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Element-specific XMCD study of Fe-doped ZnO/Ti_3C_2 composites

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1 Introduction

ZnO, a wide-band-gap semiconductor with excellent electrical, magnetic, and optical properties and a high exciton binding energy, makes it the most appropriate material for spintronics and optoelectronic applications [1,2]. Oxide-based semiconductor materials are preferred for achieving room-temperature ferromagnetism (RTFM) because they can be extensively doped with carriers to tune its property. Additionally, oxide-based semiconductors can grow at low temperatures, which will aid in limiting the sample to a single phase. ZnO is used in LEDs, solar cells, ultraviolet lasers, piezoelectric devices, transparent conducting oxide (TCO), etc., even though many NPs show their applicability in diverse technical areas [3,4]. To further understand the origin of FM in ZnO-based semiconductors, diluted magnetic semiconductors (DMS) were characterised and analysed, particularly through magnetic characterization. The magnetic property in ZnO was studied by doping with transition metals (TMs) like Mn, Cr, Co, Fe, etc [5,6]. In TM-doped ZnO, the interaction between the unpaired *d*-electron of the TM and the *s* and *p* carriers of the host semiconductor occurs, which mediates ferromagnetic ordering according to the bound magnetic polaron model, and defects such as oxygen vacancies and zinc interstitials affect the magnetic properties. TM-doped ZnO has emerged as a potential material for detecting RTFM in spintronic devices, based on both theoretical and practical investigations. However, the microscopic origin of ferromagnetism is still debated because observable magnetic properties are highly dependent on dopant concentration, defect chemistry, synthesis conditions, and the possibility of secondary phase development. Fe has drawn a lot of interest due to its strong interaction, high magnetic moment, and numerous oxidation states (Fe^{2+}/Fe^{3+}). Fe doping modifies the electrical structure, defect distribution, and exchange, which will affect ZnO's magnetic characteristics. However, there are still conflicting findings about the presence and origin of RTFM in Fe-doped ZnO/Ti_3C_2 composites, which makes it crucial to use element-specific characterisation techniques to study the local electronic and magnetic states of Fe ions.

In addition to Fe doping, making composites with Ti_3C_2 also tailors the properties of the host matrix. Ti_3C_2 is a promising material for improving photocatalytic performance due to its distinct 2D structure, efficient conductive conjugated system, large specific surface area, and non-toxicity. In addition to improving charge transport and interfacial coupling, adding Ti_3C_2 to ZnO significantly alters the local electrical environment through strong heterointerface interactions. Fe-doped ZnO/Ti_3C_2 composites are a promising method for studying the connection between electronic structure and magnetism, as these effects can impact defect formation, electronic hybridization, and magnetic exchange interactions. There is a strong interest in ZnO/Ti_3C_2 heterostructures, although research on the intrinsic magnetic behavior and element-specific contributions in Fe-doped ZnO/Ti_3C_2 composites is limited. In this work, we investigated the electronic configuration and magnetic properties of Fe-doped ZnO/Ti_3C_2 composites by using X-ray Absorption Spectroscopy (XAS) and X-ray Magnetic Circular Dichroism (XMCD) techniques. This provided direct information on the origin of ferromagnetism and the role of Fe ions and Ti_3C_2 heterointerfaces in controlling the magnetic behavior of the composite system.

2 Experiment

We synthesized Fe-doped ZnO/Ti_3C_2 composites by using a wet chemical method. Ferric nitrate nonahydrate, Titanium carbide, and Zinc oxide were used as the primary precursors for the preparation of composite samples. Firstly, ferric nitrate nonahydrate was dissolved in ethanol and stirred for 1.5 hours. To enhance Fe introduction into the ZnO lattice, the resultant precursor was completely ground with ZnO powder after drying and then annealed. The annealed Fe-doped ZnO powder was combined with Ti_3C_2 and ground for 2-3 hours to create a homogeneous composite. The resultant product was employed for magnetic characterization after being finely ground into a powder. The electronic and magnetic properties of Fe-doped ZnO/Ti_3C_2 composites were studied using advanced techniques. XAS and XMCD were performed at the Fe $L_{2,3}$ edges utilising the undulator beamline 16A (BL-16A) at the Photon Factory (KEK), Japan, for thorough element-specific magnetic research. The XMCD reflects the spin and orbital polarisations of the local electronic states and is an effective instrument for studying element-specific local magnetic interactions. The total electron yield (TEY) mode was used for surface-sensitive measurements, and the probing depth was around 5 nm. The XAS and XMCD measurements were collected using an out-of-plane configuration in a magnetic field of 2 T.

3 Results and Discussion

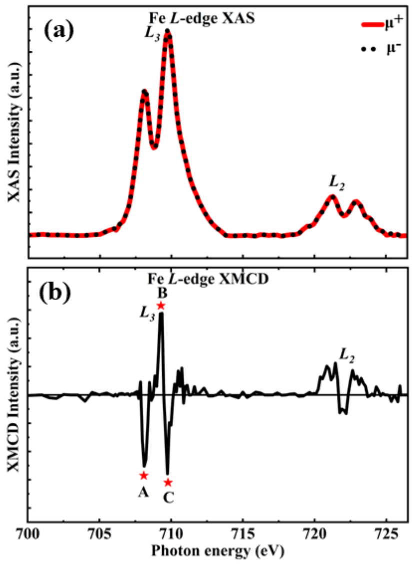

Figure 1: (a) XAS spectra and **(b)** XMCD spectra of Fe-$L_{2,3}$ edges at 2T.

The magnetic properties of Fe-doped ZnO/Ti_3C_2 composites depend on the valence state of Fe ions and their local coordination symmetry. To study the electronic and magnetic nature of Fe dopants, an XAS and XMCD study was performed at the Fe-$L_{2,3}$ edges, which correspond to 2*p*-to-3*d* electronic transitions and can offer precise information regarding the 3*d*-electronic configuration of the dopant Fe ions. The magnetic polarization of Fe 3*d* states can be directly understood using element-specific XMCD measurements. The XMCD signal is defined as the difference in XAS spectra recorded with left- and right-circularly polarized X-rays under an applied magnetic field of 2T. **Figure 1(a)** shows the Fe-$L_{2,3}$ edges XAS spectra, and **Fig. 1(b)** shows the Fe-$L_{2,3}$ edges XMCD spectra. The spectra are divided into the L_3 and L_2 edges by the Fe 2*p* spin-orbit coupling. The magnetism is mainly due to Fe^{3+} ions, with a minor contribution from Fe^{2+} ions. Peak A is attributed to the Fe^{3+} ions at octahedral sites with a small contribution from Fe^{2+} tetrahedral sites. Peak B and C are attributed to Fe^{3+} at tetrahedral and octahedral sites. The shape of the spectral line corresponds to the 3*d* electronic configuration of Fe, suggesting that Fe mainly exists in the 3+ oxidation state with minor contribution from 2+ and substitutes for Zn^{2+} in the ZnO lattice. The spin and orbital magnetic moments, as well as element-specific local magnetic interactions, are determined using the XMCD and sum rules [7,8,9].

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