doi:10.1246/cl.2010.594

# Room Temperature Ferromagnetism at the Interface between Nonmagnetic Semiconductors

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We show experimentally that room-temperature ferromagnetism can be induced in ZnO/ZnS core/shell nanoparticles without any magnetic components. This ferromagnetism could be attributed to p–p coupling interactions between S 3p and O 2p electrons arising from the redistribution of charges between Zn and O or S atoms. Our present findings possibly open up a new way for introducing magnetism in semiconductor-based "spintronics" devices.

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The discovery of paramagnetism or ferromagnetism caused by electronic reconstruction at the interface between organic and inorganic compounds which are both originally nonmagnetic has attracted a lot of interest. The first report by Naaman et al. showed that thiol-capped gold surfaces exhibited a giant paramagnetism. This unusual phenomenon has been explained as resulting from charge transfer between the substrate and the thiols during the adsorption process. After that, observations of such kinds of magnetism at organic–inorganic interfaces have been reported in a variety of systems.[1] In particular, the thiol-capped ZnO system is of considerable importance in analogy with diluted magnetic semiconductors (DMS), which can take advantage of both the charge and the spin of the electrons. Bcause of its wide band gap and electronic and optical properties, ZnO was predicted to be an ideal candidate for diluted magnetic semiconductors which show ferromagnetism at room temperature.[2] As a basic strategy for introducing ferromagnetism, ZnO has been studied theoretically and experimentally by doping with many kinds of transition metals such as Mn, Co, V, Ti, and Cu.[3] Additionally, recently, it has surprisingly been discovered that ferromagnetism can be also introduced by doping nontransition metals with ZnO, such as carbon, sulfur, or nitrogen.[4] In these reports, it has been mentioned that the magnetic moments mainly localizes at the nontransition metal dopant itself and that the ferromagnetism occurs due to the p–p interactions between the p electrons of the O atom in the host ZnO and the C, S, or N dopant atoms. Similar results also have been observed in carbon-doped ZnS systems.[5]

Since room-temperature ferromagnetism in ZnO materials has been realized in organic molecule-passivated or nontransition metal-doped systems, it must be possible to realize room-temperature ferromagnetism at the interfaces between ZnO and another inorganic semiconductor. Following this scenario, in this letter we experimentally show that room-temperature ferromagnetism can be induced in ZnO/ZnS core/shell nanoparticles (ZnO/ZnS NPs) without any magnetic components.

ZnO/ZnS NPs were synthesized by the following two-step reaction. ZnO core NPs were prepared by sol–gel process,[1d] and then ZnS shells were grown on the surface of ZnO core NPs by using successive ion layer adsorption and reaction SILAR.[6] The shell thickness of ZnS was designated in terms of the percentage of the precursor ions with respect to ZnO core. ZnO/6%ZnS, ZnO/17%ZnS, and ZnO/32%ZnS core–shell NPs corresponding to ca. 2, 5, and 10 layers, respectively, were synthesized.

