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H mediated room temperature ferromagnetism in $\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$

Hua Zhang^a, Zheng Wen^b, Xiaosi Qi^c, Lifang Si^a, Liguu Xu^d, Wei Zhong^c, Di Wu^b, Kai Shen^d,
Mingxiang Xu^a, Teng Qiu^a, Qingyu Xu^{a,e,*}^a Department of Physics, Southeast University, Nanjing 211189, China^b Department of Materials Science and Engineering, Nanjing University, Nanjing 210008, China^c Department of Physics, Nanjing University, Nanjing 210008, China^d School of Materials Science and Technology, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, China^e Key Laboratory of MEMS of the Ministry of Education, Southeast University, Nanjing 210096, China

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ABSTRACT

$\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$ powders have been synthesized by microemulsion method. The room temperature ferromagnetism was significantly suppressed, compared with the ZnO powders prepared by the same method. Enhanced room temperature ferromagnetism has been obtained after annealing in H_2 atmosphere at 500 °C for 2 h. The structural characterizations have confirmed the incorporation of the interstitial H and the suppression of the O vacancies. The possibility of the O vacancy mediated room temperature ferromagnetism has been excluded. Our results clearly demonstrated that the observed ferromagnetism originates from the neighboring Cu ions mediated by the interstitial H ions.

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1. Introduction

Dilute magnetic semiconductors (DMS) have been suggested to be a possible solution to realize ferromagnetism in conventional semiconductors, which provide the simultaneous control of charge and spin of electrons and thus have important applications in semiconductor spintronics [1]. After the theoretical prediction by Dietl that Mn doped ZnO may have Curie temperature above room temperature [2], extensive research work has been done to search for the room temperature ferromagnetic ZnO by 3d transition metal (TM) doping [3]. Due to the limits of the general structural characterization methods, the previous reported room temperature ferromagnetism in 3d TM doped ZnO was attributed to the ferromagnetic impurities [4–7]. Furthermore, with 3d TM ions substituted in ZnO lattices, generally the interaction between the neighboring spins through O^{2-} is superexchange antiferromagnetic. Thus, lacking of ferromagnetism has been reported in high-quality 3d TM doped ZnO single crystals and epitaxial films [8–10].

Generally, Zener-RKKY free-carrier exchange or bound magnetic polarons are always used to explain the observed ferromagnetism in ZnO-based DMS [8]. However, the lacking of ferromagnetism in epitaxial Co-doped ZnO films with wide electron concentration range indicates that the itinerant conduction band electrons alone are not sufficient to induce ferromagnetism [8,9]. Besides the

possible ferromagnetic contribution from the defects in ZnO, the defects have also been considered to be responsible for the ferromagnetic exchange interaction between the neighboring spins [11–16]. To obtain the ferromagnetism, high concentration defects are needed. The defects in ZnO are still being intensively studied [17], and the highly defective ZnO will lead to low crystalline quality, which will strongly decrease the carrier mobility and limits its practical applications. Efficient ferromagnetic exchange interaction between the substituted 3d TM ions are searched to realize the ferromagnetism in high quality crystalline ZnO. Park has theoretically predicted that interstitial H in ZnO might provide ferromagnetic exchange interaction between the neighboring 3d TM ions [18]. Several experimental works on Co-doped ZnO and Mn-doped ZnO annealed in H_2 demonstrated the possible H mediated ferromagnetism in ZnO, but the mechanism is still under debate [19,20]. The magnetic characterization of Cu doped ZnO annealed in H_2 atmosphere is still lacking. In this paper, we have prepared $\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$ powders by microemulsion. After annealing in H_2 atmosphere, enhanced room temperature ferromagnetism has been observed. By careful structural characterization, the ferromagnetism has been clearly attributed to the ferromagnetic exchange interaction mediated by the interstitial H.

2. Experimental details

$\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$ powders were synthesized by microemulsion method [21]. All chemicals are analytical grade (AR) and purchased from commercial sources without further treatment. In a typical procedure, 0.86 g butanol and 0.12 g cetyl

* Corresponding author at: Department of Physics, Southeast University, Nanjing 211189, China.

