

Mesoscopic Materials Research Laboratory Seminar

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Photoluminescence Study of In-Situ Defect Evolution and its Relation to the Room Temperature Ferromagnetism in Undoped TiO₂ Nanoribbons

We study the origin of intense visible and near-infrared (NIR) photoluminescence (PL) in undoped TiO₂ nanoribbons by monitoring the defect evolution during PL measurement under vacuum and air environment and identify the defect responsible for the room temperature (RT) ferromagnetism (FM) observed in these nanoribbons. TiO₂ nanoribbons are grown by a low temperature solvothermal method followed by calcination at different temperatures. Structural studies reveal the TiO₂(B), anatase-rutile mixed phases of TiO₂ structure. High resolution electron microscopy reveals TiO₂ nanoribbons with uniform pores and nanopits/ nanobricks on the surface. These samples exhibit strong visible and near-infrared PL and ferromagnetic hysteresis at RT depending on the growth and processing conditions. Interestingly, a clear correlation is found between the visible PL intensity and the FM, both of which dramatically enhanced after vacuum annealing, confirming the origin of visible PL to oxygen vacancies. This is further confirmed from temporal evolution of the visible PL intensity during laser exposure in air. Samples calcined at higher temperature exhibit stronger visible absorption and a strong NIR PL band centered at 1.44 eV, intensity of which goes down with laser heating under vacuum, as monitored during PL measurements at low temperatures. The NIR PL is attributed to Ti interstitial defects in TiO₂ identified for the first time. Direct evidence of oxygen vacancies and related Ti³⁺ defects are obtained from X-ray photoelectron spectroscopy analysis. The observed RT FM in undoped TiO₂ nanoribbons could be quantitatively explained through a model involving bound magnetic polarons (BMP). Our analysis indeed shows that the calculated BMP concentration scales linearly with concentration of oxygen vacancies and this constitutes an unambiguous evidence of oxygen vacancy induced RT FM in TiO₂ nanostructures. The development of such porous TiO₂ nanoribbons with strong visible absorption, controllable visible-NIR PL and RT FM demonstrates its immense potential as one of the most important next-generation multifunctional materials.