## List of Figures

Figure 1.1: The classification of nanostructured materials based on quantum confishape, and size.	nement, 3
Figure 1.2: The classification of nanostructured materials based on the materials	4
Figure 1.3: The application of nanostructured materials	5
Figure 1.4: The properties of nanostructure materials	9

*Figure 1.5*: The properties of nanostructure semiconductor materials under UV excitation. 10

*Figure 1.6:* The classification plasmonic nanostructure with semiconductor (a) the metal NPs embedded in the semiconductor (ii) the metal NPs are buried in the semiconductor, and (iii) isolated from the semiconductor 11

**Figure 1.7:** Surface-plasmon decay, generation and injection of hot-electron in the metallic nanostructure, (a), Localized surface plasmons can decay radiatively via reemitted photons and non-radiatively via excitation of hot electrons, (b) In plasmonic nanostructures, non-radiative decay can occur through or through interband excitations resulting from transitions between other bands (for example, d bands) and the conduction band or intraband excitations within the conduction band, (c) Plasmonic energy conversion at the metal (Ag)-semiconductor (n-TiO<sub>2</sub>) interface. 12

**Figure 1.8:** (a) Basic principle of water splitting for  $H_2$  generation (b) The complete circuit of the  $H_2$  generation mechanism (c) the band structure of some semiconductor with redox potential. 15

**Figure 1.9:** (a) The ideal band edge positioning of  $H_2$  and  $O_2$  evolution photo-catalysts (b) The band edge positions of pure metal oxide (TiO<sub>2</sub>) with respect to water redox potential towards  $H_2$  production. 16

*Figure 1.10:* The type of photodetector (a) Photoconductor, (b) Photodiode, and (c) Phototransistor 19

Figure 2.1: The schematic steps for the substrate cleaning process	25

Figure 2.2: The schematic steps for the LTO solution preparation	. 27
------------------------------------------------------------------	------

**Figure 2.3:** Schematic growth process of in-situ grown Ag-TiO<sub>2</sub> thin film in five successive steps (a) TiO<sub>2</sub> thin film on FTO coated glass by spin coating of sol-gel precursor or TiO<sub>2</sub> NP followed by annealing (b) dip coating of precursor of LTO thin film (c) annealing of precursor film at 550 °C for 1 hour to obtain polycrystalline Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>thin film (d) ion exchange process to exchange Li<sup>+</sup> ion of Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> by  $Ag^+$  of solution. (e) Reduction process that converts  $Ag^+$  to  $Ag^o$  to form Ag-TiO<sub>2</sub> thin film containing Ag NCs inside TiO<sub>2</sub> thin film.

**Figure 2.4:** Schematic growth process of in-situ grown  $Ag_2S$ -TiO<sub>2</sub>thin film in four successive steps (a) Dip coating precursor of LTO on the FTO, TiO<sub>2</sub> (sol-gel)/FTO and TiO<sub>2</sub> (NPs)/FTO) coated glass substrate followed by annealing respectively at 550 °C for 1 hour to obtain polycrystalline Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> thin film (b) for ion exchange process to exchange Li<sup>+</sup> ions by  $Ag^+$  (c) in this step sample dip for sulfurization process that convert  $Ag^+$  to Ag and to form  $Ag_2S$  inside TiO<sub>2</sub> thin film (d) this thin film wash with DI water to remove extra Na<sub>2</sub>S solution from the samples. 5

**Figure 2.5:** Schematic growth process of in-situ grown  $Cu_2S$  (NPs)-TiO<sub>2</sub> thin film in three successive steps (a) LTO precursor coated on the three different including FTO, TS/FTO, and TN/FTO, ZnO coated glass or glass substrate by dip coating followed by annealing respectively at 550 °C for 1 hour to obtain polycrystalline Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> thin film (b) for ion exchange process to exchange Li<sup>+</sup> ions by metal ion (Li<sup>+</sup>  $\leftarrow Cu^+$ ), from metal solution) to form Cu<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> thin film. (c) For sulfurization process that converts Cu<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> to Cu<sub>2</sub>S-TiO<sub>2</sub> thin films respectively and these thin films containing Cu<sub>2</sub>S NCs inside TiO<sub>2</sub> thin film (d), these samples wash with DI water to remove extra Na<sub>2</sub>S solution from the surface 32

*Figure 2.6:* The schematic diagram of IPCE or EQE, Responsivity measurements for PEC cell or photodetector 35