E-mail address: xuqingyu@seu.edu.cn (Q. Xu).

trimethyl ammonium bromide (CTAB) were added into 60 ml octane, and the solution was then subjected to magnetic stirring at room temperature for 0.5 h. After that, the solution was divided into two identical parts. 1.1 g $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and 0.019 g $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ were completely dissolved into 10 ml deionized water. We obtained two microemulsions by adding the latter solution into one part of the former solution and aqueous ammonium into the other. After mixing the two microemulsions, hydroxide nanoparticles of Zn and Cu were yielded and precipitated. The hydroxide nanoparticles were extracted from solution by a centrifugation, and washed first with deionized water then alcohol. The hydroxides nanoparticles were converted to $\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$ powders (ZnCuO) by heating at 393 K for 12 h, and finally dried at 393 K for 24 h. The annealing of $\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$ powders were performed in H_2 (ZnCuO-H) or in Ar (ZnCuO-Ar) flow at 500 °C for 2 h. Part of ZnCuO-H powders was annealed in air at 500 °C for another 2 h (ZnCuO-air). The low temperature of 500 °C was selected for the annealing to avoid the possible metallic impurity formed by the annealing in H_2 at high temperature [22]. The structures were studied by X-ray diffraction (XRD) with θ - 2θ scans using a Cu K α source, transmission electron microscope (TEM, FEI Techni-S20), and X-ray photoelectron spectroscopy (XPS, ThermoFisher SCIENTIFIC) with Al K α X-ray source ($h\nu = 1486.6$ eV). The samples for XPS measurements were kept in the high-vacuum chamber overnight to remove the absorbed air. The photoluminescence (PL) spectra of the samples were acquired at room temperature with acquisition time of 0.1 s by excitation with the 340 nm line of a Xe lamp (Horiba Jobin Yvon Fluorolog-3). The magnetization has been measured by a physical property measurement system (PPMS-9, Quantum Design) at 300 K.

3. Results and discussion

Fig. 1 shows the XRD patterns of ZnCuO powders before and after annealing in H_2 atmosphere. All the peaks can be indexed to pure wurtzite structure without any impurity phase, which was further confirmed from the XPS survey spectra (not shown here). A broad peak locating at around 23° can be observed in the as prepared ZnCuO powders, indicating a small fraction of amorphous phase. After annealing in H_2 atmosphere, the broad peak disappeared, indicating the improvement of the crystallization. To see clearly the structural evolution of ZnCuO powders on the annealing, the (103) peaks of the samples are displayed in the inset of Fig. 1(b). It can be seen that the peak slightly shifts to the larger 2θ value for ZnCuO-H, which is consistent with our previous study on the pure ZnO annealed in H_2 [23]. This can be attributed to a decrease in the concentration of O vacancies by annealing in H_2 [24]. The calculated average crystallite size was almost the same using Debye-Scherrer equation (23 nm for ZnCuO and 21 nm for ZnCuO-H), indicating no crystallite growth during the annealing.

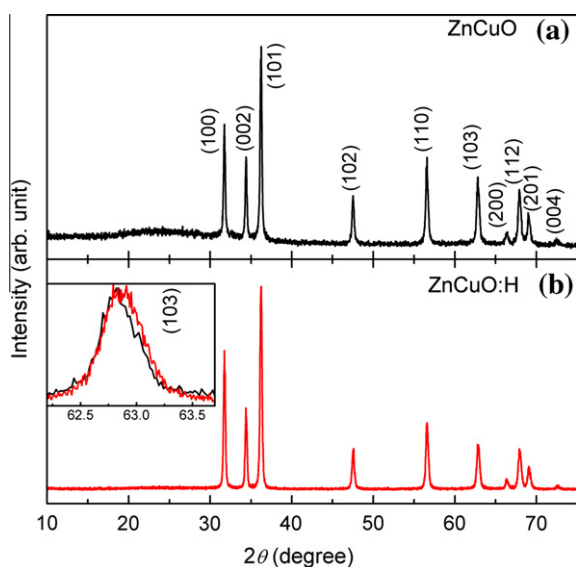


Fig. 1. XRD patterns of (a) ZnCuO and (b) ZnCuO-H powders. The inset shows the enlarged view of (103) peaks of ZnCuO and ZnCuO-H powders.

