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Artificial Photosynthesis: Solar Fuels Nanomaterials

Jia Jia[1,2], Gilberto Casillas[3], Miguel Yacaman[3], Geoffrey Ozin[1] and Doug D. Perovic[2]

[1.] Department of Chemistry, University of Toronto, Toronto, Canada.
[2.] Department of Materials Science and Engineering, University of Toronto, Toronto, Canada.
[3.] Department of Physics, University of Texas, San Antonio, Texas, U.S.A.

The objective of this research is an in-depth exploration of semiconductor photo-catalysts that are able to convert CO_2 and H_2O and sunlight to energy rich and transportable fuels, such as CH_4, CH_3OH and HCO_2H. The main focus is on the synthesis, structure determination, physical property characterization and photocatalytic testing of different classes of semiconductor photo-catalysts, with and without the presence of co-catalysts that bear distinct and well defined nanocrystal (NC) morphologies. Shape-controlled TiO_2 nanocrystals have been explored, involving the synthesis and characterization of TiO_2 nanocrystals with different populations of {001}, {101} and {010} crystal facets (Fig. 1). The integration of shape-controlled TiO_2 nanocrystals with co-catalysts exemplified by Pt and Cu has also been explored. A variety of analytical techniques, such as TEM, HRTEM, PXRD, XPS-UPS, BET and UV-Vis have been employed to characterize properties of these nanomaterials that are considered to be key to understanding, controlling and optimizing their photoactivity. TEM and HRTEM are extremely important in identifying the structure of these semiconductor photo-catalysts, especially when the co-catalysts are too small to be characterized by other techniques.

Literature reports are mixed regarding which facet orientation contributes to a higher photocatalytic activity because of inconsistencies between the various reaction conditions investigated. The synthesis of TiO_2 NCs with controlled shapes was accomplished using a solvothermal method (Fig. 2). Titanium butoxide (TB) was chosen as the source of titanium. The key feature of this approach is the use of water vapor as hydrolysis agent to increase the reaction rate and the use of both oleic acid (OA) and oleylamine (OM) as distinct capping surfactants to control the relative rates of growth of different crystal facets in the resulting nanocrystals.

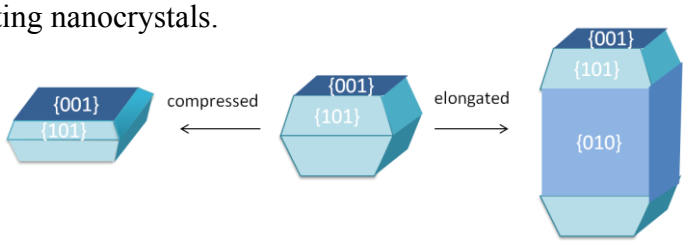

Figure 1: Illustration of Anatase TiO_2 crystal morphologies with different percentages of {101}, {001}, and {010}/ {100} crystal facets

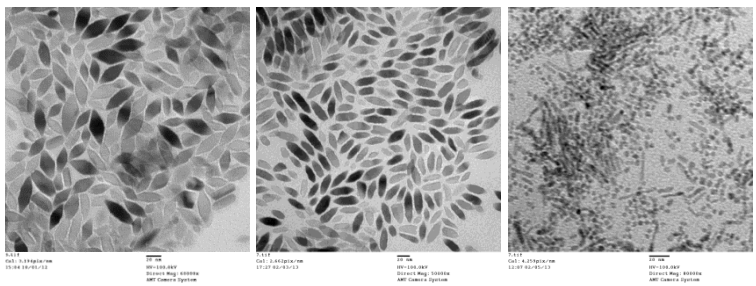

Figure 2: TEM images for rhombic, elongated rhombic and spherical TiO2 NC

An effective method for improving photocatalytic activity is to form a co-catalyst heterojunction structure. Pt-TiO_2 (Fig. 3) and Cu-TiO_2 (Figs. 4 and 5) NC hetero-junctions have been synthesized by photo-deposition and microwave-assisted deposition. The overall photocatalytic activity is made more effective because co-catalysts not only promote charge separation but also accelerate the surface chemical reaction. The roles of co-catalysts will be elucidated and the mechanism of the photocatalysis for NC TiO_2 integrated with co-catalysts will be explained.

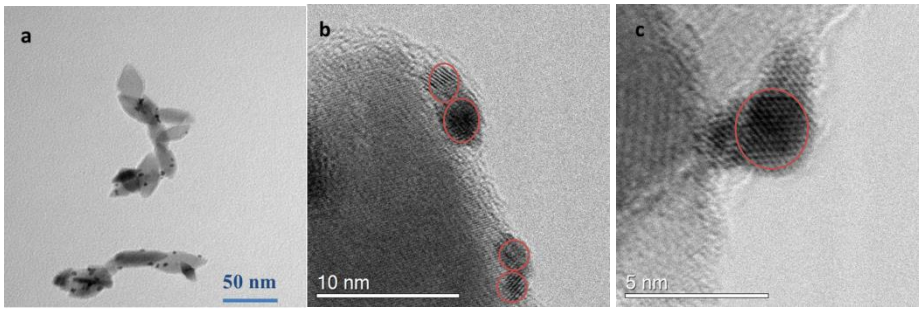

Figure 3a): TEM image for Pt-TiO_2 b) HRTEM image for Pt-TiO_2 c) HRTEM image for Pt-TiO_2

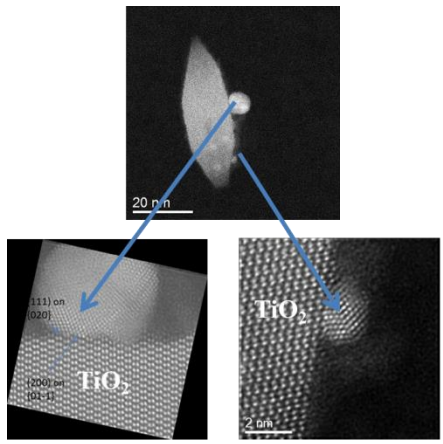

Figure 4: HRTEM images for Cu-TiO2

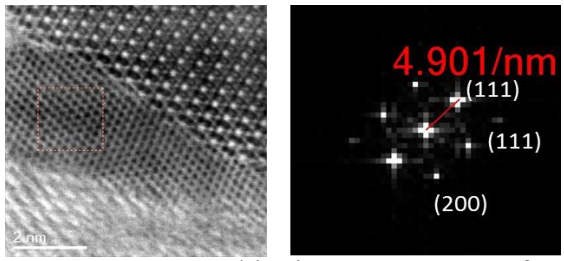

Figure 5: HRTEM and lattice measurement for Cu-TiO_2

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