TiO_2/QDs nanocomposites for sustainable reactions: synthesis and characterization

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Significance and Relevance

Sunlight reaching Earth each hour could meet global annual energy needs if were captured and stored affordably. Drawing inspiration from nature, this study investigates TiO_2 polymorphs enhanced with heavy-metal-free quantum dots (QDs) for two sustainable reactions: CO_2 reduction to solar fuels and biomass valorization. By coupling TiO_2, a well-studied photocatalyst, with non- toxic QDs, known for their excellent optoelectronic properties to harvest and deliver solar energy, this research aims to explore potential photocatalytic synergies between these nanoscale semiconductors. Preliminary experimental and modeling results indicate that selectivity and yield vary depending on the TiO_2 polymorphic type and QD concentration.

Preferred and 2nd choice for the topic: Photocatalysis and photoelectrocatalytic approaches, solar energy utilization

Green chemistry and biomass transformation, renewable resources conversion

Preferred presentation: (Oral only / Oral preferred or Short Oral / Poster) Oral preferred or Short Oral

Introduction and Motivations

In recent decades, the twin challenges of climate change and increasing energy demands have become critical global issues. TiO_2, known for its low toxicity and affordability, is widely used as a photocatalyst to exploit solar energy for sustainable chemical reactions. Its main drawback is its large band gap which prevents it from absorbing photons in the visible range. To address this limitation, this study explores both the presence of different TiO_2 crystalline phases—anatase, rutile, and brookite—and the coupling with copper-based quantum dots that emit in the NIR range, to enhance light absorption and photocatalytic performance.[1]

Materials and Methods

TiO_2/$CuInS_2$ nanocomposites (TiO_2/CIS) were obtained at low temperatures without the use of template. Different titanium precursors, such as titanium tetrachloride and titanium tetraisopropoxide[2,3], were used to synthesize nanometric TiO_2.[4] Sodium oxalate and sodium lactate, as chelating agents, and urea, as in situ OH^- source, were added to tune the polymorphs percentages. $CuInS_2$ quantum dots were synthesized through one-pot synthesis method in inert atmosphere.[5] The two nanometric semiconductors were coupled in a controlled atmosphere at different temperatures.[3] Characterization of the studied nanomaterials has involved either theoretical calculations or experimental techniques such as X-ray powder diffraction (XRPD), quantitative phase analysis via Rietveld refinement, diffuse reflectance (DR) UV-Vis spectroscopy, N_2 adsorption/desorption, ζ-potential measurement for electrophoretic mobility in water, X-ray photoelectron spectroscopy (XPS), and electron microscopy. Photocatalytic performance assessment has been conducted under simulated sunlight at 1 Sun intensity (100 mW/cm^2).

Results and Discussion

By adjusting the chelating agents, aging time, and calcination temperature, we successfully controlled the quantity of polymorphs, allowing us to produce either single-phase or multiphase nanoscale TiO_2. These powders were coupled with $CuInS_2$ quantum dots (CIS-QDs) to enhance their photocatalytic activity. The influence of homo-(among the different TiO_2 polymorphs)[6] and hetero-junctions (between TiO_2 and CIS QDs) in the photocatalytic performance of the nanocomposites has been investigated through experimental techniques coupled with Kohn-Sham density functional calculations. KS-DFT calculations were used to model the different surfaces of the titania polymorphs to quantify their influence on the work function. We have been testing these nanocomposites for two sustainable reactions: i) CO_2 conversion in solar fuels; ii) lignin conversion into fragrances. Preliminary chromatographic analysis for CO_2 reduction revealed different amounts of C_1 and C_{2+} products, depending on the types of polymorphs present in the nanocomposite with CIS QDs. Furthermore, TiO_2/CIS nanocomposites appear to catalyze the conversion of dihydroeugenol to vanillin.

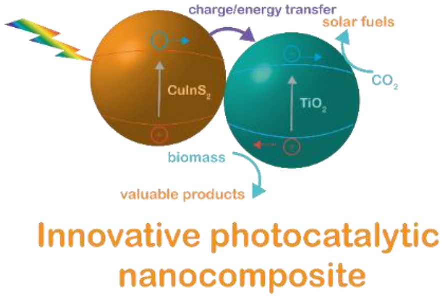

Figure 1 Sketch of the nanocomposite

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