Supplementary Information for

Large Enhancement of Ferromagnetism under Collective Strong Coupling of YBCO Nanoparticles

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1 - Methods

The superconducting powder $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) was purchased from Can Superconductors and used without further purification. The powder was ground well in a mortar before use. The polymers, polystyrene (PS, analytical standard for GPC; MW 200,000) and polymethyl methacrylate (PMMA, MW 120,000), and their solvent, toluene were purchased from Sigma Aldrich/Merck. Toluene was distilled and dried before use. Silicon (Si) wafers (4-inch diameter, 500 µm thick) purchased from TEDPELLA were cut into 2x2 cm pieces and cleaned by sonication in water and subsequently in isopropanol. The cleaned Si wafers were dried in a hot air oven and used as substrates for thin film making. The thin films of YBCO nanoparticles embedded in different polymers were prepared as follows. The YBCO powder (50 % by wt. compared to the polymer) was added to freshly prepared homogeneous solutions of polymer (PS or PMMA, 20 wt%) and sonicated for 4 minutes (20 kHz, 10 second ON - 5 second OFF sequence) and then stirred for at least six hours at room temperature. Metal (Au) deposition onto the cleaned Si substrates was done by sputtering technique using an Emitech K575X sputterer (Parameters: Current 60 mA; the Au thickness was varied from 20 nm to 100 nm by changing the sputtering time). The films (4 µm thick) were prepared by spin casting (RPM: 1000, time: 2 minutes) the YBCO-polymer mixture onto Si substrates (for reference samples) and Au coated Si substrates (for strongly coupled samples). The samples were stored in a vacuum box before measuring the magnetic properties. To measure the magnetization properties of the samples, the spin casted films were cut into small pieces (ca. 4x4 mm) : few of them were then inserted into a gelatine capsule, sealed using Kapton tape.

The temperature-dependent magnetization (ZFC and FC) at 100 Oe magnetic field and the field-dependent magnetization measurements were done in ISIS, Strasbourg (using MPMS SQUID Quantum Design magnetometer), in IPCMS, Strasbourg and Quantum Design Europe, Darmstadt (using MPMS3 SQUID magnetometer). The infrared spectra were recorded using a Bruker Vertex70 FTIR spectrometer, in transmission and ATR mode. The dispersion curves of the strongly coupled samples were measured in ATR mode with a Variable Angle Reflection Accessory (“Bruker” A513/Q). For the dispersion measurements, a right-angle ZnSe prism, sputter-coated with 10 nm of Au and spin-coated with a thick YBCO embedded polymer layer (5 µm) at the bottom, was placed at the sample position. The angle of incidence on the prism was varied from 20° to 40° with steps of 0.5° for both TM and TE polarizations. By recording the reflection of an Au film sputter-coated at the bottom of the ZnSe prism, the instrument response of the reflection accessory was measured and subtracted from the sample data. Scanning Electron Microscopy (SEM) characterization was done using SEM model Quanta FEG 250, FEI / Thermo Fisher Scientific), equipped with an Energy-
Dispersive X-ray detector (EDX, EDAX company). X-ray Photoelectron Spectroscopy was achieved using a Thermo Scientific K-Alpha XPS system. The AlKα source produces X-rays (hv = 1486.7 eV). The level of vacuum was $10^{-8}/10^{-9}$ mbar in the main chamber. The spot size of the X-ray beam was fixed at 400 μm. The YBCO powder was also characterized by X ray diffraction to analyze carefully its composition. The PXRD measurements were carried out on a D8 Discover_Bruker powder diffractometer in the Bragg-Brentano geometry. The diffractometer was equipped with a front monochromator (Cu Kα1 wavelength $\lambda = 0.154\ 056$ nm) and a LynxEye XE-T linear detector.

