample composition	XRD size (nm)
Pure ZrO_2 at 230°C (Z230)	3.1
Pure ZrO_2 at 300°C (Z300)	3.7
Y-doped ZrO_2 at 300°C (Y300)	3.5

Table 1: ZrO_2 nanoparticles mean size determined using the Scherrer equation.

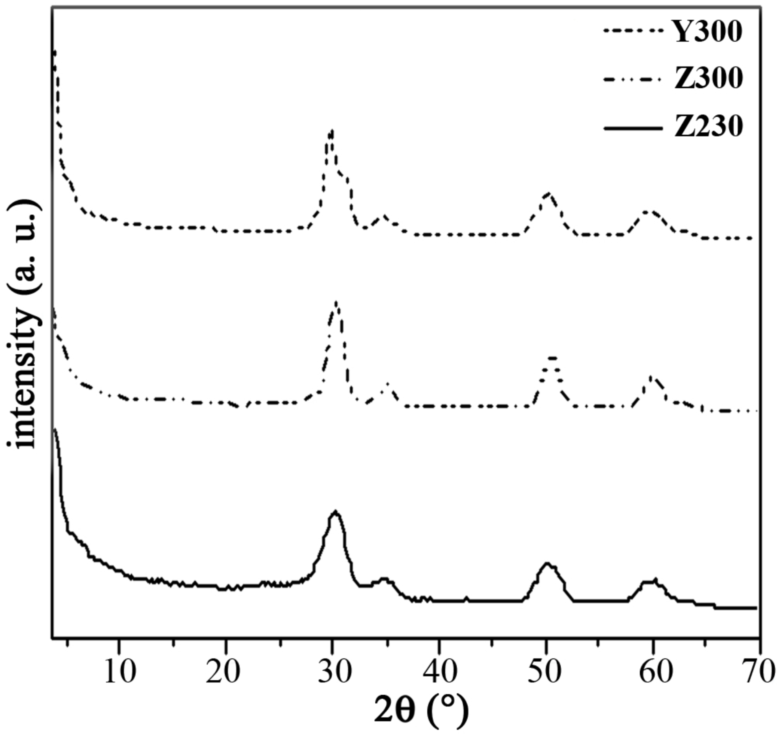

Figure S1: XRD diffractograms of the samples studied in the present work. Patterns of bare and doped ZrO_2 nanoparticles are reported from bottom to top, respectively

2 SEM

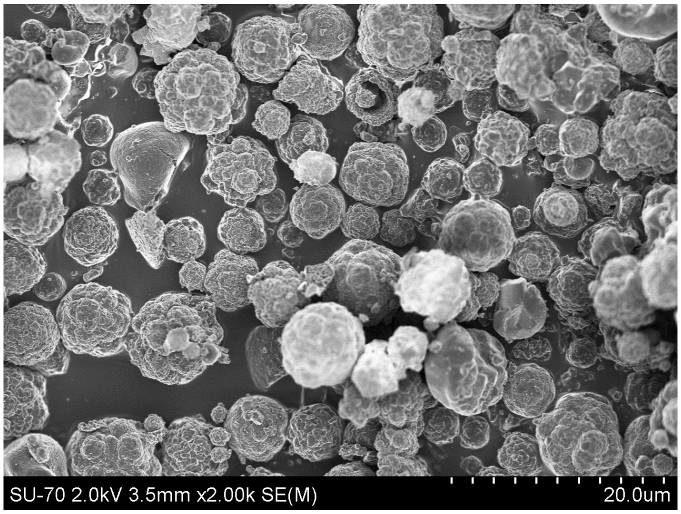

Figure S2: SEM image of Y300.

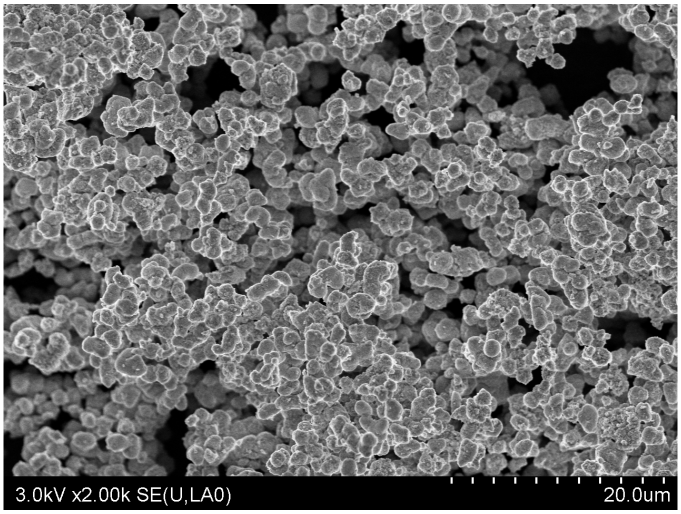

Figure S3: SEM image of Z300.

