**Bottom-up Nanostructures for Sustainable and Biomedical Engineering**

**Associate Professor Timothy TAN**

Associate Chair (Academic)

Director (Outreach)

School of Chemical and Biomedical Engineering

Nanyang Technological University, Singapore

Email: tytan@ntu.edu.sg

Bottom-up fabrication techniques have enabled the synthesis and tailoring of functional nanostructures from basic building blocks such as atoms or/and molecules. Tuningthe morphology, interfaces, crystallinity, porosity and/or composition of nanostructures have been shown to enhance material performances in energy harvesting, waste remediation and medical applications. This talk will focus on selected bottom-up strategies developed in our labto prepare multifunctional nanostructures for enhanced solar/bio energy conversion andwater treatment,and to innovate novel nanotheranostics to tackle ongoing challenges in medicine.

Our lab has synthesized several types of graphene based hierarchical nanostructures, which showed significant improvement in energy harvesting when they were applied as electrodes. For example, 2 nm size TiO2-graphene photoanodes showed high photoconversion efficiency (PCE) in dyes-sensitized solar cells, and their size-dependent nanoscale electron transport mechanism were elucidated1,2. In another work, a hierarchically porous graphene-chitosan scaffold showed a significantly higher power density when applied as a bioelectrode in microbial fuel cells3. The above examples demonstrate that the incorporation of high charge transport materials such as graphene into composite materials, together with judicious materials selection and nanostructuraltuning, will enable breakthrough in materials performance. Zero-dimensional (0D) graphene quantum dots (GQDs) exhibit distinctive electronic and optical properties owing to their large edge effects and quantum confinement.We have prepared graphene quantum dots composite materials which showed significantly enhanced biofilm resistant properties4 and enhanced PEC hydrogen evolution.

Photon upconversion in lanthanide (rare-earth) nanomaterials is ananti-Stokes process when two or more lower energy photons (typically in the near-infrared region) are sequentially absorbed (excitation),leading to the emission of light at shorter wavelengths (typically ranges from UV to visible to near-infrared). We haveengineered lanthanide-based nanostructures with multiple functionalities, and demonstrated their potential applications in simultaneous near-infrared (NIR) activated upconversionoptical imaging5,6, X-ray Computed Tomography (CT)7and magnetic resonance imaging (MRI)8-10. By encasing the lanthanide-based nanocrystalswith a nitrogen-doped TiO2 photosensitizer and functionalizing with a cancer-targeting antibody, our lab has innovated anovel photo-enablednanodevicewhich wasconferred with targeted anti-tumor property and activated by NIR irradiation (808 and 980 nm), which is non-phototoxic and havea deeper tissue penetration (~5 cm, 1 W/cm2)11. This work is currently supported by Singapore National Research Foundation, and is collaborated with clinicians fromSingapore National Skin Centre, with a goal to translatelanthanide upconversion-based technology into novel tools and devices for cancer immunotherapy.

**Reference**

**1.**Ziming He, Hung Phan, Jing Liu, Thuc-Quyen Nguyen, and **Timothy Thatt Yang Tan\*,** Understanding TiO2 Size-Dependent Electron Transport Properties of a Graphene-TiO2Photoanode in Dye-sensitized Solar Cell Using Conducting Atomic Force Microscopy***Advanced Materials***, 2013 25 47 p6900

**2.**ZM He,GH Guai, J Liu, CX Guo, SCJ Loo, CM Li, **TTY Tan\***, Nanostructure control of graphene-composited TiO2 by a one-step solvothermal approach for high performance dye-sensitized solar cells, ***Nanoscale***, 2011, 3 (11), 4613 – 4616.

**3.**Ziming He,Jing Liu,Yan Qiao,Chang Ming Li and **Timothy Thatt Yang Tan**\*, Architecture engineering of hierarchically porous chitosan/vacuum-stripped graphene scaffold as bioanode for high performance microbial fuel cell, ***Nano Letters*** 2012, 12 (9) p4738

**4.**Zeng et al, “Graphene Oxide Quantum Dots Covalently Functionalized PVDF Membrane with Significantly-Enhanced Bactericidal and Antibiofouling Performance,” Scientific Reports, *in press*.

**5.**Gautom Kumar Das and **Timothy Thatt Yang Tan\*** “Rare-Earth Doped and Co-Doped Y2O3 Nanomaterials as Potential Bio-Imaging Probe” ***J. Phys. Chem. C****,* 2008, 112 (30), 11211–11217.

**6.**Gautom Kumar Das,Yan Zhang, Loyola D’Silva, ParasuramanPadmanabhan, Boon Chin Heng, Joachim Say Chye Loo, Subramanian Tamil Selvan,Kishore K. Bhakoo, and **Timothy Thatt Yang Tan\***, Single-Phase Dy2O3:Tb3+ Nanocrystals as Dual-Modal Contrast Agent for High Field Magnetic Resonance and Optical Imaging, ***Chemistry of Materials*** 2011**,** *23* (9), pp 2439–2446

**7.**Wei Wei, Yan Zhang, Rui Chen, Julian Goggi, Na Ren, Ling Huang, Kishore K. Bhakoo, Handong Sun, **Timothy Thatt Yang Tan**\* “Cross Relaxation Induced Pure Red Upconversion in Activator- and Sensitizer-Rich Lanthanide Nanoparticles” ***Chemistry of Materials***2014, 26 (18) p5183**.**

**8.**Yan Zhang,Gautom Kumar Das,VimalanVijayaragavan, Qing Chi Xu,Parasuraman Padmanabhan, Kishore K. Bhakoo,and Subramanian Tamil Selvan,*\****Timothy Thatt Yang Tan\****,* “Smart” Theranostic Lanthanide Nanoprobes with Simultaneous Upconversion fluorescence and Tunable T1-T2 Magnetic Resonance Imaging Contrast and Near-Infrared Activated Photodynamic Therapy, ***Nanoscale***, 2014, 6 12609.

**9.**Yan Zhang, Jing Dong Lin, VimalanVijayaragavan, Kishore K. Bhakoo, and **Timothy Thatt Yang Tan\***, Tuning sub-10 nm single-phase NaMnF3nanocrystals as ultrasensitive hosts for pure intense fluorescence and excellent T1 magnetic resonance imaging, ***Chem. Commun*.**, 2012,48, 10322-10324.

**10.**Zhang, W Wei, GK Das, **TTY Tan**\*, “Engineering Lanthanide-based Materials for Nanomedicine”, ***Journal of Photochemistry and Photobiology C: Photochemistry Reviews***, 2014, 20 p71-96.

**11.**Qing Chi Xu, Yan Zhang, Ming Jie Tan, Yang Liu, Shaojun Yuan, Cleo Choong, Nguan Soon Tan, **Timothy Thatt Yang Tan**\* “Anti-cAngptl4Ab-conjugated N-TiO2/NaYF4:Yb,Tm Nanocomposite for Near Infrared-Triggered Drug Release and Enhanced Targeted Cancer Cell Ablation” ***Advanced Healthcare Materials****,* 2012 1 (4) p470.