Nanophotonics and Plasmonic Hot Electrons for the Production of Solar Fuels

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BACKGROUND

1. Photonic crystals are composed of periodic dielectric nanostructures with oscillatory dielectric constants. The periodic nature of these systems influences photon propagation in a manner similar to electron motion in semiconductor crystals. Consequently, various interesting optical characteristics and phenomena including the photonic band gap (PBG) as well as the inhibition of spontaneous emission can be observed.
2. Plasmonic systems exploit "hot electrons" from the resonant interaction of light with the collective and coherent motion of electrons in metal nanostructures, to enhance and support photocatalytic activity.

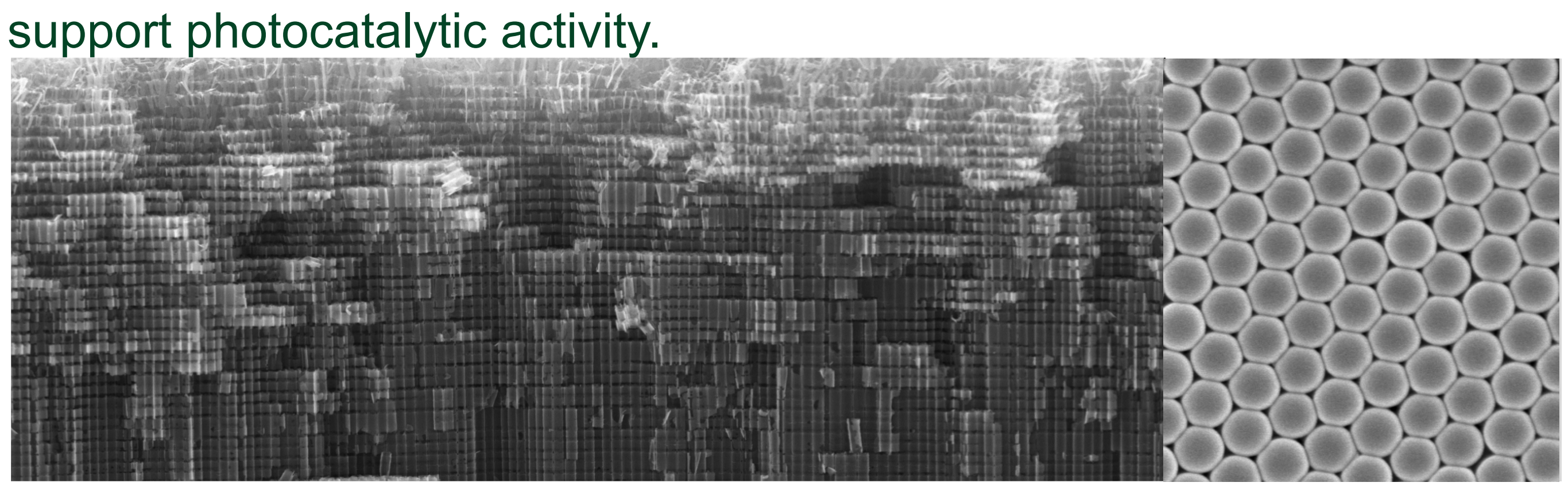

Fig.1

AIMS AND OBJECTIVES

Incorporating Nanophotonics and Plasmonics in the Photoreduction of CO_2

Our research focuses on the utilization of suitable photocatalysts, and their incorporation in hybrid plasmonic nanostructures, such as photonic crystals, to promote efficient solar harvesting. Lumerical FDTD simulations provide a healthy vantage point from which the predictive design of said hybrid structures, and their optical properties can be analyzed, while exploiting hot electrons to improve photocatalytic performance efficiencies. This is based on a working hypothesis that PBG provides for optimal light trapping at resonance wavelengths that excite hot electrons in metallic nanostructures