2 – SEM characterization of YBCO powder

![SEM images of YBCO powder](image)

**Figure S1.** A and B are SEM images of the YBCO powder. C is an EDX spectrum of the same powder. Clusters of powder can have a size as large as 10µm (image A, scale bar is 1µm) but are composed of smaller nanoparticles having an average size around 200nm (image B, scale bar is 100nm). EDX spectra were also recorded (image C) and did not show any impurity into the powder (Al and C elements are coming from the sample holder and adhesive tape used to fix and hold the powder into the vacuum chamber of the SEM)

3 – XRD characterization of YBCO powder

The YBCO powder was also characterized by X ray diffractometry to analyze carefully its composition. Initial powder showed two main phases: Y123 and Y211 as well as a few others phases (Copper Oxide, Barium Copper Oxide, etc.). Note however that the critical temperature of this powder (Tc=92K) is not affected by those different phases.
Figure S2. XRD diagram of the YBCO powder. Full black line: experimental data. Color vertical lines correspond to phase identification (in red and bright green are the Y123 and Y211 phase respectively, blue, pink, orange and olive green correspond to copper oxide, barium copper oxides and barium copper hydroxide). Numbers in the figure caption refer to the JCPDS number for each phase.

4– FTIR spectrum of YBCO powder

Pellets of KBr ground with YBCO powder were prepared (15 mg of YBCO in 100 mg of KBr) and measured. The peaks at 697 cm$^{-1}$, 846 cm$^{-1}$ and 1400 cm$^{-1}$ are typical of CO$_3$ (see also Ref. 1).
Figure S3. FTIR spectrum of a pellet of YBCO/KBr showing peaks typical of carbonate ions.

5 – XPS analysis of YBCO powder

XPS was used to analyze the YBCO powder and to estimate its CO$_3$ content. First the survey only showed the presence of expected elements plus carbon, that is always found in samples, proving one more time the purity of the powder in terms of composition (Table S1).

Table S1: Survey of the elements detected by XPS, with the peak position (in eV) and atomic content (% of the total area probed).

| Name | Peak Binding | Energy (eV) | Atomic % |
|------|-------------|-------------|-----------|
| Ba $3d_5$ | 780.09 | 10.83 |
| O $1s$ | 531.21 | 53.1 |
| Cu $2p_3$ | 934.04 | 9.5 |
| Y $3d$ | 158.4 | 3.14 |
| C $1s$ | 285.37 | 23.43 |
Then following the orbitals C 1s and Ba 3d, we confirmed the presence of carbonate into the powder. There is a clear signature of CO$_3$ in the C 1s fitting (peak at 289eV; Ref. 2). In addition, the fitting of the Ba 3d spectrum reveals that most of the Ba$^{2+}$ ions contained in the powder are bonded to CO$_3$ (peaks at 780eV and 795eV) because we see no trace of the pure Ba$^{2+}$ orbital at 778eV.

**Figure S4.** XPS spectrum (in black) of the YBCO powder: the peak at 289eV is fitted by CO$_3$ (in red) and the peak at 285eV is fitted by C-C (in green) and is typical of adventitious carbon. The peak at 300 eV corresponds to the orbital Y3p$_{3/2}$.

**Figure S5.** XPS spectrum (in black) of the YBCO powder: the peaks at 780eV and 795eV (doublet) are fitted by Ba$^{2+}$ bonded to CO$_3$ (in green and red). The doublet of pure Ba$^{2+}$ ions should stand at slightly lower energies (i.e. 778 and 793eV).
References

(1) Masuda, Y.; Ogawa, R.; Kawate, Y.; Matsubara, K.; Tateishi, T.; Sakka, S. The Effect of Residual Carbon on the Superconducting Properties of YBa$_2$Cu$_3$O$_{7-x}$ Powders. J. Mater. Res. 1993, 8, 693-698.

(2) Fukuda, Y.; Nagoshi, M.; Suzuki, T.; Namba, Y.; Syono, Y.; Tachiki, M. Chemical States of YBa$_2$Cu$_3$O$_{7-\delta}$ Studied by X-Ray Photoelectron Spectroscopy. Phys. Rev. B 1989, 39, 11494–11497.