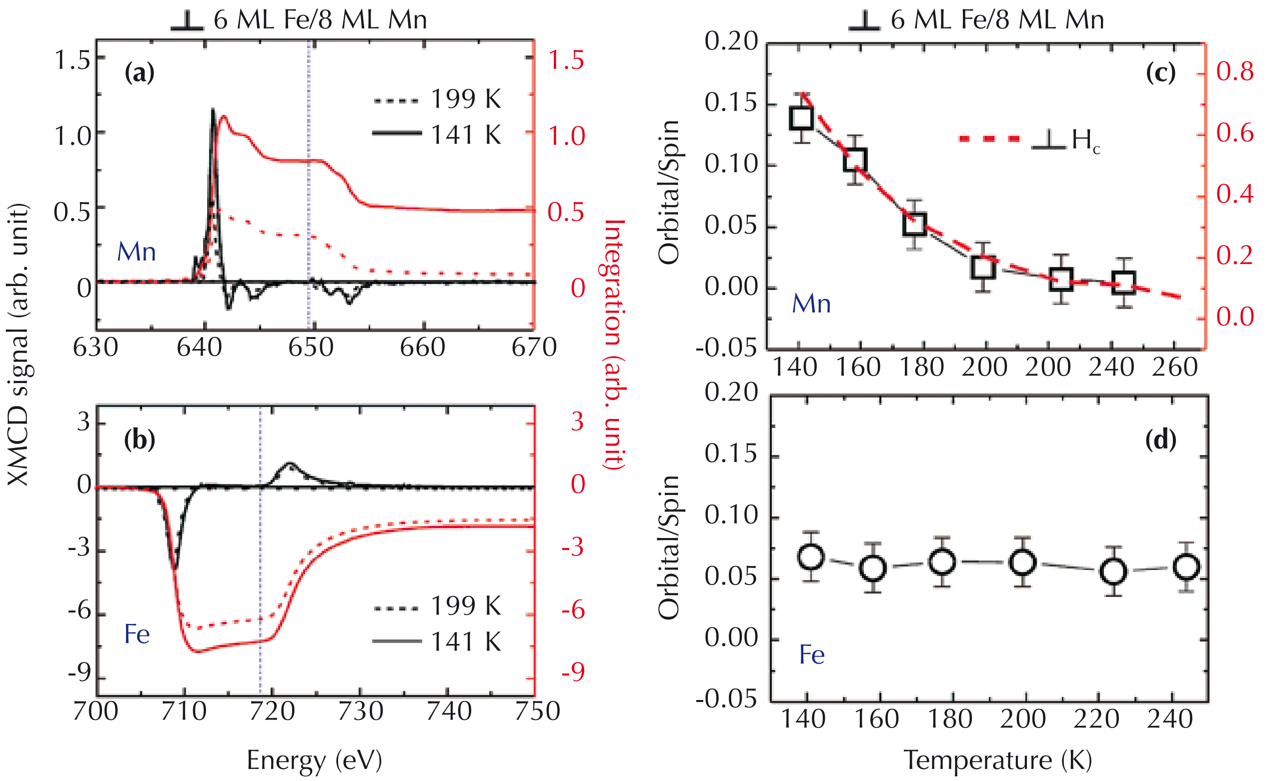

Fig. 3: (a) and (b): Curves represent Mn and Fe XMCD at 178 K and 199 K, respectively. (c) and (d): Ratio m_o/m_s of Mn and Fe moments, respectively, calculated from the XMCD curves; the red dashed line indicates H_c of a 6 ML Fe/8 ML Mn bilayer measured in the out-of-plane direction. (Reproduced from Ref. 4)

and exchange bias, but also indicates a new direction for the control of perpendicular magnetization in magnetic devices, which is the key to achieve a great recording density.

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Hydrogen Powers the Future

This report features the work of Hao Ming Chen and his co-workers published in Small ***9****, 2926 (2013).*

Hydrogen is regarded as a clean fuel because its only byproduct is water. The drawback is, however, that to generate hydrogen via water splitting requires the traditional fossil fuels. Splitting water in photoelectrochemical cells (PEC) with solar energy as fuel has therefore become an ultimate goal of sustainable energy. The impediment appears to be a lack of high-performance PEC electrodes. By recording X-ray absorption spectra at **BL01C1** of the TLS, researchers from National Taiwan University, Academia Sinica and NSRRC have demonstrated a novel plasmonic photoelectrode that exhibits a significantly enhanced production of solar hydrogen.