The morphologies of ZnCuO and ZnCuO-H powders are shown in Fig. 2. As can be seen, both samples show spindle shape with length of about 1 μm and width of 500 nm. No significant change has been observed for the shape and size of the particles after annealing in H_2 atmosphere. The particle size is much larger than the value determined by XRD. The inset of Fig. 2(a) shows clearly the aggregation of small crystallites, confirmed by the spotty ring like diffraction pattern taken from one particle (inset of Fig. 2(b)).

The field dependent magnetic hysteresis M - H loop of ZnCuO measured at 300 K is shown in Fig. 3(a). The positive slope at high fields indicates the dominating paramagnetism in ZnCuO powders. After annealing in H_2 atmosphere, the slope at high field changes to negative, indicating the dominating diamagnetism. After subtracting the diamagnetic or paramagnetic contributions, the ferromagnetic magnetization is shown in Fig. 3(b). The saturate ferromagnetic magnetization (M_s) of ZnCuO is about 0.25 memu/g, which is much smaller than that of ZnO powders prepared under the same process (1.4 memu/g) [23]. After annealing in H_2 , clear ferromagnetic hysteresis loop can be observed and M_s significantly increases to about 3 memu/g, which is one order enhanced.

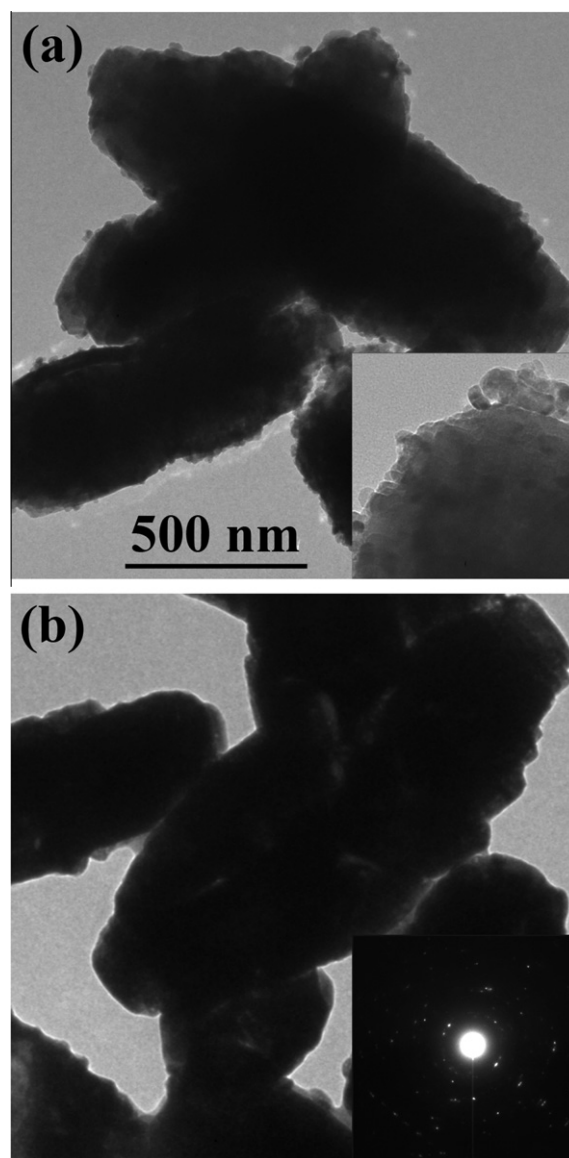


Fig. 2. TEM images of (a) ZnCuO and (b) ZnCuO-H powders. The inset in (a) shows the enlarged view of one particle of ZnCuO, and in (b) shows the diffraction pattern from one particle of ZnCuO-H.