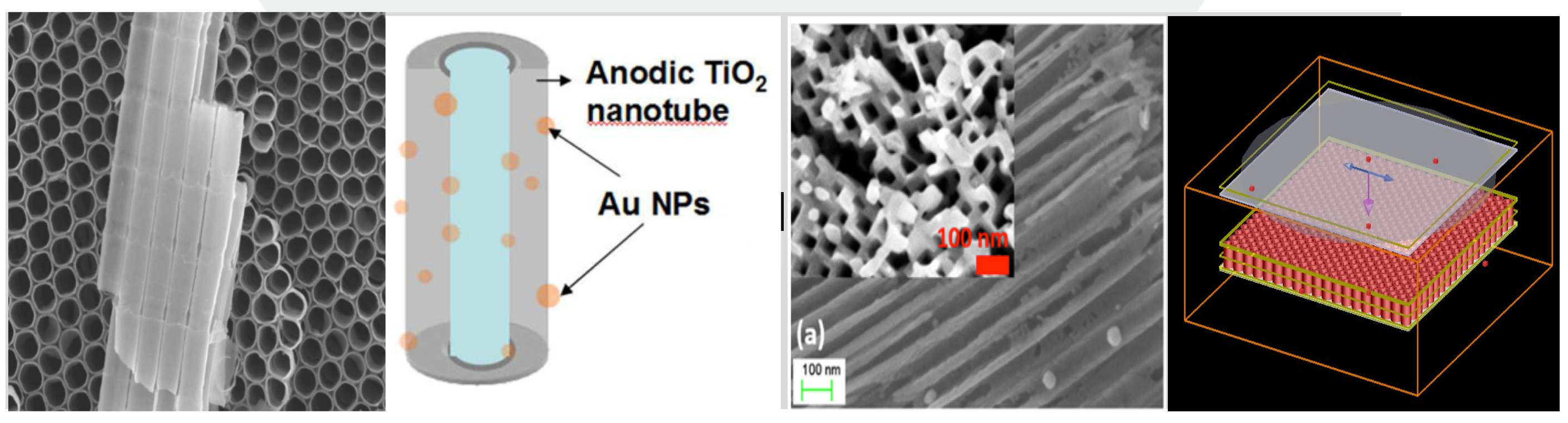

Fig.2

RESULTS

Visible Light Harvesting and Production of Solar Fuels

1. Lumerical FDTD simulations assist in analyzing the predictive optical characterization of various hybrid plasmonic nanostructures (Fig. 3a & 3b) providing a measure of comparative assessment on selective nanostructures that are fabricated at the Shankar lab, for example, the measurement of plasmon resonance in gold nanoparticles (Fig. 3c), while providing for analysis of novel structures that show promise and potential for efficient photocatalytic light harvesting.
2. Gold nanoparticles decorated TiO_2 nanotube arrays have provided for substantially improved photocatalytic activity, enhanced nonlinear optical coefficients, and increased light harvesting. The high Q-factor plasmonic resonance of gold nanoparticles at a wavelength of ~590 nm is directly observed, and agrees with FDTD simulation results. Further research has indicated that Ti-Au nanocomposites are highly promising in photoelectrochemical water splitting under 550 nm LED illumination.
3. Our Periodically Modulated TiO_2 Nanotubes (PMTiNT) also provide outstanding photoactivity. Coupling bimetallic coatings with these PMTiNT, we have achieved remarkable photoreduction of CO_2 to hydrocarbons (~166 μmol·g^{-1}·h^{-1}).