To meet future demands for energy without the combustion of fossil fuels depends on an efficient production of solar energy. The photolysis of water using semiconductors has been investigated as a clean process to convert renewable energy, by storing solar energy in chemical bonds such as those of hydrogen. Hydrogen that is produced by the splitting of water using solar energy is clearly attractive as a clean energy vector, and various attempts have been made to construct viable molecular and biomolecular devices to produce hydrogen. The development of an artificial mechanism of photosynthesis, based on splitting water into hydrogen and oxygen, is highly desirable. Hao Ming Chen indicates that the field of plasmonics has expanded rapidly because of the ease of tailoring and shape-dependent optical properties. Many materials have been found to have plasmonic applications, such as plasmonic lasers, surface-plasmon-enhanced light-emitting diodes, metamaterials, plasmon focusing, plasmon waveguides, among others. Chen and co-workers recently revealed that introducing plasmonic materials into a photochemical reaction can markedly enhance the photolytic response to split water with solar energy.[1] Chen further indicated that the mechanism of this enhancement is proposed to involve either charge transfer between metal and oxide or plasmon-induced heating and establishment of an electromagnetic field. “Understanding the mechanism of the plasmonic enhancement is a crucial aspect and useful for the future development of photovoltaic devices,” said Chen. “Distinguishing among independent photoresponses to solar radiation associated with various plasmonic effects is, however, a key challenge.”

For this purpose, Chen and co-workers overcame the challenge by exploiting three important strategies. First, a PEC was used as a platform rather than a photocatalyst in evaluating photoactivity, as a PEC can extract an electric signal directly from photoactive materials upon irradiation without the need to measure the production of gas. The splitting of water into hydrogen and oxygen directly by sunlight in a PEC is an ideal method to produce hydrogen that integrates the collection of solar energy with the electrolysis of water at a single photoelectrode. Accordingly, a PEC enables independent photoresponses to be associated with recognizable plasmonic effects. Second, a plasmonic photoelectrode is measured with illumination polarized along various axes because the localized plasmon oscillation depends on the polarization; these measurements were readily combined with a theoretical simulation to evaluate a plasmon-induced effect. Third, as a localized plasmonic oscillation generates an electromagnetic field at the surface of plasmon materials, modifying the interface between the plasmon metal and a semiconductor, it might alter the electronic structure of a semiconductor, to generate thereby a localized transition state. A paper on this subject “Plasmonic ZnO/Ag Embedded Structures as Collecting Layers for Photogenerating Electrons in Solar Hydrogen Generation Photoelectrode” reporting X-ray absorption spectra recorded at **BL01C1** at the TLS, was published in *Small*, 2013.[2] The research team included participants from National Taiwan University, Academia Sinica and NSRRC. Chen and co-workers from National Taiwan University designed a new fabrication strategy in which Ag plasmonics were embedded in the interface between ZnO nanorods; a conducting substrate was experimentally demonstrated using a plasmonic ZnO/Ag photoelectrode induced with a femtosecond laser.[2] These researchers demonstrated that this technique is applicable to generate patternable plasmonic nanostructures to improve their effectiveness in generating hydrogen. Such a plasmonic ZnO/Ag nanostructure photoelectrode represented a photocurrent of a ZnO-nanorod photoelectrode increased more than 85 % at 0.5 V. Both a localized surface plasmon resonance in the metal nanoparticles and plasmon polaritons propagating at the metal/semiconductor interface are available to improve the capture of sunlight and the collection of charge carriers. Plasmon-induced effects enhanced the photoresponse by simultaneously both improving optical absorbance and facilitating the separation of charge carriers.

According to their results,[2] an enhancement of the spectrum of incident-photon-to-current efficiency (IPCE) was found when the ZnO/Ag photoelectrode was used (Fig. 1(a)). Two possible mechanisms are involved – a scattering effect and a plasmonic effect. An enhancement at 350 nm was clearly observed in the IPCE spectra. At this wavelength, Ag shows strong electron damping and a lack of surface plasmon resonance. The other mechanism of enhancement is plasmonic-induced resonant-energy transfer (PIRET), as Ag particles served as nanoantennae and captured the energy of the incident waves at a plasmonic resonance. The enhancement about 420 nm is thus attributed to the presence of a plasmon-induced electromagnetic field, as an efficient wavelength of plasmonic resonance of Ag nanostructures is located in this region. This result agrees with the results of a finite-element simulation (inset in Fig. 1(a)), and with the intensity of the electric field calculated with a full-wave 3D Maxwell-equation solver. The results of simulation show a field enhancement of the Ag nanostructure at the surface of the ITO embedded in ZnO under irradiation at 410 nm. In addition, to simulate a real system of chemical reactions, all calculated modules were constructed according to the SEM image (Fig. 1(b)). Figure 1(c) shows the distribution of the intensity of the electric field corresponding to Fig. 1(b) under *x*-polarized illumination at wavelength