**Figure 2.7**: Schematic representation of three-electrode systems for I-V Characterization. In this figure, three different photoanodes used as a working electrode (Ag-TiO<sub>2</sub>, Ag<sub>2</sub>S-TiO<sub>2</sub>, and Cu<sub>2</sub>S-TiO<sub>2</sub>), platinum as a counter electrode and Ag/AgCl as a reference electrode. 2

*Figure 3.1*: (a) The XRD pattern of LTO and Ag-TiO<sub>2</sub>, (b) and normalized UV-VIS absorption spectra of different photoanodes coated with TiO<sub>2</sub>, Ag-TiO<sub>2</sub>, Ag-TiO<sub>2</sub>/TiO<sub>2</sub> solgel, and Ag-TiO<sub>2</sub>/TiO<sub>2</sub>NP, respectively. (c) The images of Ag-TiO<sub>2</sub> and TiO<sub>2</sub> thin films, (d) UV-VIS absorption spectra of Cu-TiO<sub>2</sub> thin film. 41

**Figure 3.2** The microstructure and surface morphology of the (a) Ag-TiO<sub>2</sub> (dip coated) thin film on Si substrate (b) Particle size distribution of Ag-NP (c) Energy dispersive spectra of Ag-TiO<sub>2</sub> thin film, an elemental composition that obtained from EDS shown in the inset. (d) EDS mapping of Ag-TiO<sub>2</sub> thin film (i) original SEM image (ii) for O, (iii) for Ag, and (iv) for Ti 42 **Figure 3.3** (a) Transmission electron microscope image of Ag NPs-TiO<sub>2</sub> (b) particle size distribution of Ag NP, (c) high-resolution image of Ag NP-TiO<sub>2</sub>, the green circle indicates the lattice spacing d-fringe of Ag and yellow circle for TiO<sub>2</sub> (d) selected area electron diffraction (SAED) pattern of Ag NP-TiO<sub>2</sub> 43

*Figure 3.4: High-resolution XPS spectra of Ag-TiO*<sub>2</sub> *sample (a) Ag 3d (b) Ti 2p and (c) O Is. (d) the full scan of XPS for the Ag-TiO*<sub>2</sub> *thin film* 44

**Figure 3.5** (a) Current density vs. (V vs.RHE) potential of different Ag-TiO<sub>2</sub> thin film under light and dark in 1 M KOH solution (b) schematic diagram of photocatalytic water splitting mechanism by Ag-TiO<sub>2</sub> based photoanode due to the SPR effect of Ag NP. (c) IPCE data for different photoanode in the range of 350 nm to 800 nm under -1.0V external bias with 1 M KOH electrolyte solution. Inset shows the magnified IPCE data in the wavelength range from 390 nm to 510 nm. (d) Mott–Schottky (M-S) plot for different photoanodes in 1 kHz operation under dark condition. 47

**Figure 3.6**: (a) Current density vs. (V vs. RHE) potential of Ag-  $TiO_2$  and  $TiO_2$  thin film under light and dark in 1 M KOH solution, (b) The EIS spectra for Ag- $TiO_2$  and  $TiO_2$ photoanodes. (c) The EIS spectra of three different Ag- $TiO_2$  photoanodes. The inset shows the equivalent circuit. (d) Volumetric hydrogen generation over the time in five different cycles for Ag- $TiO_2/TiO_2$  NPs/FTO photoanode under one sun white light irradiation. 53

**Figure 3.7**(*a*) Photostability tested for Ag-TiO<sub>2</sub>/TiO<sub>2</sub> NPs/FTO thin film under continues light illumination in 1M KOH solution. (b) Time response of different photoanode under light (100 mw/cm<sup>2</sup>) and dark with -0.3 V external bias, (i) for TiO<sub>2</sub>/FTO (ii) for Ag-TiO<sub>2</sub>/TiO<sub>2</sub> sol-gel /FTO (iv) for Ag-TiO<sub>2</sub>/TiO<sub>2</sub> NPs/FTO. 54

**Figure 4.1**: (a) The XRD pattern of bare TiO<sub>2</sub>, LTO and Cu<sub>2</sub>S-TiO<sub>2</sub> (CSTO) thin films on the FTO substrate (b) Normalized UV-VIS absorption spectra of TiO<sub>2</sub> only and Cu<sub>2</sub>S-TiO<sub>2</sub> coated with three different substrate including FTO, TS/FTO, and TN/FTO nanocomposite thin films (b-d) Taue plot from UV-VIS absorption spectra of (b)TiO<sub>2</sub> only (c)Cu<sub>2</sub>S-TiO<sub>2</sub> coated thin films 59

Figure 4.2 The microstructure and surface morphology of the (a)  $Cu_2S$ -TiO<sub>2</sub> (dip coated) thin film on Si substrate (b) Particle size distribution of Ag-NP (c) Energy dispersive spectra of  $Cu_2S$ -TiO<sub>2</sub> thin film, an elemental composition that obtained from EDS is shown in the inset. (d) EDS mapping of  $Cu_2S$ -TiO<sub>2</sub> thin film (i) Cu(ii) for S, (iii) for Ti, and (iv) for O.