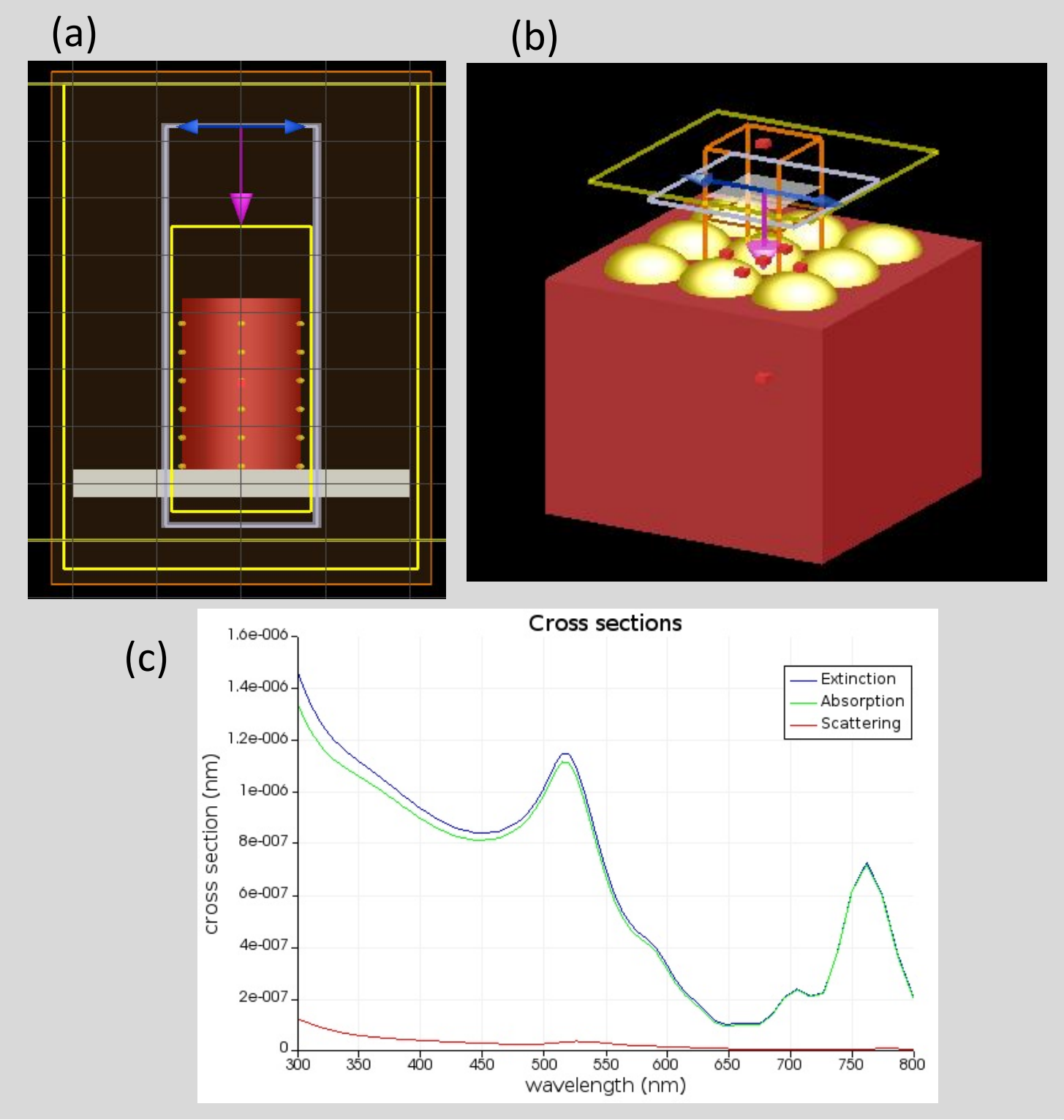

Fig.3

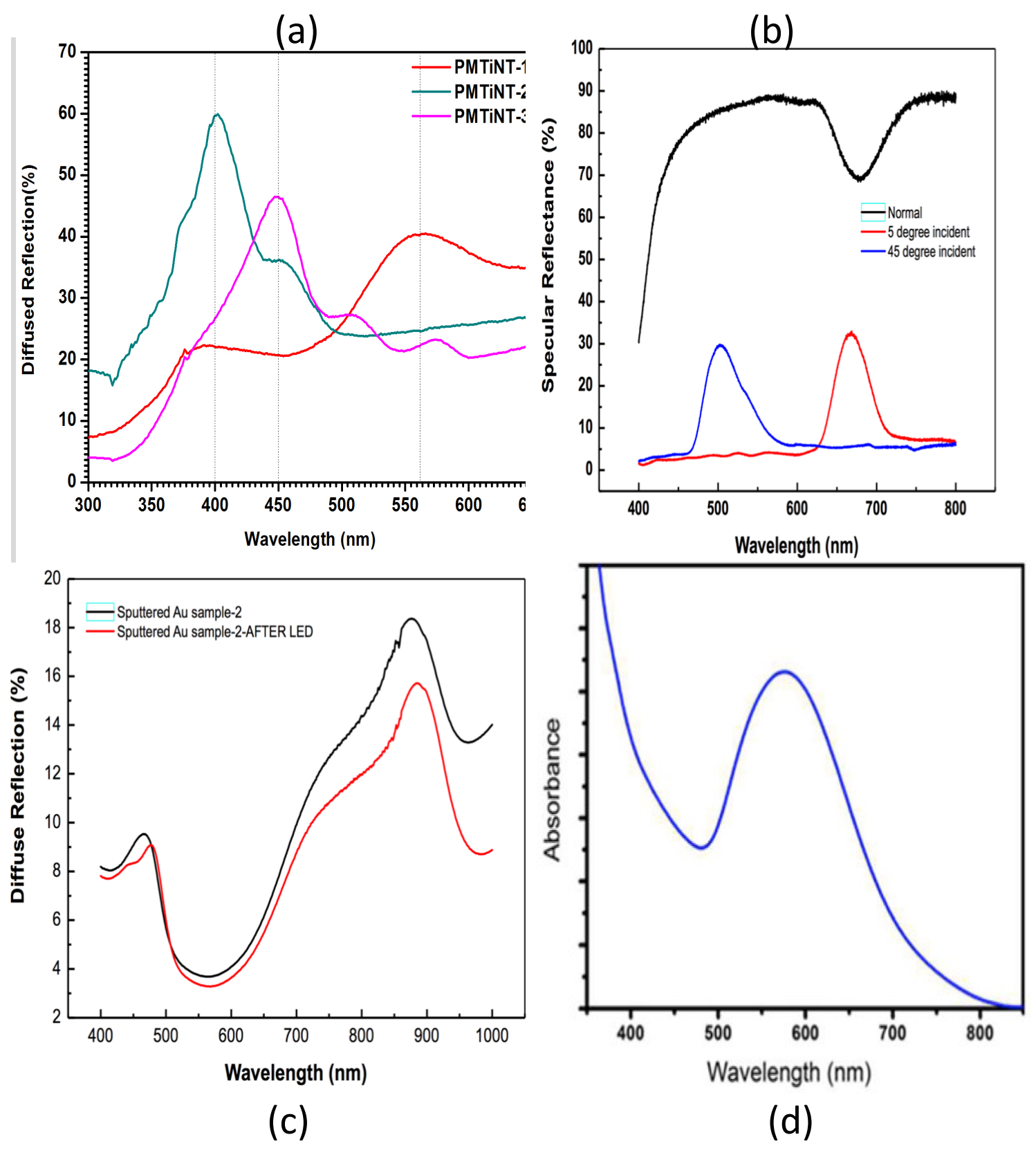

Fig.4

FUTURE DIRECTIONS

1. Further progress in advanced Lumerical FDTD simulations transitioning from isolated nanostructures to complex hierarchical nanosystems in arrays and complexes, from which selective effective architectures can be chosen and facilitated for fabrication.
2. Advanced fabrication methods including Atomic Layer Deposition (ALD) and Glancing Angle Deposition(GLAD), are under consideration for utilization in the future fabrication of complex nanostructures such as inverse opal 3D photonic crystals, helical nanorod arrays.
3. Exploiting other materials for high activity photocatalysts including but not limited to Titanium Nitride, Zinc Oxide, Nickel Oxide, Carbon Nitride, Cellulose nanocrystals and etc. This will be supplemented by further research on suitable plasmonic materials that can help take advantage of plasmonic resonance mechanisms in nanophotonics.
4. Better light management for solar energy harvesting and more applications by utilizing nanophotonics and plasmonic resonance phenomena, such as CO_2 photoreduction, photoelectrochemical water splitting, dye degradation, solar cells, SERS and etc.

PARTNERS

1. Prof. Ken Cadien research group, in the Chemical & Materials Engineering Dept. at the University of Alberta, is helping us with ALD ultra-thin high quality metal oxide conformal coatings on photonic crystal platforms.
2. Prof. Jingli Luo group in Chemical & Materials Engineering Building at the University of Alberta: We are collaborating on photoelectrochemical CO_2 reduction using semiconductor nanomaterials.