To understand the structural origin of the enhanced ferromagnetism in ZnCuO–H powders, the PL spectra of ZnCuO and ZnCuO–H in the wavelength range of 370–650 nm were taken and shown in Fig. 4. A small sharp peak at around 380 nm and a strong peak at around 420 nm can be observed for both samples. The UV emission originates from the exciton-related recombination [25]. The blue emission might come from the defects of Zn interstitial (Zn_i^+) and the formation of the energy level due to Cu doping [26], suggesting the substitution of Cu in ZnO lattice. The peak position of the blue emission shift from 410 to 436 cm^{-1} after annealing in H_2 atmosphere, as similar phenomenon observed in hydrogenated ZnO [27], confirming the structural influence of the hydrogenation. A broad emission peak with center at around 550 nm has been observed for ZnCuO, but disappears in ZnCuO–H, which can be attributed to singly charged and doubly charged O vacancies [15]. The disappearance of the green emission suggests the strong suppression of the O vacancies in ZnCuO–H [28], similar to ZnO powders annealed in H_2 [23]. However, due to that the emission arising from excitons bound to interstitial H is very close to the free-exciton related UV emission peak [28], the incorporation of H in ZnCuO–H cannot be directly determined from the PL spectra at room temperature.

To clearly resolve the electronic structure of each element, XPS spectra of each element were taken, and are shown in Fig. 5. All the XPS spectra were referenced to the surface impurity C 1s line (284.8 eV) binding energy [29]. Fig. 5(a) shows the O 1s spectra from ZnCuO and ZnCuO–H, respectively. As can be seen, double peaks have to be applied to fit the peaks. The lower binding energy component (denoted as O_A) corresponds to the stoichiometrically bonded O^{2-} , and the higher binding energy component (denoted as O_B) is attributed to the O^{2-} in the O deficient regions within the matrix of ZnO [30]. After annealing in H_2 , the concentration of O^{2-} in the deficient region decreases from 61.51% to 53.61%, indicating the decrease of the concentration of the O vacancies. This is consistent with the XRD and PL results. After annealing in H_2 atmosphere, the binding energy of the O_A and O_B peaks shift

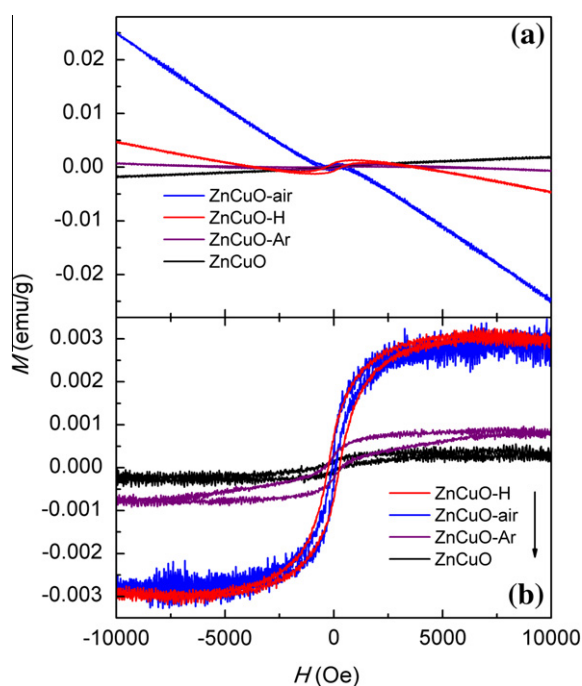


Fig. 3. (a) The M – H curves and (b) the ferromagnetic magnetization after subtraction of the diamagnetic or paramagnetic contribution from the high field linear part of ZnCuO, ZnCuO–H, ZnCuO–Ar, and ZnCuO–air powders.

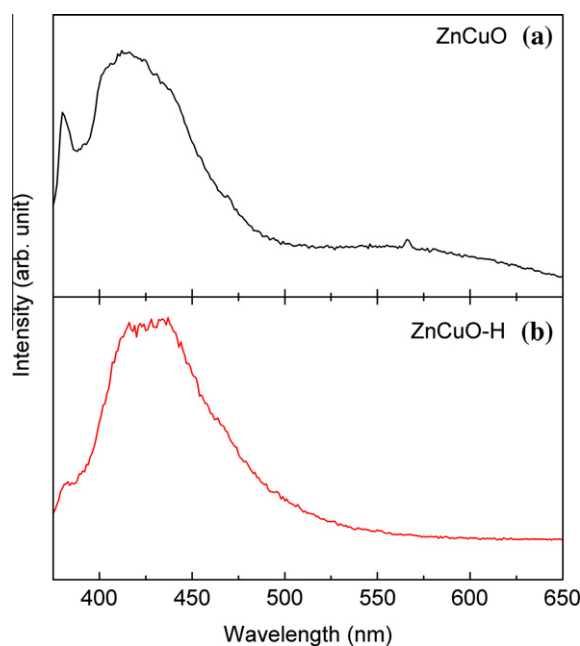


Fig. 4. PL spectra of (a) ZnCuO and (b) ZnCuO–H powders.