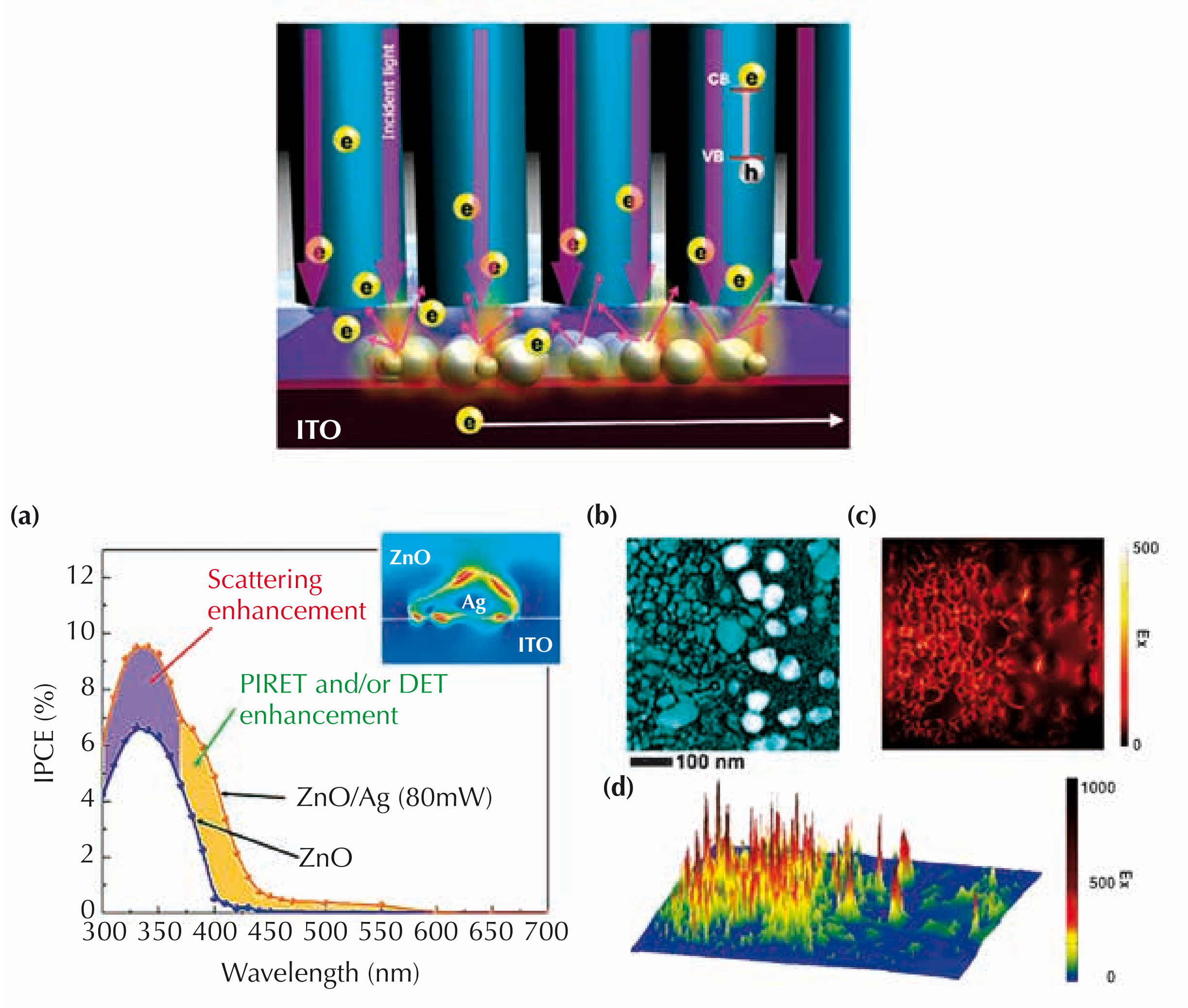

Fig. 1: (a) IPCE spectra. (b) SEM image of laser-treated Ag plasmonic nanostructures. (c) Corresponding maps of the distribution of the electric field. (d) Maps of hotspot distribution of panel (c). (Reproduced from Ref. 2)