3 TEM

Statistical analysis performed on pure ZrO_2 nanoparticles synthesized at 230°C. The particles average size is 3.5 nm.

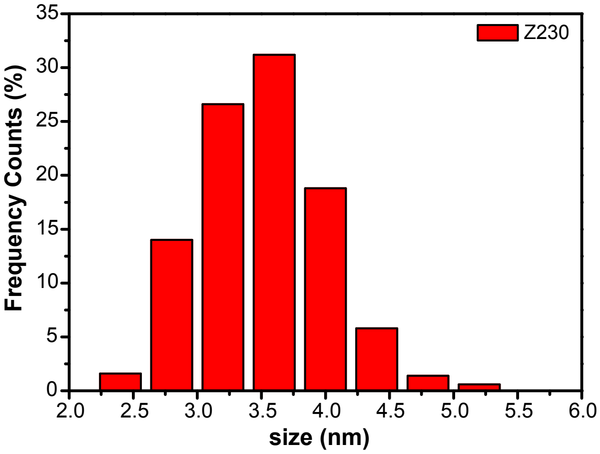

Figure S4: Statistical analysis performed on pure ZrO_2 nanoparticles synthesized at 230°C (Z230). The particles average size is 3.5 nm.

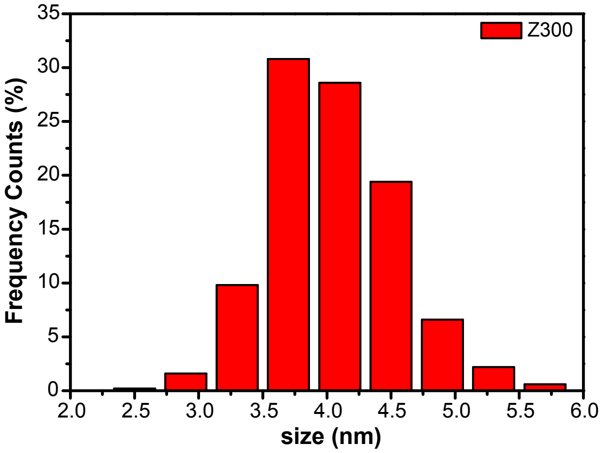

Figure S5: Statistical analysis led on ZrO_2 nanocrystals obtained at 300°C (Z300). The particles average size is 4.0 nm.

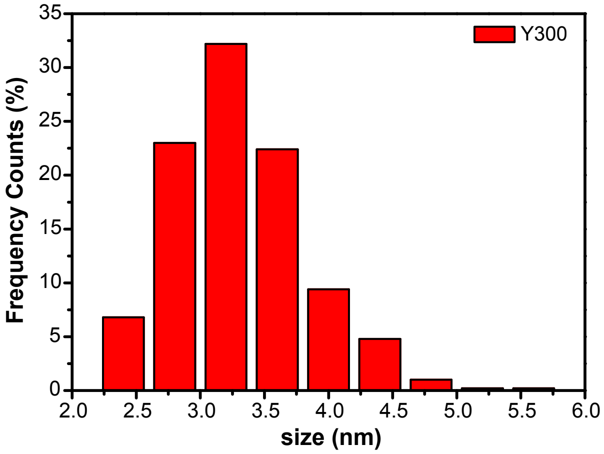

Figure S6: Statistical analysis conducted on Y-doped ZrO_2 nanocrystals achieved at 300°C (Y300). The particles average size is 3.3 nm.

4 FT-IR and Raman spectra in the 1500 cm^{-1} frequency range

The chemical environment that surrounds the nanoparticles has been disclosed by means of FT-IR analysis. It can be noted the presence of two strong absorption features due to the symmetric and asymmetric stretching bands of the carboxylate groups at 1410 and 1530 cm^{-1}, respectively. Moreover, the stretching signal due to the vibration of phenyl ring is observable at 1600 cm^{-1}.

