Hybrid InN/TiO_2 Nanoparticle Films as Blue/Near UV Light Emitters

Dye sensitized solar cells cost relatively low attributed to the high efficiency of light-to-electric energy conversion. The factors including low cost, various applications and photo stabilities of TiO_2 attract the study for photo induced phenomena of TiO_2 related nano-materials. The enhancement of photoluminescence from anatase TiO_2 films covered by InN nanoparticles using plasma-enhanced chemical vapor deposition was observed in this research. The measured UV-Visible absorption spectra indicate that the InN particles increase in absorption in the visible light region and may sensitize the TiO_2 films.

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TiO_2 has been studied widely due to its potential applications in photo-electrolysis. Many investigations have focused on the enhancement of the photo-response and improvement of the photo-activity of TiO_2. Hence, TiO_2-based materials are pivotal to the fields of biomaterials, photo-catalysis, and dye sensitized solar cells (DSSCs). As it is an indirect-band semiconductor, band-edge luminescence from TiO_2 is very difficult to observe. The emission probabilities of indirect transitions are lower than those for direct transitions. In this work, we report blue/near UV photoluminescence (PL) of TiO_2 thin films covered with InN nanoparticles. The PL emission of TiO_2 thinfilms can be significantly enhanced without largely changing the emission wavelength by depositing InN particles of an appropriate thickness. Complete characterization of these materials was performed using scanning electron microscopy (SEM), X-ray diffraction (XRD), UV-Visible (UV-Vis) absorption spectroscopy, and PL.

A comparison of PL spectra of various other related nanoparticles obtained under the same conditions is demonstrated in Fig. 1. The PL spectrum of InN nanoparticles showed no emission in the spectral region 300-600 nm, as shown in Fig. 1(a), but substantial emission at around 600 and 660 nm which has been observed and assigned to donor-bound excitation from α-InN grains and band-edge emission respectively in previous literatures. A broad and weak emission was observed from the TiO_2 particles alone. This weak emission displayed obscure bands around 419 nm (2.96 eV) and 476 nm (2.50 eV). These were assigned to phonon incident lines and an oxygen defect trap exciton peak, respectively.

Compared to weak or near zero emissions from individual InN or TiO_2 nanoparticles, the PL spectrum obtained from InN/TiO_2 nanoparticles exhibits a strong blue/near UV emission with significant bands at 420 and 474 nm, a shoulder close to 400 nm and an onset near 300 nm. It can also be seen that the emission band features of InN/TiO_2 nanoparticles were similar to those of TiO_2 nanoparticles alone. PLE measurements were performed to provide further information

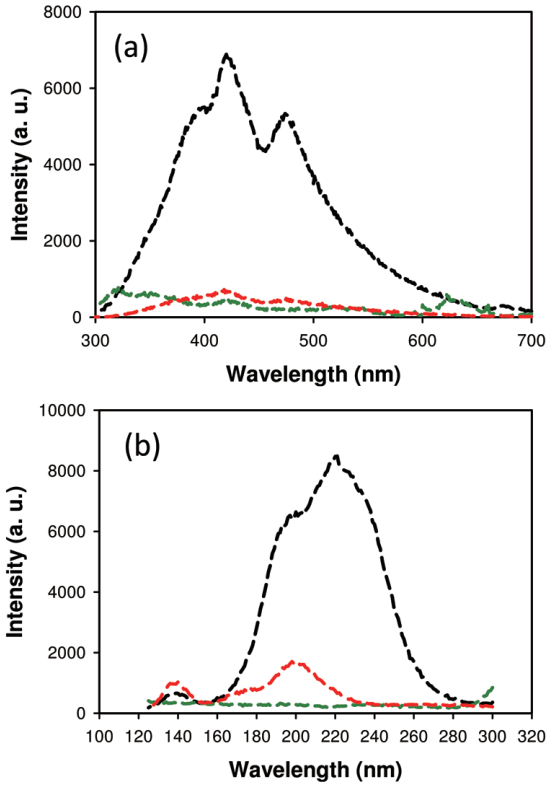

Fig. 1: (a) PL spectra and (b) PL excitation spectra of InN/TiO_2 (black), pure InN (red), and pure TiO_2 (green). The excitation wavelength of all nanomaterials for the PL spectra was set at 200 nm. The monitored emission of InN/TiO_2 and pure TiO_2 was set at 420 nm and 660 nm for pure InN.

