

on the thickness of the Ag film can be understood in that the gap state occurs at the intersection between the QWS band and the Ge band edge, which must vary as the entire QWS band shifts in energy with the thickness of Ag. Figure 4(b) displays the dependence of gap states and the second-layer, highest-occupied-molecular-orbital (HOMO) positions on the thickness of the Ag film for CuPc/Ag films/Ge(111) and CuPc/Ag films/Au(111). This dependence produces a possibility of tuning the Fermi-level pinning position at the interface via altering the Ag thickness. As shown in Fig. 4(b), the measured second-layer HOMO position shifts to decreased energy with increasing Ag thickness, like the gap state, for Ag films on Ge(111), whereas that for Ag films on Au(111) remains con-

stant. The reason is that the energy position of the gap state with respect to the Fermi level is directly related to the density of the gap state at the Fermi level, which is the key determining the ELA.

The research team performed the photoemission experiment at BL08A1 in the TLS. For further information, please refer to the principal reference and related references.

References

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A New Way to Create Multifunctionality

*This report features the work of Heng-Jui Liu and his co-workers published in ACS Nano **6**, 6952 (2012) and Adv. Mater. **25**, 4753 (2013).*

Self-assembled vertical heteroepitaxial nanocomposites (VHN) become objects of fascination because of their large ratio of interface to volume, according to the scheme in Fig. 1. The couplings of spin, orbital, charge and lattice degrees of freedom at interfaces provide many possibilities to explore new condensed physics or multifunctionality. Of particular interest are self-assembled perovskite-spinel nanostructures, posing promising applications over a wide range. A famous case proposed by Zheng *et al.* has demonstrated an enhanced and controllable magnetoelectric effect, revealed in the ferroelectric BaTiO₃-ferrimagnetic CoFe₂O₄ VHN.¹ The multifunctionality of this magnetoelectric effect indicates that the magnetic properties can be altered with an electric field, and *vice versa*. The origin of such multifunctionality in nanostructures of this kind has been confirmed to correlate strongly with the intimate structural coupling between these two constituents. The research team from National Chiao Tung University in this report has demonstrated multifunctionality of a new

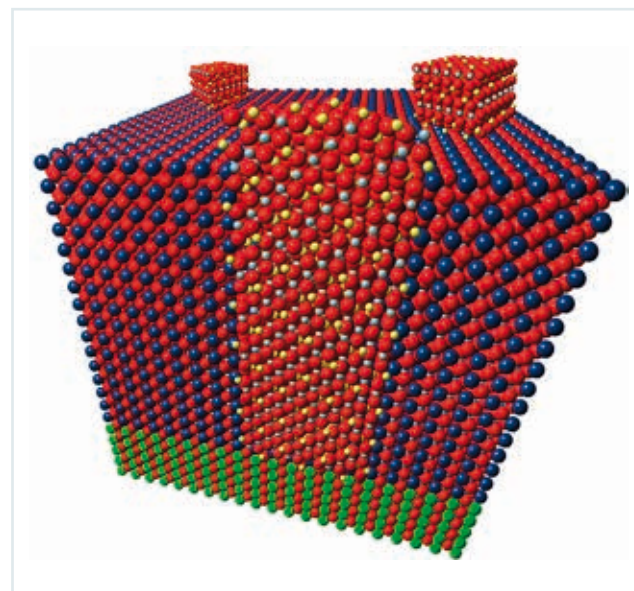


Fig. 1: Typical scheme of self-assembled vertical heteroepitaxial nanocomposites.

kind, a photomagnetic effect and spectacularly large magnetoresistance, on fabricating VHN composed of SrRuO₃ (SRO) and CoFe₂O₄ (CFO). High-resolution

X-ray diffraction and X-ray absorption techniques were practised to reveal the lattice and electronic interaction inside the VHN, which are important tools to realize the mechanism of the corresponding multifunctionality.