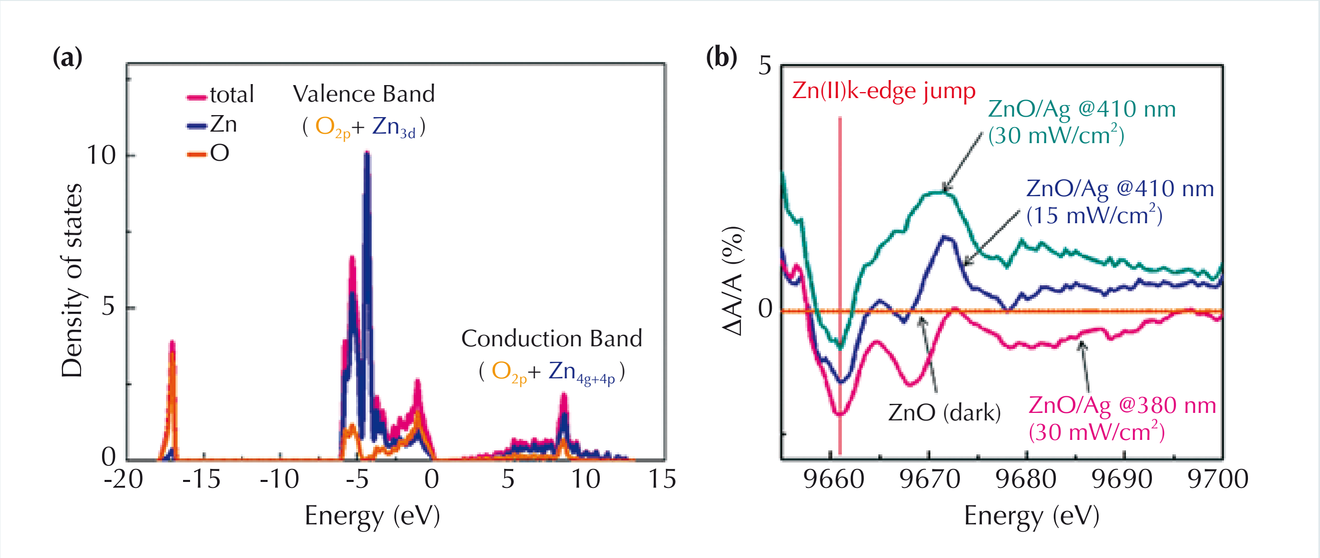

Fig. 2: (a) Density of states for ZnO. (b) The relative vacancies for ZnO and ZnO/Ag nanorods. (Reproduced from Ref. 2)

410 nm. A 3D diagram of the field intensity is plotted also in Fig. 1(d) to demonstrate clearly the spatial distribution of the electric field. It also reveals that the density of plasmonic hotspots in the laser-treated area is much larger than that in the unilluminated area.

The densities of states (DOS) of the ZnO calculated with density-functional theory (DFT) indicated that the conduction band comprises mainly Zn^{4s}+ Zn^{4p} states (Fig. 2(a)). K-edge absorption of Zn involved a transition from 1s to 4p states, such that a greater XANES intensity indicates the presence of more numerous vacancies in 4p states and the conduction band of ZnO. The researchers defined the difference spectra of bare ZnO nanorods and those of the ZnO/Ag photoelectrode as the relative vacancy ($\Delta A/A$) (Fig. 2(b)). The extent of relative vacancy decreased as the ZnO nanorods absorbed UV irradiation, which is attributed to an excitation of photoelectrons and their injection into the conduction band, which decreased the number of vacancies and revealed the photoexcitation in ZnO under UV irradiation at 380 nm. With irradiation at 410 nm, the spectra exhibited a significantly increased relative vacancy, indicating that a plasmonic-inducing electromagnetic field can modify the electronic structure and increase the vacancies in the conduction band. With increasing intensity of illumination, more vacancies were generated. This plasmonic-inducing vacancy served as a trap of charge carriers and provided a driving force to photogenerate electrons, and rapidly collected photoelectrons to facilitate effectively the transport of photogenerated electron-hole pairs.

This work demonstrated the independent contributions from various plasmonic effects under solar irradiation, explaining how the coupling of hot electrons formed by plasmons with the electromagnetic field effectively increased the probability of the photochemical reaction in the splitting of water. The hot electrons that were generated by the plasmons were injected from the plasmonic materials into the conduction band, while the plasmon-induced electromagnetic field created vacancies in the conduction band, promoting the separation of photogenerated electrons and holes.