**Figure 4.3:(a)** Transmission electron microscope image of  $Cu_2S$  NP-TiO<sub>2</sub> (b) size distribution of  $Cu_2S$  NP-TiO<sub>2</sub> (c) high resolution image of  $Cu_2S$  NP-TiO<sub>2</sub>, white circle indicates the lattice d-fringe of  $Cu_2S$  and magenta circle for TiO<sub>2</sub> (d) selected area electron diffraction (SAED) pattern of  $Cu_2S$  NP-TiO<sub>2</sub>. 61

*Figure 4.4*: (a) The Image of the samples, bare  $TiO_2$ , and  $Cu_2S$ - $TiO_2$  (CSTO) thin films on the FTO substrate, (b) Survey scane of XPS for the  $Cu_2S$ - $TiO_2$  thin film 63

*Figure 4.5*: *High-resolution XPS spectra of*  $Cu_2S$ - $TiO_2$  *sample (a)* Cu 2p *(b)* S 2p *(c)* Ti 2p *and (d)* O 1s. 63

**Figure 4.6 (a-b)** Current density vs. (V vs. RHE) potential of different Cu<sub>2</sub>S-TiO<sub>2</sub> thin film under light and dark in 1 M KOH solution with three different substrates (a) for HER evolution, (b) for OER evolution (b) Schematic charge transfer process of Cu<sub>2</sub>S-TiO<sub>2</sub> interface and H<sub>2</sub> evalution, (d) IPCE of bare TiO<sub>2</sub>, Cu<sub>2</sub>S-TiO<sub>2</sub> with three different substrate. 64

**Figure 4.7**: The comparative study of (a) current density vs. (V vs. RHE) potential of bare TiO<sub>2</sub> and Cu<sub>2</sub>S-TiO<sub>2</sub> thin film (b) EIS data of bare TiO<sub>2</sub> and Cu<sub>2</sub>S-TiO<sub>2</sub> thin film (c) electrochemical impedance spectroscopy (EIS) measurement for three different Cu<sub>2</sub>S-TiO<sub>2</sub>photoanodes under light and dark conditions in 1 M KOH solution (d) The Mott–Schottky (M-S) plot for different photoanodes in 1 kHz operation under dark condition inset show the positive slop. 69

**Figure 4.8:** (a)The time response of different photoanodes (b) the photostability of  $Cu_2S$ -TiO<sub>2</sub>/TiO<sub>2</sub> sol-gel, (c) The volumetric hydrogen generation under one sun white light irradiation over the time for three different photoanodes. (d) For five successive cycle by  $Cu_2S$ -TiO<sub>2</sub>/TiO<sub>2</sub> NPs photoaode. 70

**Figure 5.1**: (a) The XRD pattern of bare  $TiO_2$ , LTO and  $Ag_2S$ - $TiO_2$  thin films (b) Normalized UV-VIS absorptionspectra of  $TiO_2$  and  $Ag_2S$ - $TiO_2$ nanocomposite thin films. 77

Figure 5.2 The surface morphology of the (a)  $Ag_2S$ -TiO<sub>2</sub> (dip coated) thin film on FTO coated glass substrate (b) Particle size distribution of  $Ag_2S$ -TiO<sub>2</sub> NPs (c) Energy dispersive spectra of  $Cu_2S$ -TiO<sub>2</sub> thin film, an elemental composition that obtained from EDS is shown in the inset. (d) EDS mapping of  $Ag_2S$ -TiO<sub>2</sub> thin film (i)O (ii) for S, (iii) for Ag, and (iv) forTi.