The first photomagnetic effect in a material system of this kind depends on a concept of product property: photostrictive SRO \times magnetostrictive CFO. To drive this effect, SRO and CFO must have a strong structural coupling. As shown in Fig. 2, a map of the X-ray reciprocal space around the (112) reflection of a SrTiO₃ (STO) substrate obtained at BL17B1 in the TLS clearly exhibits two extra diffraction spots that are identified as SRO (112) and CFO (224). The

ϕ -scans in Fig. 2(b) show that all constituents present four-fold symmetry, indicating that the SRO and CFO grew on STO with a relation cubic on cubic. From the map, the corresponding lattice parameters of SRO and CFO are extracted as $a = b = 3.93(4)$ Å, $c = 3.92(7)$ Å and $a = b = 8.45(2)$ Å, $c = 8.27(3)$ Å, respectively, compared to bulk SRO ($a = b = c = 3.93$ Å) and CFO ($a = b = c = 8.39$ Å); this result implies that SRO is almost free from strain and that CFO suffers a large compressive strain along a direction out of plane that comes from the SRO part. Based on this structural information, the presence of a photomagnetic effect in this system is then ascribed to an interaction at the interface between these two materials.²

This nanocomposite system possesses another interesting phenomenon, which is a large magnetoresistance. SRO and CFO are originally a metallic and an insulating oxide, respectively, and both lack an evident magnetoresistance effect, but, in this system, the research team has discovered that the magnetoresistance of SRO becomes greatly enhanced on interaction with the magnetic CFO nanopillars. To disclose the underlying physics, X-ray absorption is essential. As shown in Fig. 3, the Co-L_{2,3}, Fe-L_{2,3} and Ru-L₃ edges were recorded at Dragon beamline BL11A1 in the TLS to derive the electronic structural information and the valence of the Co, Fe and Ru ions. On comparison with standard samples, these profiles show clearly the mixed valence of Co²⁺/Co³⁺ and Ru⁴⁺/Ru⁵⁺ in this system. These atoms hence become rearranged under deposition as there is no mixed valence observed in bulk SRO and CFO. These rearranged atoms have a strong magnetic coupling in either SRO or CFO, and thus induce an unexpectedly large magnetoresistance – ~ 40 % at applied field 0.5 T.³

Such nanocomposite systems can provide numerous possibilities to design or to create new multifunctionality and future devices if the materials for combination are appropriately selected. The research team has demonstrated elegantly the potential of material systems of this kind and confirmed the mechanism of interaction with the aid of synchrotron radiation at NSRRC. The cooperation of application and

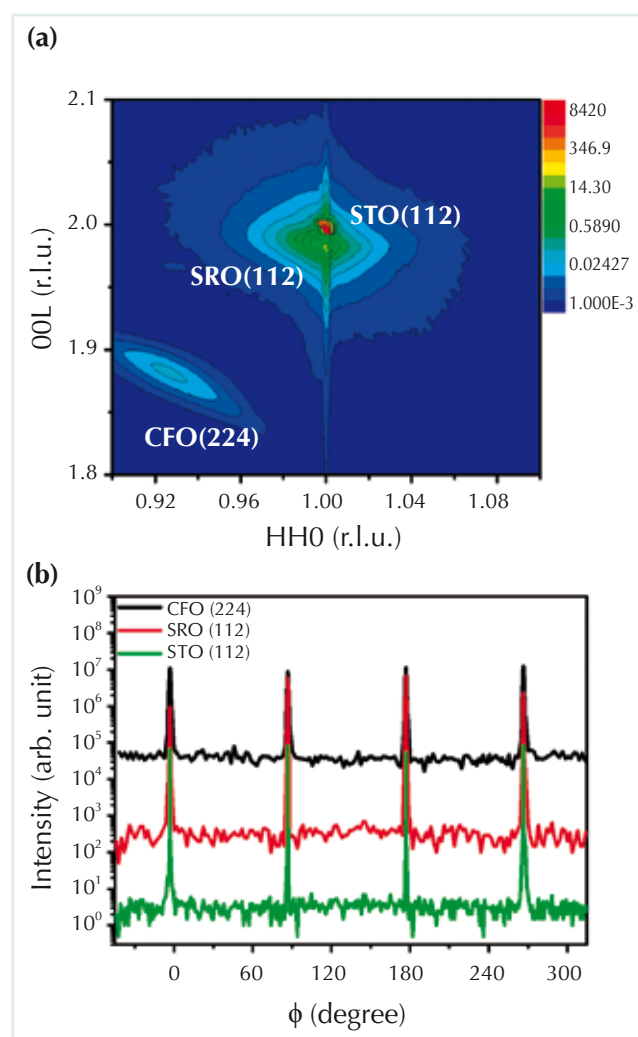


Fig. 2: (a) Reciprocal space map (RSM) around the (112) reflection of the STO substrate. (b) ϕ scans of STO (112), SRO(112), CFO(224) indicate these constituents to be well connected with a relation cubic on cubic. (Reproduced from Ref. 2)

