

Synthesis of organic-inorganic hybrids via high-pressure-ramp process: Effect of inorganic nanoparticles loading on structural and photochromic properties

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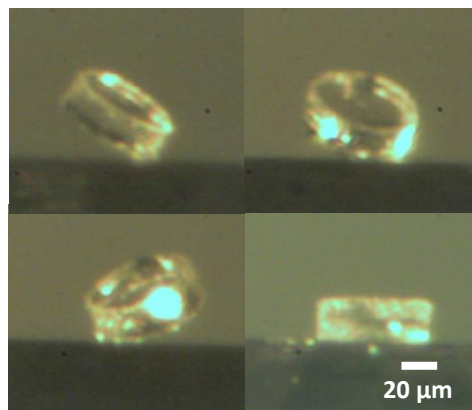
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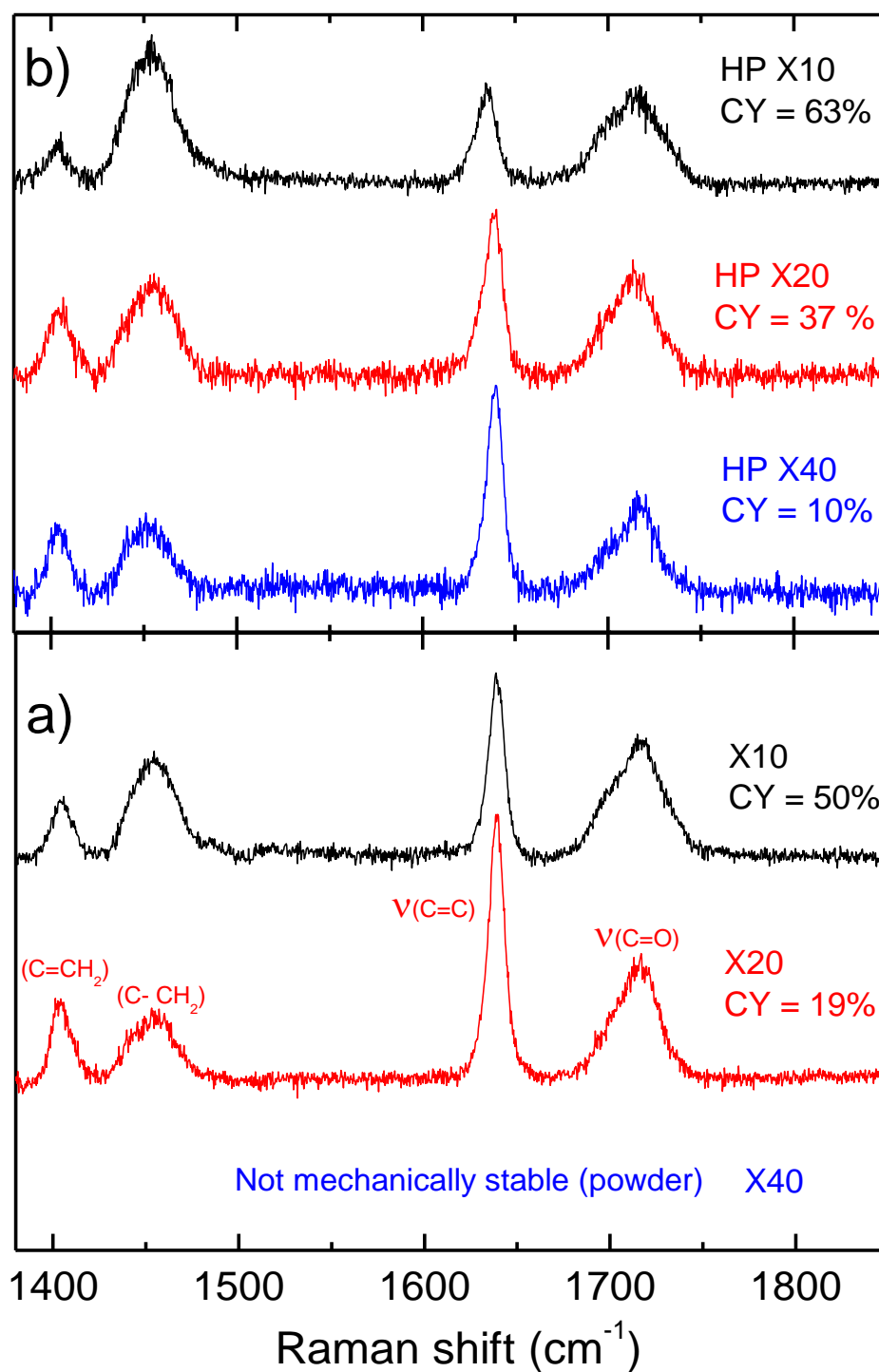
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Photos of hybrid samples synthesized by HPR induced polymerization