**Figure 5.3**(a) Transmission electron microscope image of  $Ag_2S$  NP-TiO<sub>2</sub> (b) high resolution image of  $Ag_2S$  NP-TiO<sub>2</sub>, green circle indicates the lattice d-fringe of  $Ag_2S$  and pinck circle for TiO<sub>2</sub>.(c) Slected area diffraction pattern of  $Ag_2S$  NPs-TiO<sub>2</sub> (d) Size distribution of  $Ag_2S$  NPs-TiO<sub>2</sub>. 79

*Figure 5.4*:*High-resolution XPS spectra of Ag*<sub>2</sub>*S-TiO*2 *sample (a) Ag 3d (b) O 1s. (c) Ti 2p and (d) S 3p* 80

**Figure 5.5** (a) Current density vs. (V vs. RHE) potential of different  $Ag_2S$ -TiO<sub>2</sub> thin film under light and dark in 1 M KOH solution (b) schematic diagram of photocatalytic water splitting mechanism by  $Ag_2S$ -TiO<sub>2</sub> based photoanode (c) IPCE data for different photoanode in the range of 350 nm to 800 nm under -1.0V external bias with 1 M KOH electrolyte solution. (d) The Mott–Schottky (M-S) plot for different photoanodes in 1 kHz operation under dark condition. 83

**Figure 5.6:**(a) The comparative study of current density vs. (V vs. RHE) potential of bare TiO<sub>2</sub> and Ag<sub>2</sub>S-TiO<sub>2</sub> thin film (b) The EIS spectra TiO<sub>2</sub> and Ag<sub>2</sub>S TiO<sub>2</sub> photoanodes. The inset shows the equivalent circuit, (c) The electrochemical impedance spectroscopy (EIS) measurement for three different Ag<sub>2</sub>S-TiO<sub>2</sub>photoanodes under light and dark conditions in1 M KOH solution (d) The images of the Ag<sub>2</sub>S-TiO<sub>2</sub> and TiO<sub>2</sub> (NP) photoanodes 87

**Figure 5.7:** (a) Time response of same photoanode with different substrates under light (100 mW/cm<sup>2</sup>) and dark with -0.5 (b)Photostability tested for  $Ag_2S$ -TiO<sub>2</sub>/TiO<sub>2</sub> sol-gel/FTO photoanode V external bias in 1M KOH medium, the volumetric hydrogen generation under one sun white light irradiation with the time (c) for three different photoanodes. (d) in five successive cycles by  $Ag_2S$ -TiO<sub>2</sub>/TiO<sub>2</sub> NP photoanode 88

*Figure 6.1:* The XRD pattern of (a) Cu<sub>2</sub>S- TiO<sub>2</sub> and pure LTO (b) UV-Vis spectra of LTO, TiO<sub>2</sub>, and Cu<sub>2</sub>S- TiO<sub>2</sub> thin films. 95

**Figure 6.2.** (a) SEM image of  $Ag_2S$ -TiO<sub>2</sub> thin film b) transmission electron microscope image of  $Cu_2S$  NP-TiO<sub>2</sub> b) high-resolution image of  $Cu_2S$  (NP)-TiO<sub>2</sub>, the greenish circle indicates the lattice d-fringe of  $Cu_2S$  and pink circle for TiO<sub>2</sub>. d) Selected area diffraction pattern of  $Cu_2S$  (NP)-TiO<sub>2</sub>. 96

**Figure 6.3:** Size distribution of  $Ag_2SNP$  inside  $TiO_2$  thin film from (a) SEM image,(b) TEM image,(c)Photoconductivity of Glass/ZnO/TiO\_2-Cu\_2S/Al, Glass/ZnO/LTO/Al, Glass/ZnO/Al under dark and light conditions,(d) The elemental and composition analysis show the spectrum and table of Cu\_2S-TiO\_2. 97

**Figure 6.4:**(*a-b*) Semi log plot shows the photoconductivity of a)Glass/ZnO/TiO<sub>2</sub>-Cu<sub>2</sub>S/Al, b)Glass/ZnO/Al under dark and light conditions. Band alignment, band bending, and charge separation of (c) Al/Cu<sub>2</sub>S-TiO<sub>2</sub>/ZnO (d) Al/ZnO heterostructure photodetector devices. 100

**Figure 6.5:** Cu<sub>2</sub>S-TiO<sub>2</sub>/ZnO lateral heterojunction photoconductor device performance (a) External quantum efficiency (EQE) vs. Wavelength, (b) Extracted responsivity vs wavelength (c) Extracted detectivity vs wavelength and d) Transient time response of these same set of devices structures Glass/ZnO/TiO<sub>2</sub>-Cu<sub>2</sub>S/Al, Glass/ZnO/LTO/Al, and Glass/ZnO/Al. 101