Chapter 6

Conclusion and Outlook

In conclusion, this thesis work investigated novel schemes to control the ultrafast switch in complex materials upon photo-excitation. In particular, two cases were addressed: first, the control process is based on a suitable coupling between the out-of-equilibrium state of the material, due to photo-injected free-carrier population, and its geometry. In the second case, we addressed the coherence of the electronic degree of freedom in correlated materials as an additional tool to control the photo-induced phase transition. Indeed, the coherent excitation scheme is capable to couple not only to the band population, but also to the short-living macroscopic polarization.

More specifically, in the former case, we have studied the photo-induced sub-ps optical modulation of the Fano resonance formed by the coupling of an excitonic state with Mie modes in halide perovskite NPs. In particular, we have demonstrated that the ultrafast modification of the optical properties induced by the *band gap renormalization* and *band filling* mechanisms, dramatically depends on the geometry of the NPs. In the low-q resonance Fano condition, the contribution of the two effects to the relative transmittivity variation is completely reversed with respect to the high-q resonant case and to what was previously observed in thin films and bulk materials. Importantly, this is the demonstration of the ultrafast control of the optical response in nanoparticles where Mie resonances are coupled with excitons. In previous studies, the ultrafast all-optical switching in Mie-resonant nanoparticles was carried out with standard semiconductors like amorphous silicon and gallium arsenide, for which excitonic effects are negligible at room temperature. Beside the physical effects arising from the coupling between exciton and Mie modes, there is important advantage of high absorption and sharp band-edge in $CsPbBr_3$ perovskites, allowing us

to greatly reduce the fluence required to observe ultrafast tuning. $CsPbBr_3$ nanoparticles exhibit an amplitude of the transmittivity modulation that is two order of magnitude larger as compared to that measured in silicon-based Mie resonators under similar photo-excitation conditions.

Although in this work we focused on $CsPbBr_3$ nanoparticles, the results and modeling discussed simply rely on the geometry-driven overlap between the exciton line and the continuum of Mie resonances. As a consequence, the present results can be promptly extended to a wider class of perovskites-based nanonstructures. The present results offer insights into the photophysics of halide perovskite nanoparticles and provide an additional parameter to control their optical properties at frequencies as high as few THz, with impact on perovskite-based optoelectronic devices, metamaterials and switchable nano-antennas.

On the latter case, we presented and applied an interferometric time-resolved pump-probe (ITRPP) scheme as a coherent-control method to photo-induce the insulator-to-metal transition in the prototypical Mott insulator V_2O_3. Compared to previous approaches in which the light-assisted transition temporally evolves according to incoherent pathways, here the transition towards the final state of the system is triggered by coherent orbital manipulation on the ultrafast timescale (faster than dephasing processes), thus allowing to investigate the effect of the electronic quantum coherence on the photo-induced phase transition. Specifically, a pair of coherent pump pulses is employed to induce an electronic orbital population imbalance which in turns triggers the transition from the insulating to the metallic metastable state. In our experiments, we focused on the orbital population involved in two optical transitions of the low-temperature V_2O_3 phase involving $3d$ electrons: the first at $\sim 1.6\,\text{eV}$ (*NIR Optical Transition*) and the second at $\sim 2.4\,\text{eV}$ (*VIS Optical Transition*). Moreover, the experimental results have been complemented by a theoretical model based on the numerical solution of a set of Optical Bloch Equations (OBE) describing the light-matter interaction, in which a phase-locked pulse pair excitation manipulates the population of a two-level system.

In the interferometric scans, the signal shows a temporal envelope wider than that exhibited by the excitation pattern (pump interferogram). This temporal widening corresponds to a *spectral narrowing* when the time domain data are Fourier Transformed in the energy domain. This narrowing is a direct effect of a non-vanishing quantum coherence and it indicates that the phase delay between the two pump pulses (t_1) represents an additional control parameter. Moreover, when the pump spectrum is non-resonant with the optical transition, the signal exhibits oscillations with a different frequency than that corresponding to the optical cycle of the pump beam. Therefore, in the energy domain, the spectra have different positions. In particular, the signal spectrum is shifted from the

pump one towards the position of the peak ascribed to the optical transition. For the antiferromagnetic low-temperature phase of V_2O_3 ($T = 100\,K$), the results from the ITRPP measurements allows to extract a coherence time value on the order of $4 - 5\,fs$, which is in agreement with previous estimations in the case of transition-metal-oxides compounds ($2 - 6\,fs$, [Gandolfi et al., 2017]). In addition, when the temperature increases, an increasing value of the shift is obtained in the ITRPP experiments. Based on numerical simulations, this behaviour is ascribed to both an increase of the coherence time (up to $\sim 10\,fs$) in the insulating-metallic cohexisting region and a (temperature-driven) redshift of the peak related to the optical transition. These results demonstrates the presence of a non-vanishing quantum electronic coherence and its effect can be detected through the ITRPP approach.

Under an experimental point of view, although the values of the dephasing time are on the order of few femtoseconds, they are comparable with currently available pulse widths. Therefore, this may pave the way to the application of the coherent-control scheme to the insulator-to-metal transition in other cathegories of correlated materials. In addition, the coherent-control scheme we presented can be applied also to other classes of transitions, such as the superconducting one. Indeed, the transition from the normal to the superconductive state is driven by the electronic degree of freedom, whose coherent dynamics can be monitored by an ITRPP scheme.