X-ray absorption spectroscopy and materials science: recent advances

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A description and understanding of the local atomic and electronic structure is essential for knowledge – based design of advanced materials. X-ray absorption spectroscopy (XAS) and related techniques can play a crucial role in this context, allowing an atomistic understanding of materials function. In this talk I will review recent advances in the application of XAS and related techniques to materials for photocatalysis.

TiO_2 is one of the most studied oxide semiconductors for photocatalysis. However, because of its wide band gap only a small fraction of the solar spectrum can be harvested. This limitation can be overcome by doping or inclusion of metallic nanoparticles. By using XAS, including ab – initio full potential simulations, we have shown that V dopants in TiO_2 nanoparticles and thin films occupy substitutional sites, irrespective of whether the oxide matrix has a rutile, anatase or mixed structure; N dopants, instead, are found both in substitutional anionic sites and as N_2 dimers [1, 2]. These structural studies are complemented with a quantification of materials functionality, correlated to the charge carrier dynamics studied by ultra fast optical spectroscopy [3]. We have also applied a high resolution XAS method with differential illumination to prove that sub-bandgap visible light absorption is predominantly due to excitation of electrons from V ions to defective and long-lived Ti sites, thus identifying an element-specific photoexcitation channel [4]. Inclusion of metallic nanoparticles in the oxide matrix extends light absorption to the visibile range thanks to the excitation of the surface plasmon resonance. By using high resolution XAS in TiO_2 sensitized by Au nanoparticles, we have demonstrated charge transfer from Au nanoparticles to long – lived states localized on defective sites localized on the oxide surface [5].

Inclusion of plasmonic nanoparticles can be used also to sensitize CeO_2, a photocatalyst characterized by the ability of Ce to reversibly change between the 4+ and 3+ oxidation states. Using static XAS we have performed an in - depth structural investigation of CeO_2 nanoparticles [6] and of Ag nanoparticles on the CeO_2 surface [7]. More recently, using time resolved XAS with ~ 100 fs time resolution using the FERMI free electron laser, we have demonstrated electron trasfer from plasmonic Ag nanoparticles to the CeO_2 matrix [8].

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