to higher energy, also the Zn 2P peaks shift to higher energy. Similar phenomena have been observed in our previous research on ZnO powders annealed in H_2 atmosphere [23]. Annealing in H_2 atmosphere will incorporate H atoms into ZnO and locate at the interstitial sites as H_i or form V_O –H complex [31]. Considering the electronegativity of Zn (1.65) and H (2.20) [32], the Zn–H has higher bonding energy than Zn–O binding energy [27]. And the increase of the O 1s binding energy is due to the O–H related bonding [27]. Similar phenomena have been observed in the hydrogenated Co-doped ZnO, which has been ascribed to the H bonding with 1 eV increment of the binding energy [33]. Besides the main 2P 1/2 and 2P 3/2 peaks, two satellite peaks can be observed locating at the binding energy of about 9 eV higher, which is a typical characteristic of the materials having a d^9 configuration in the ground state [34,35]. This indicates the +2 valence state of the doped Cu ions in ZnCuO. However, the binding energy of Cu^{2+} (931.0 eV) is smaller than the generally reported value of 933.6 eV in CuO [36]. Recently, Ciatto has experimentally demonstrated that the O vacancies tend to locate close to the doped Co atoms in ZnO [37]. We suggested that the O vacancies may also locate close to the doped Cu atoms in ZnO, which decrease the binding energy of the outer shell d electrons of Cu^{2+} ions. Annealing in H_2 atmosphere significantly suppresses the O vacancies, the binding energy of the Cu ions shift to higher energy. However, the satellite peaks disappear, suggesting the lost of the d^9 configuration. Since the peak position of Cu 2P 3/2 is very close to that of Cu^+ in Cu_2O , indicating that the doped Cu ions are mainly in +1 valence state [35,36].

Based on the above structural results, we try to explore the mechanism of the magnetic properties in Cu-doped ZnO. The room temperature ferromagnetism has been reported in ZnO, and the ferromagnetic origin has been generally attributed to the oxygen vacancies [15]. In our previous study on ZnO powders prepared by the same method, clear room temperature ferromagnetism has been observed, which has been explained by the singly charged O vacancies mediated O vacancy clusters [23]. With 2% Cu doping in ZnO, the ferromagnetic magnetization was strongly suppressed, similar to the Mn-doped and Co-doped ZnO, and 3d TM doped CeO_2 [38–40]. The XPS results suggest the neighboring tendency of doped Cu^{2+} and O vacancies, thus the spatial-charge density