3. Prof. Jon Veinot Group in the Department of Chemistry at University of Alberta: They are providing us silicon and germanium nanocrystals for use as sensitizers to broaden the visible light absorption of TiO_2.
4. Shankar Group graduate students received $20,000 from CMC Microsystems for research projects by writing funded proposals.

FES PROJECT OVERVIEW

T12:P02 Artificial Photosynthesis Using Semiconductor Nanomaterials:

Plasmonic photocatalysts boost performance through visible light sensitization, vibrational activation of adsorbed reactants and the amplification of local electromagnetic fields. Plasmon-enhanced photocatalytic systems focus on taking advantage of "hot electrons", a result of the resonant interaction of light with the collective and coherent motion of electrons in metal nanostructures such as noble metal nanoparticles, to further enhance and support photocatalytic activity including sunlight-driven CO_2 photoreduction and water-splitting. We have built new platforms to exploit hot electrons for photocatalysis that also benefit from photonic crystal mediated light trapping effects. Periodically Modulated TiO_2 NanoTubes (PMTiNTs) provide for a high active surface area, facile heterojunction formation with noble metal nanoparticles, efficient light trapping and slow photon propagation, which are optimally suitable for incorporation with plasmonic resonances, to achieve effective solar light harvesting and high photocatalytic performance. The unique structure and electronic properties of PMTiNTs also offer opportunities to engineer selectivity in the distribution of products from CO_2 reduction.

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