regarding the electronic structures of these nanoparticles. The dotted black line in Fig. 1(b) shows the PLE spectrum of the InN/TiO_2 film, in which maximum emission occurs with excitation at 220 nm (5.64 eV). Comparing the strong signal observed from the InN/TiO_2 films, the TiO_2 particles exhibited a relatively flat and weak PLE spectrum, as shown in Fig. 1(b), whereas the PLE spectrum of InN particles exhibited clear bands which peaked at 200 and 139 nm.

The above control experiments clearly demonstrated the unusual enhanced emission intensity from the hybrid InN/TiO_2 nanoparticles. Moreover, PLE spectra of the two individual materials and the hybrid one indicated the importance of the interface between the InN and TiO_2 films, which may not only control the efficiency of the recombination of photo-induced electrons and holes, but also energy transfer. It has been proven that TiO_2 has a direct forbidden energy gap degenerated by an indirect allowed transition. The indirect allowed transition of TiO_2 controls its optical property near the absorption edge, and thus the PL intensity of TiO_2 is very weak. One way to enhance the PL intensity of TiO_2 is through energy transfer from upper layers of sensitizers, ie. InN nanoparticles. The absorption of InN nanoparticles induced the separation of electrons and holes (carriers). It is thought that the temporary carriers may induce transport to the TiO_2 film and enhance the localization of impurities and/or defect-trapped excitons. Strong PL emission of the TiO_2 anatase phase thin films was therefore observed. To examine our assumption of the emission mechanism, time-resolved experiments will need to be performed in the future.

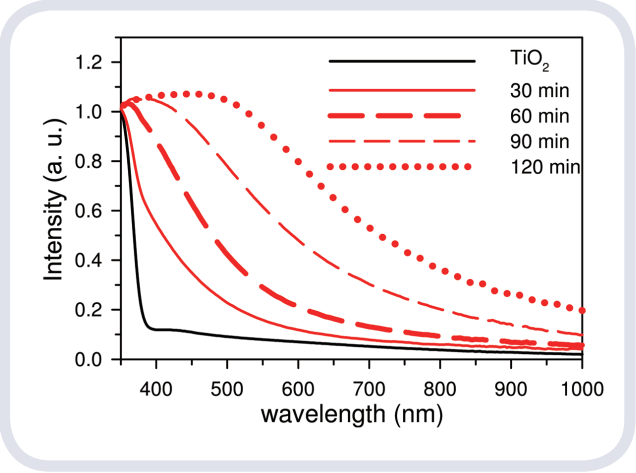

Fig. 2: UV–Vis spectra of a TiO_2 film and InN/TiO_2 films with various durations of deposition. The spectrum is normalized at 350 nm.

Figure 2 gives a comparison of UV–Vis spectra of TiO_2 and InN/TiO_2 films with varying periods of deposition. The absorption spectrum of pure TiO_2 nanoparticles showed a weak absorption in the visible light region and an increased absorption from 390 nm into the UV region. The absorption spectra of TiO_2 films with the addition of InN nanoparticles showed a remarkable enhancement of broad absorption in the visible light region and the absorption shifted toward the red as the deposition increased.

In summary, we have demonstrated the synthesis of a hybrid InN/TiO_2 nanoparticle film through a combination of sol-gel and plasma-enhanced chemical vapor deposition methods. The structure of the hybrid material was characterized via SEM and XRD. We also observed the intense emission of blue/near UV light from this hybrid nanomaterial. The UV-Vis and PLE spectra suggested that the enhanced PL emission of TiO_2 was activated through photo-induced delocalized carriers from the InN layer.[1]

Beamline 03A1
PLS end station

Reference

1. C.-W. Wu, C.-W. Lu, Y.-P. Lee, Y.-J. Wu, B.-M. Cheng, and M. C. Lin, J. Mater. Chem. **21**, 8540 (2011).

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