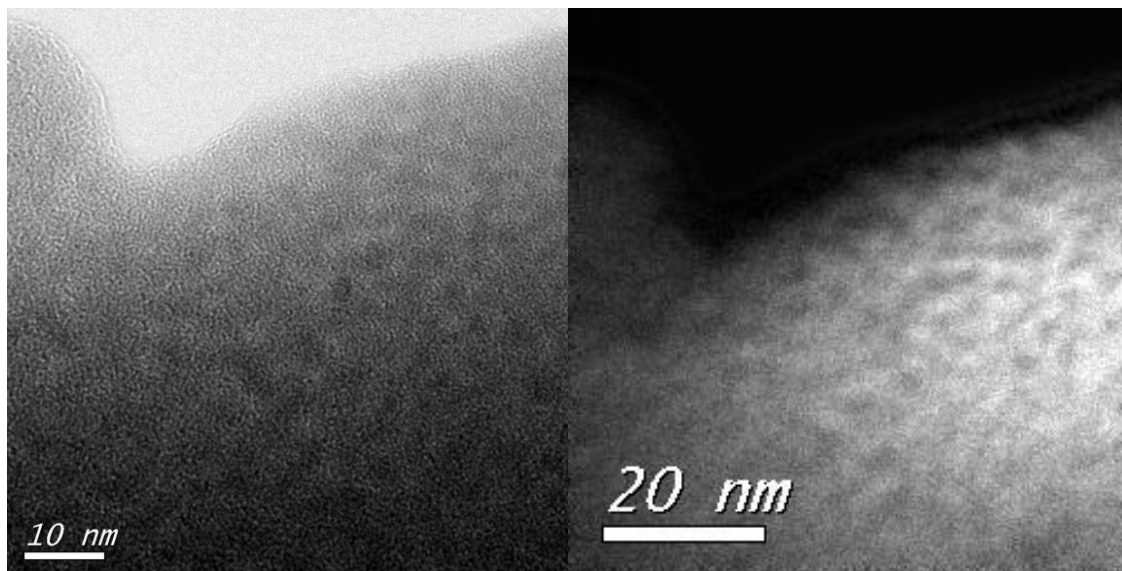
Supplementary Figure S.1: Photography of a recovered sample (HPX2).

Raman spectra of thermally polymerized hybrids



Supplementary Figure S.2: Comparison of Raman spectra of pHEMA-TiO₂ hybrids (a) synthesized at ambient pressure with a thermal initiator (AIBN) and (b) synthesized using the HPR induced polymerization.