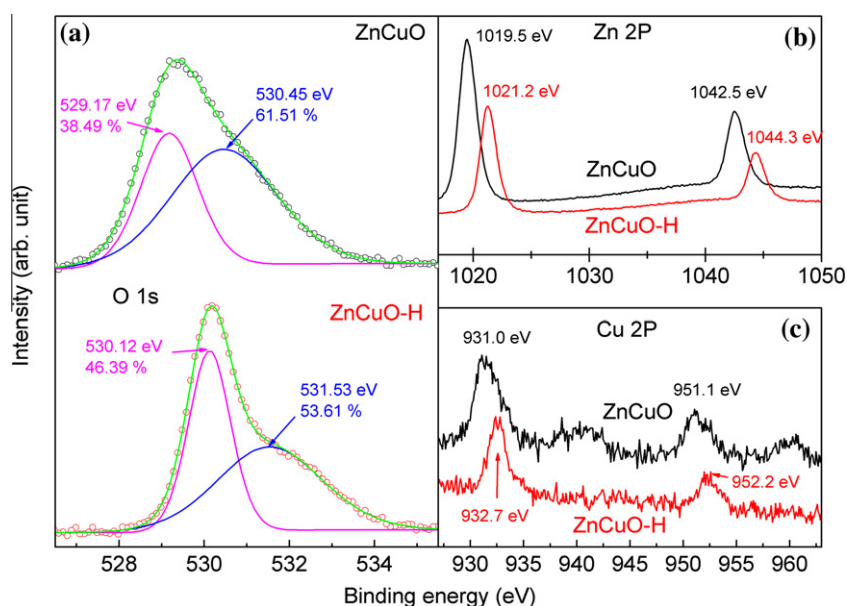


Fig. 5. XPS of (a) O 1s, (b) Zn 2P, and (c) Cu 2P for ZnCuO and ZnCuO-H powders. The fitted peak position and relative atomic concentration of O 1s are indicated. The peak position of Zn 2P and Cu 2P are also indicated.

distribution around the O vacancies are significantly changed. This might significantly decrease the magnetic moment and the radius of the electron orbital around the O vacancies, and affect the electronic ground state of the ferromagnetic system of the network of the O vacancies [38]. In ZnCuO powders, the valence state of Cu ions is +2, which has d^9 electronic configuration and net magnetic moment. The observed paramagnetism in ZnCuO is contributed from the O vacancies and Cu^{2+} ions. After annealing in H_2 atmosphere, the O vacancies were significantly suppressed, and the valence state of Cu ions is mainly +1. Since the Cu^{1+} ions have the d^{10} electronic configuration, which has no magnetic moment, the paramagnetism was strongly suppressed and diamagnetism of bulk ZnO dominated. Though in ZnCuO-H, the Cu ions are mainly in the valence state of +1, small portion of Cu ions may still be in the valence state of +2. Park et al. has predicted theoretically that the interstitial H can mediated a strong short-ranged ferromagnetic spin-spin interaction between neighboring magnetic impurities through the formation of a bridge bond [18]. Thus the ferromagnetism might be attributed to the interstitial H mediated Cu^{2+} ions.

There is another possible ferromagnetic contribution from the O vacancies [15,23]. To clarify this, we further annealed the ZnCuO-H powders in air for 2 h at 500 °C (ZnCuO-air). The $M-H$ curve of ZnCuO-air is shown in Fig. 3. As can be seen clearly, the $M-H$ curve is nearly the same as that of ZnCuO-H. In our previous study on the ZnO powders annealed in H_2 , the ferromagnetism was totally lost after the following annealing in air for 2 h at 500 °C. This clearly confirms that the observed ferromagnetism in ZnCuO-H is not from the O vacancies. Similar phenomena have been observed in hydrogenated Co-doped ZnO [19], indicating the highly thermal stability of the interstitial H mediated room temperature ferromagnetism. As O vacancies are generally considered to be the possible media for the ferromagnetism [14], we also annealed ZnCuO powders in Ar atmosphere at 500 °C for 2 h. As can be seen in Fig. 3, the high field slope of ZnCuO-Ar is the smallest compared with that of ZnCuO-H and ZnCuO-air, and that of ZnCuO-air is the largest, indicating that the highest concentration of O vacancies in ZnCuO-Ar and annealing in air might further suppress the oxygen vacancies [15]. However, the ferromagnetic magnetization is only about 0.8 memu/g, which is much smaller than that of ZnCuO-H.

This result clearly demonstrates that the O vacancies cannot efficiently mediate the magnetic ions ferromagnetically. Our results clearly demonstrate that the interstitial H ions can provide an efficient media for the realization of room temperature ferromagnetism in 3d magnetic TM doped ZnO.

4. Conclusion

In summary, $Zn_{0.98}Cu_{0.02}O$ powders have been synthesized by microemulsion method. The room temperature ferromagnetism was significantly suppressed, compared with the ZnO powders prepared in the same method. Enhanced room temperature ferromagnetism has been observed after annealing in H_2 atmosphere at 500 °C for 2 h. The structural characterizations have confirmed the incorporation of the interstitial H. The possibility of the O vacancy mediated room temperature ferromagnetism has been explicitly excluded. Our results clearly demonstrated that the observed ferromagnetism originates from the neighboring Cu ions ferromagnetically mediated by the interstitial H, which open a new route for the realization of the ZnO-based ferromagnetic semiconductors with high crystalline quality.

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