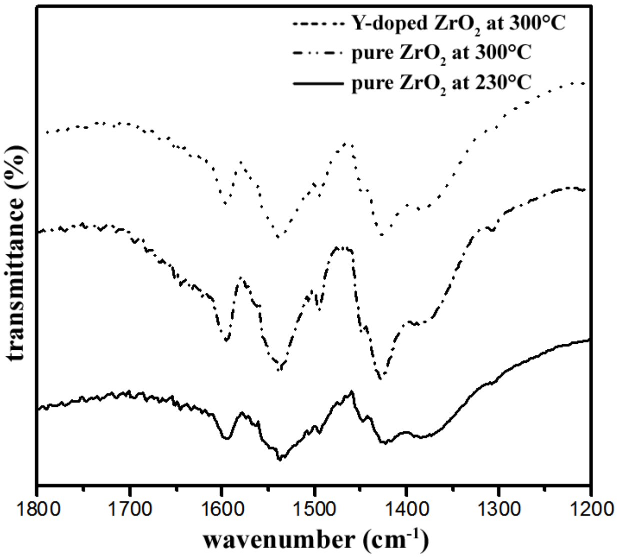

Figure S7: FT-IR spectra of bare (solid and dashed-dot lines) and doped ZrO_2 nanoparticles (dashed trace), respectively.

In Figure S8, the Raman spectra between 1800 and 1200 cm^{-1} are reported. Three main peaks are detectable. The first two signals between 1550 and 1400 cm^{-1} can be assigned to the asymmetric and symmetric stretching vibrations of the carboxylate groups bound to the ZrO_2 surface. The third band can be assigned to the stretching modes of the phenyl rings. The relative position of the two broad bands can be related to the geometry of the carboxyl-metal center coordination[1]. A difference of about 120 cm^{-1} between the frequencies of the asymmetric and the symmetric stretching of the carboxylate group suggests the presence of bridging bidentate bonds between benzoate and zirconium ions.[2] These spectral features agree with the FT-IR measurements. However a small variation of the frequency difference between the asymmetric and the symmetric stretching can be observed in the Raman measurements.

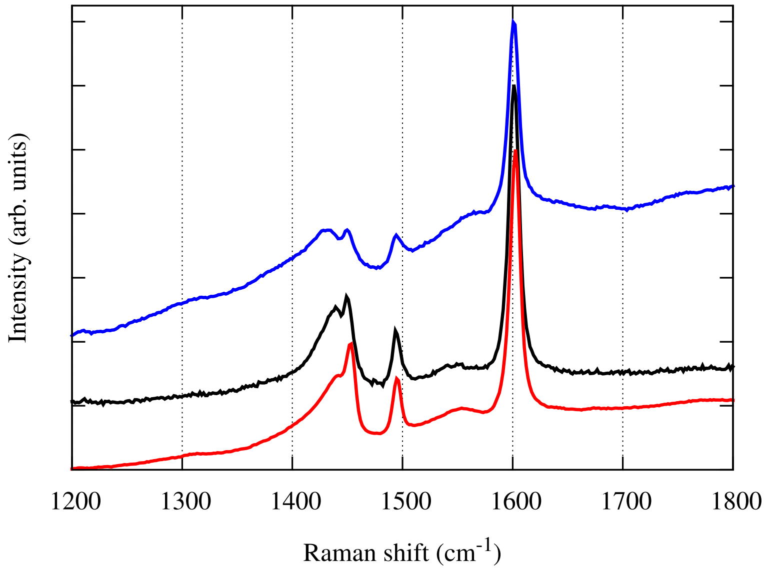

Figure S8: Raman spectra of bare ZrO_2 nanoparticles at 230 and 300°C doped ZrO_2 nanoparticles at 300°C from top to bottom respectively in the frequency range of the stretching modes of the phenyl rings of the benzoate species.

5 Assembly

TEM pictures of Y-doped ZrO_2 NPs based assemblies have been captured after the annealing step at 450°C. It has been figured out that the crystal assembly was preserved although the high calcination temperature. The particles have not been sintered, as a matter of fact they were still distinguishable.