Chen and co-workers demonstrated a new approach to investigate localized plasmon-induced effects and charge separation in a photoelectrochemical process. They exploited a localized plasmon resonance to enhance significantly the photochemical processes in photovoltaic devices. Although solar water splitting served as a platform to elucidate the mechanism of a surface plasmon resonance, this work of Chen and co-workers might provide new strategies for, and an understanding of, the transfer of photogenerated electrons.

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The Size Does Matter!

This report features the work of Shu-Jung Tang and his co-workers published in Nat. Commun. ***4****, 2925 (2013).*

Varying the electronic structures at organic-metal interfaces to engineer an organic-based electronic device has always been a main topic in organic-optoelectronic technology. Shu-Jung Tang and collaborators introduced the physical concept of quantum-size effects (QSE) to manipulate the alignment of energy levels (ELA) at interfaces between organic molecules and thin metal films.[1]

They created a novel model to explain the uniform thin metal films of Ag sandwiched between top organic films and a bottom substrate. They then systematically studied, with photoemission, the QSE on the organic-metal interface on varying three factors – the thickness of the Ag films, the types of substrates for the Ag films, and the types of adsorbates; the latter are mainly phthalocyanine-family molecules, such as copper phthalocyanine (CuPc), phthalocyanine (H_2Pc) and tetra-*t*-butyl H_2Pc (TTB-H_2Pc). These molecules are generally considered to be *p*-type electron donors. A nontrivial interfacial electronic structure is thus expected with respect to the charge transfer as a result of the interaction between the molecular-orbital state and the Ag quantum-well states (QWS) in the context of chemisorption. It was discovered also that QWS carried the influence of the Ge substrate under the Ag films to the top organic-metal interface, as manifested by the QSE.

Figures 1(a) and 1(b) show 2D photoemission

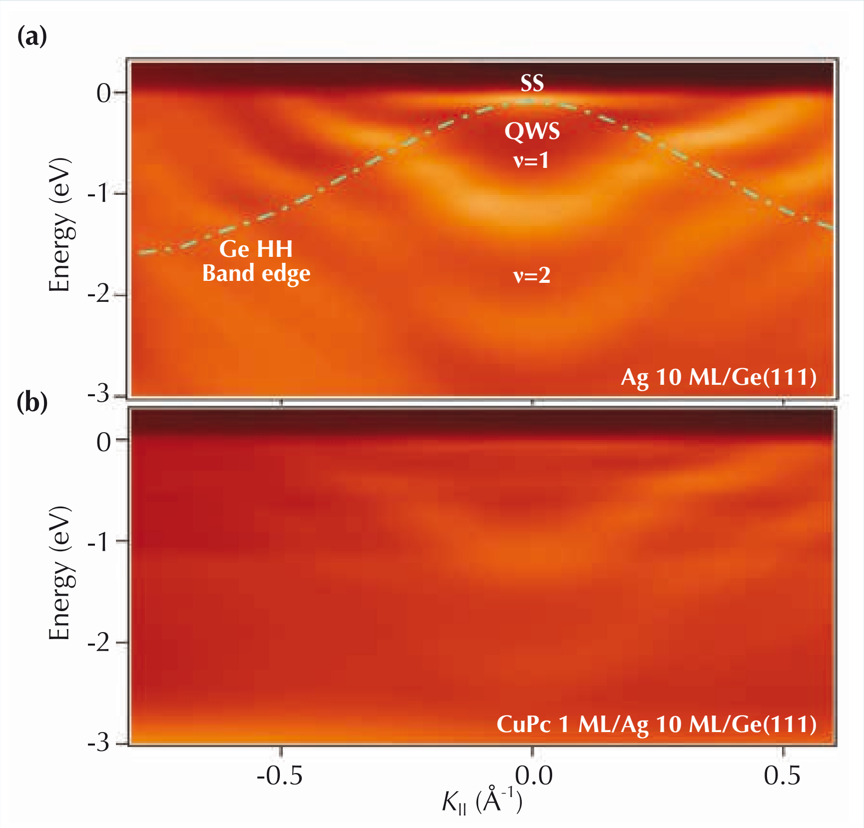

Fig. 1: Angle-resolved photoemission result along $\overline{\Gamma M}$ for (a) a 10-ML Ag thin film on Ge(111) and (b) for a 1-ML CuPc on a 10-ML Ag thin film on Ge(111).