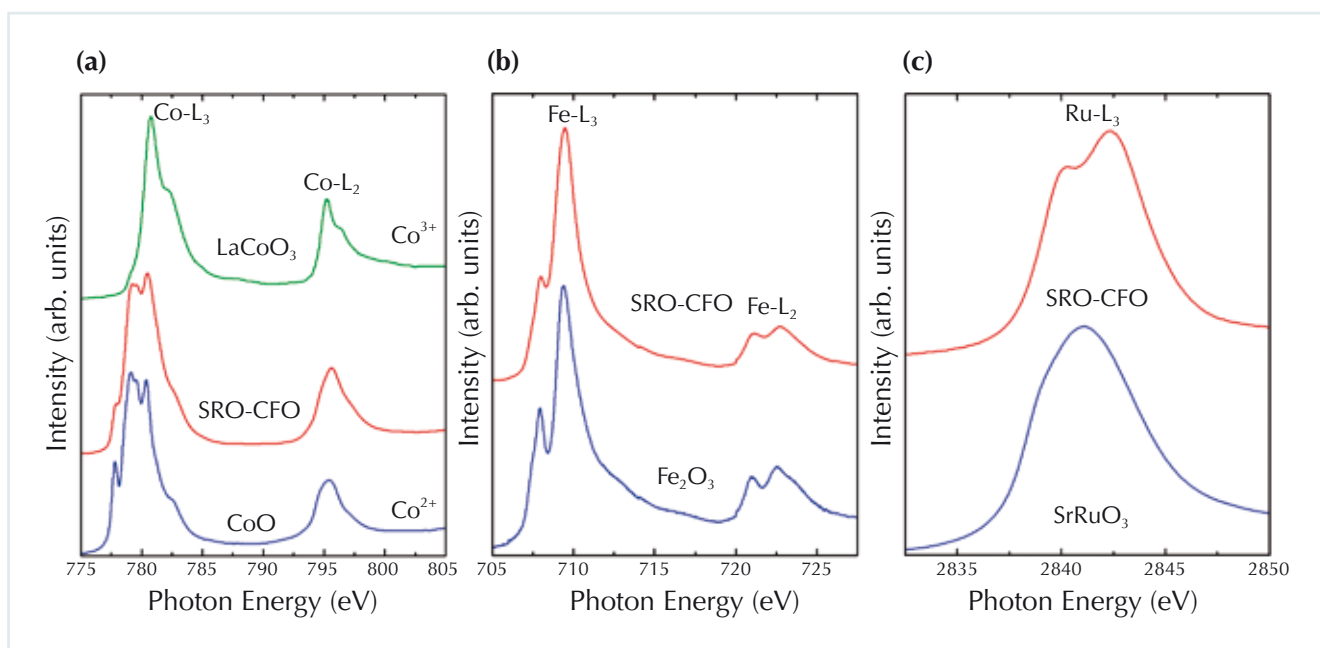


Fig. 3: X-ray absorption spectra of Co-L_{2,3}, Fe-L_{2,3} and Ru-L₃ edges: (a) The Co spectrum in SRO-CFO nanostructures compared with those of standard samples of LaCoO₃ and CoO indicates the presence of mixed valence Co²⁺/Co³⁺. (b) The Fe spectrum is near that of the standard sample of Fe₂O₃, indicating that the valence of Fe ions is all 3+ in the SRO-CFO nanostructure. (c) The Ru spectrum exhibits a split peak toward higher binding energy relative to the spectrum of pure SrRuO₃, indicating the mixed valence Ru⁴⁺/Ru⁵⁺ in this system. (Reproduced from Ref. 3)

physics would pave a path for the exploration of new functionality in hetero-epitaxial self-assembled oxide nanostructures.

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