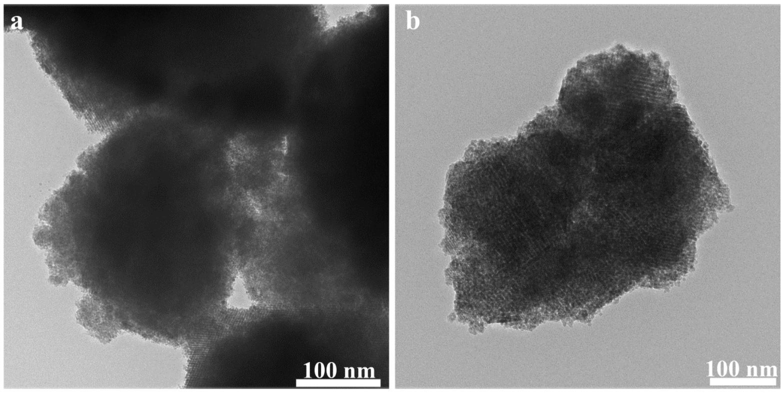

Figure S9: (a-b) Representative TEM micrographs of Y-doped ZrO_2 based superlattices after calcination at 450°C taken at different magnification.

Furthermore, in order to evaluate the particles ordering degree after calcinations of ZrO_2 powders, XRD patterns have been collected. It can be noticed the disappearance of the peak at low angle (4°) in the calcined sample (dashed line).

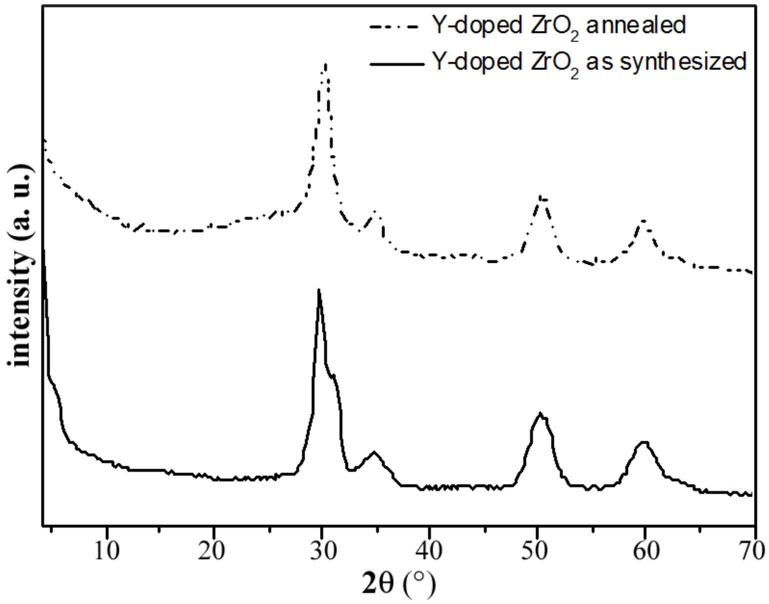

Figure S10: XRD diffractograms concerning Y-doped ZrO$_2$ nanoparticles before (solid line) and after calcination at 450°C (dashed line), respectively.

6 Low-frequency Raman spectra sodium and potassium benzoates

Figure S11 presents the Raman spectra of sodium and potassium benzoates. The spectra have been vertically shifted for clarity.

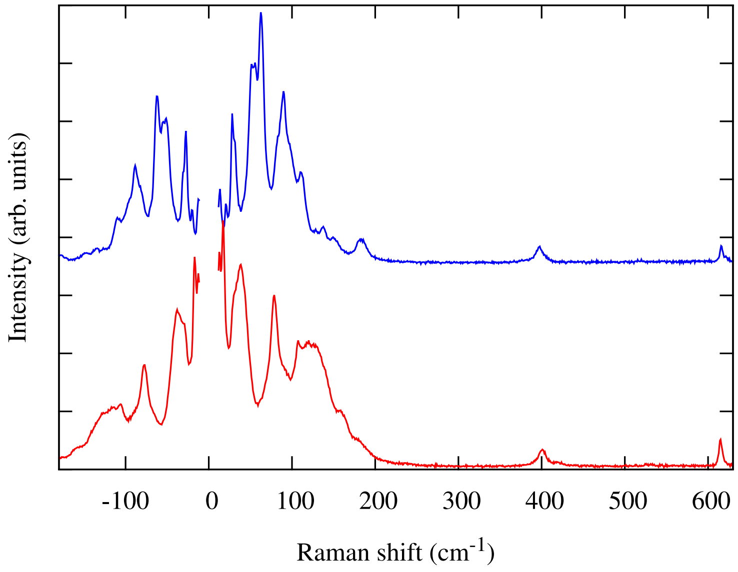

Figure S11: Low-frequency Raman spectra of solid molecular crystals of sodium benzoate (red line) and potassium benzoate (blue trace).

