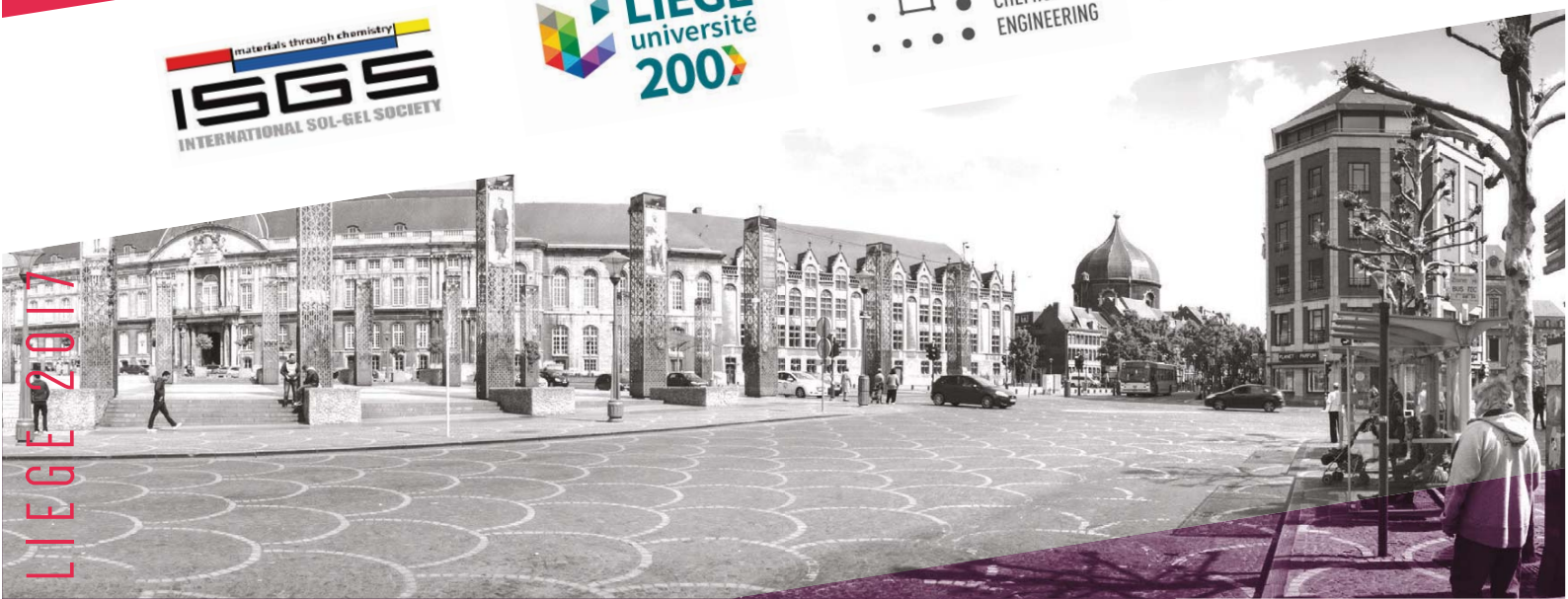


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Band gap engineering in photoactive materials. A novel approach for the synthesis of visible-light activated titanias for photocatalysis and solar-driven applications

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The quest for materials able to efficiently harvest solar light is one of the major challenges of our time. Titania (TiO_2) is one of the most promising candidates for this task, yet it presents important drawbacks. One of its major constraints is that its overall efficiency for solar-driven applications is limited to the UV range (less than 5% of the total solar irradiation) due to its wide band gap (3.2 eV, for the anatase phase).

There are two main techniques to improve the sunlight-driven photocatalytic efficiency of titania: i) band gap narrowing, i.e. doping and partial reduction of Ti(IV), and ii) photosensitization with organic dyes or coordination complexes able to absorb in the visible. Our radically new approach is based on the incorporation of organic moieties into the crystalline framework of titania semiconductors as a new tool to modify the electronic structure of the titania in order to fine tune its band gap. Based on our previous experience in the design of hybrid periodic mesoporous Metal Complex-Silica through the so-called "Sol-Gel Coordination Chemistry" approach [1], we have developed an unexplored strategy based on the one-pot co-condensation of in-situ prepared polymetallic titanium-alkoxide complexes with titanium tetrabutoxide, allowing the homogeneous incorporation of organic moieties (disruptors) within the crystal structure of titania [2-4].

Different molecules have been used as charge-transfer dyes such as organic compounds [2,3] or neutral or cationic complexes of Ru(II) or Ir(III) [2,4]. These dyes act both as disruptors of the crystalline structure of the anatase (decreasing its band gap up to 2.7 eV) and as dyes (molecular antenna). The incorporation of these chromophores inside titania provides additional protection, yielding exceptional stability against both photodegradation and leaching over those titanias that contain dyes only on their surface (conventional dye-sensitized titanias prepared by grafting). These hybrid materials present highly active and remarkably stable photocatalytic properties, even after multiple cycles under UV or visible light, exceeding, in both cases, the activity and stability of conventional dye-sensitized titania (prepared by grafting).

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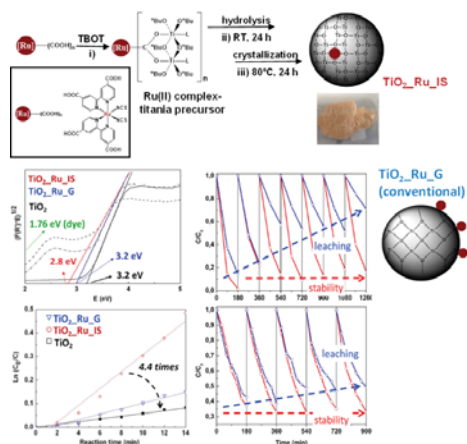


Figure: Synthesis of the in-situ $\text{TiO}_2\text{-Ru-IS}$ (red), band gap estimation and photocatalytic activity as compared with the control TiO_2 and the conventional grafted material (in blue) in the degradation reaction of an aqueous solution of R6G (5×10^{-5} M) under UV (top) and visible (bottom) irradiation.

KEYWORDS

Visible-light activated titanias-solar-driven applications-band gap engineering-Sol-Gel coordination chemistry