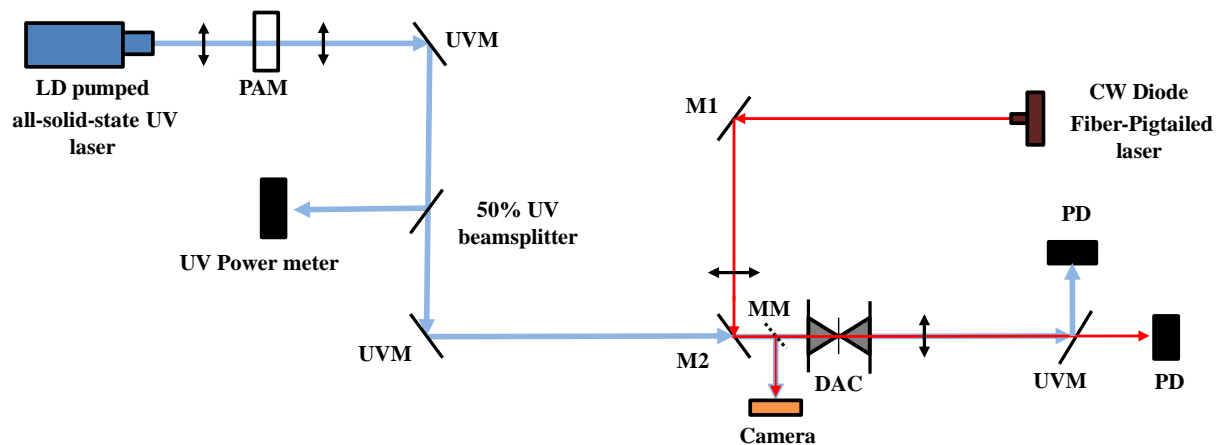
High resolution transparency electron microscope images of HPX5 sample



Supplementary Figure S.3: HRTEM image of sample HPX5 (right). Energy filtered (Ti) TEM image of the same sample HPX5 (left).