7 Diameter dependence of the low-frequency Raman intensity

We consider a simple example to derive the scaling law. For simplicity, we assume that Raman scattering is due to the radial breathing mode of a homogeneous spherical nanocrystal with zero photoelastic constants. A more general and lengthy approach exists which result in the same law. It will be presented elsewhere.

Nanocrystal dipole moment $p(t)$ and incident laser electric field $E_L(t)$ are related by $p(t) = \alpha(t)E_L(t)$ where $\alpha(t)$ is the polarizability of the nanocrystal. In the case of a homogeneous sphere,

$$\alpha(t) = 3\varepsilon_0 V(t)\frac{(\varepsilon_r - 1)}{(\varepsilon_r + 2)} \tag{1}$$

where ε_0 is the vacuum permittivity, $V(t)$ is the nanocrystal volume and ε_r is the relative permittivity of the nanocrystal. The volume varies with time due to the breathing mode. The relative permittivity of the nanocrystal is constant since in this simple example we assumed that the photoelastic constants are zero.

$\alpha(t)$ varies with time due to the vibration of the nanocrystal, from a minimum of $\alpha_0 - \delta\alpha$ to a maximum of $\alpha_0 + \delta\alpha$. The intensity of Raman scattering due to the breathing mode is determined by $\delta\alpha$. The instantaneous diameter, $D(t)$, of the nanocrystal oscillates with time. Let d denote the average diameter. $D(t)$ varies from $d - a$ to $d + a$. Since $V(t) = (4/3)\pi(D(t)/2)^3$, therefore $\delta\alpha$ scales as ad^2.

The amplitude a is determined by the fact that any single vibrational mode of an object has total mechanical energy k_BT. When the nanocrystal is at elastic equilibrium its energy is all kinetic. Apart from a dimensionless prefactor, the kinetic energy is $\rho V_0 \omega_B^2 a^2$, where ρ is the density, V_0 is the equilibrium volume and $\omega_B \sim 1/d$ is the vibrational frequency of the radial breathing motion. Therefore, a scales as $d^{-\frac{1}{2}}$. So the final result is that $\delta\alpha$ scales as $d^{\frac{3}{2}}$.

$p(t)$ includes Fourier components that vibrate at $\omega_L - \omega_B$ (Raman Stokes), ω_L (Rayleigh) and $\omega_L + \omega_B$ (Raman anti-Stokes). These dipole oscillations emit the electromagnetic waves that are observed in the detected spectrum. The Raman intensity is proportional to the square of the dipole moment, so that it scales as size cubed. Let $I(d)$ denote the Raman intensity due to a single nanocrystal of size d. Denote the experimentally-observed Raman spectrum as $I_{exp}(\nu)$, where ν is the Raman shift in wavenumbers. The size distribution function is $h(d)$, which is a histogram obtained by measuring the sizes of a large number of nanocrystals in a TEM image. Since ν varies inversely with d, there is an additional factor of d^2 which is required in order to obtain $I_{exp}(\nu) \sim h(d)d^2I(d)$. Since we know that $I(d)$ scales as d^3, it follows that $I_{exp}(\nu) \sim h(d)d^5$. In this way, it is straightforward to determine the shape of a Raman peak based on the experimental size distribution from TEM observations together with a theoretical calculation of ω_B as a function of d.

References

[1] G. Deacon and R. Phillips, *Coord. Chem. Rev.*, 1980, **33**, 227–250.

[2] A. Pucci, M.-G. Willinger, F. Liu, X. Zeng, V. Rebuttini, G. Clavel, X. Bai, G. Ungar and N. Pinna, *ACS Nano*, 2012, **6**, 4382–4391.