Photodarkening experiment

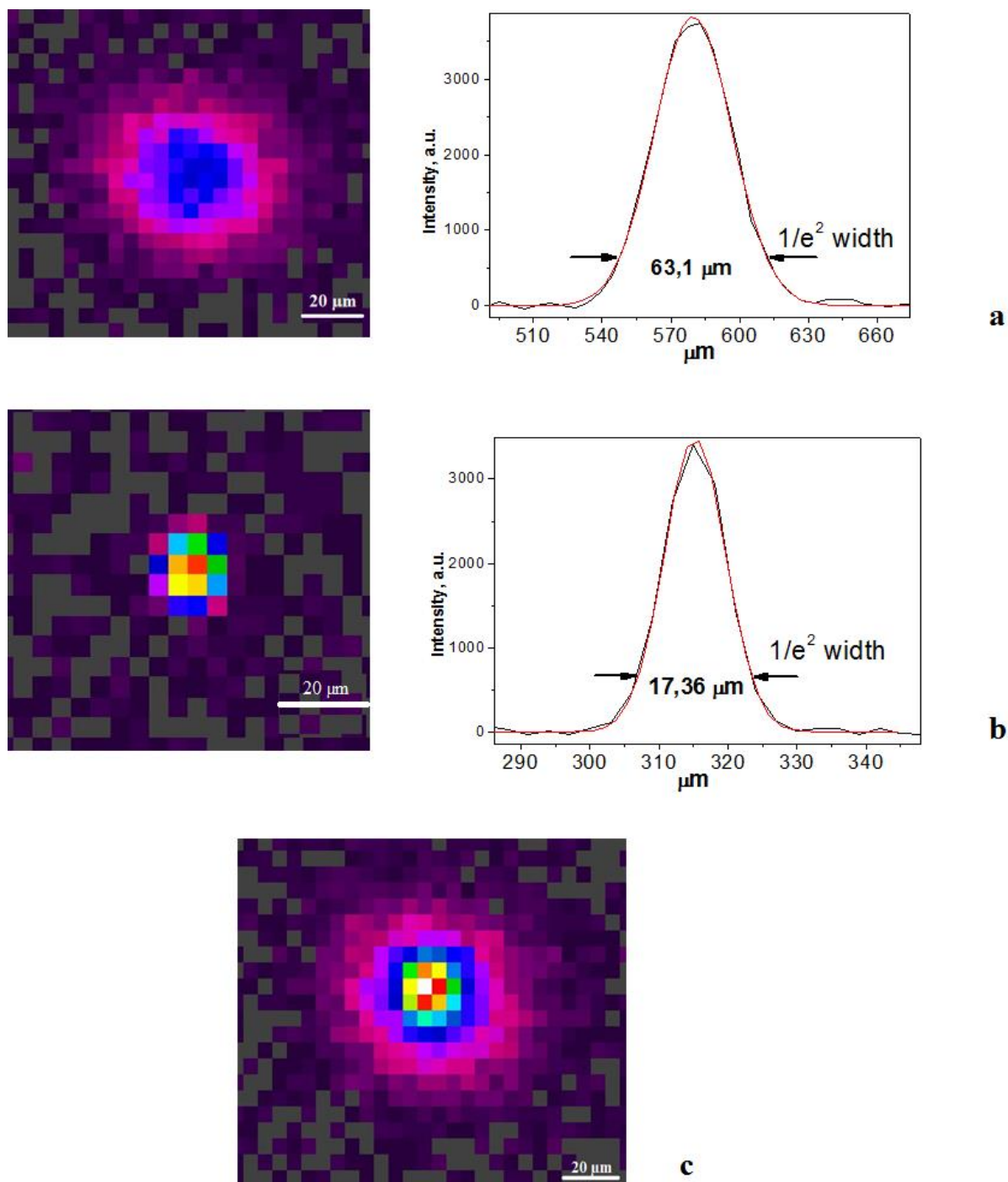
The pump-probe photodarkening experiments are based on the measurement of the absorption of the sample at 640 nm as function of the UV (355 nm) irradiation dose received by the sample. The Supplementary Figure 3 represents the general scheme of the experimental setup. Basically, a high repetition rate (4kHz) diode pump solid state (DPSS) UV laser delivers pulses of 7 ns at 355 nm (10 mW). The UV beam is collimated by a first lens and focused on the sample through a second long focal lens (75 cm). This combination of lenses ensures a Gaussian shape of the UV beam on the sample with a radius equal to $\sim 33 \mu\text{m}$ (Supplementary Figure 5.a) leading to an UV fluence on the sample of $10 \text{ mJ}/\text{cm}^2$. The UV laser power is adjusted by a variable attenuator (PAM) designed for linearly polarized laser beam. The UV irradiation dose is carefully measured and monitored from a power meter (Coherent PS10Q). The probe beam at 640 nm is delivered by a CW fiber-diode laser stabilized in power and temperature. The laser is focused on a spot of $\approx 9 \mu\text{m}$ radius on the sample inside the DAC. The transmitted beam is collimated by a short focal lens and analyzed by a Si photodiode.



Supplementary Figure S.4: Setup of the pump-probe photodarkening experiment (UVM: UV mirrors, M1: visible mirror, M2: visible mirror transparent in UV, MM: movable metallic mirror, DAC: Diamond Anvil Cell, PD: Si photodiodes, PAM: power attenuator module)

The superposition of UV and 640 nm laser beams on the sample is a critical parameter to ensure reliable measurements of the sample absorption. Due to the small sizes of beams, a mere “eyes alignment” of UV and visible beams is not sufficient. For that reason the beams superposition is checked before each experiment. A removable metallic mirror is placed in front of the DAC to reflect at right angle both UV and visible beams. The reflected beams are observed by a CCD camera placed on the focal point of the visible beam

(Supplementary Figure 4.a and b). The beams are superposed using UV mirrors (Supplementary Figure 4.c). Then the metallic mirror is removed and the DAC is placed on the focal point of the visible beam. An ocular system has been used to observe the position of the visible beam on the sample and to place the DAC in the right position.



Supplementary Figure S.5: UV laser beam and profiles (a); 640 nm laser beam profile (b); superposition of the two laser beams (c).