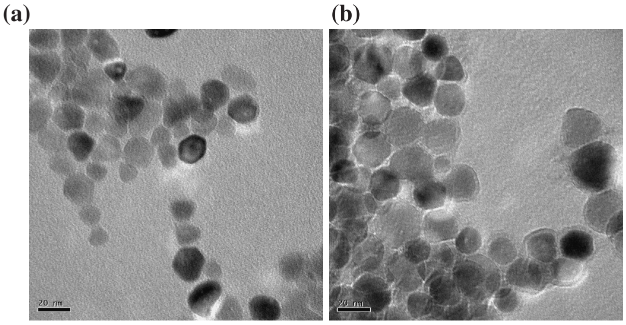

**Figure 1.** TEM images of a) ZnO core NPs and b) ZnO/17%ZnS core/shell NPs; scale bar = 20 nm.

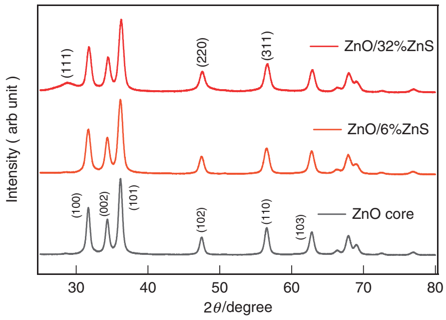

**Figure 2.** XRD patterns of ZnO core, ZnO/6%ZnS core/shell NPs, and ZnO/32%ZnS core/shell NPs.

Figures 1a and 1b show TEM images for ZnO core NPs and ZnO/17%ZnS core/shell NPs, respectively. The average size ZnO core NP is estimated to be 19 nm. In Figure 1b core–shell structure of the particles can be clearly identified, and the sizes of the nanoparticles increased to about 22 nm, meaning the shell thickness is about 1.5 nm. In light of the 0.31 nm ZnS lattice parameter, it is roughly estimated that 5 monolayers of ZnS shells were obtained as expected.

Figure 2 presents the XRD patterns of ZnO core NPs, ZnO/6%ZnS, and ZnO/32%ZnS NPs. The diffraction pattern of ZnO core NPs has six peaks which correspond to hexagonal wurtzite structures. The average particle size, calculated using the Scherrer equation ($D = K\lambda/\beta\cos\theta$) is 18.8 nm, which is in good agreement with the TEM results discussed above. The XRD patterns of ZnO/6%ZnS NPs show peaks only due to wurtzite ZnO NPs structure, while that of ZnO/32%ZnS NPs shows three new broad peaks corresponding to (111), (220), and (311) planes of zincblende ZnS structures in addition to wurtzite ZnO NPs structures.

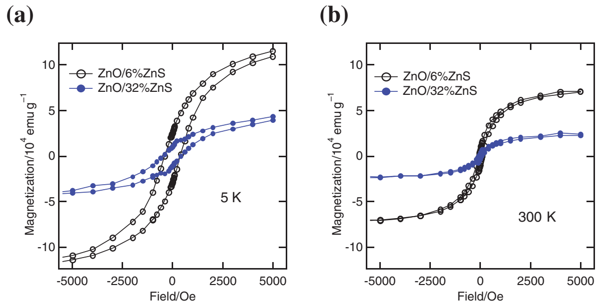

**Figure 3.** Magnetization curves of ZnO/6%ZnS and ZnO/32%ZnS core/shell NPs at a) 5 K and b) 300 K, respectively, after subtracting the diamagnetic components.

The magnetization curves of ZnO/6%ZnS and ZnO/32%ZnS NPs were measured at 5 and 300 K. In both cases, ferromagnetic contributions adding to the diamagnetic character were found even though the starting ZnO nanoparticles showed only a diamagnetic components (see Supporting Information).[7] The ferromagnetic contribution can be clearly seen after subtracting the diamagnetic component (Figure 3). Since both ZnO and ZnS are originally diamagnetic materials, it suggests that this ferromagnetism is contributed by ZnO–S bonds which formed as a result of being created core–shell structures. The differences of the saturation magnetization values reflect the difference of the shell thickness. As shell thickness increases, meaning the increase of diamagnetic ZnS, the saturation magnetization values (emu $g^{-1}$) decrease. On the other hand, the coercivity is almost the same regardless of shell thickness (400 Oe at 5 K and 70 Oe at 300 K). These observations indicate that the ferromagnetism appears only at the ZnO–ZnS interfaces.

Now we provide one possible explanation for these phenomena in analogy with the appearance of ferromagnetism in organic ligand-passivated and nontransition metal-doped ZnO, which are spin polarization in nonmagnetic elements via p–p interactions.[4a,4c–4f] The first-principle calculations by Shen et al. showed that when ZnO is doped with nonmagnetic 2p light element (N), N 2p spin, O 2p spin and O 2p hole are produced, then these spins are coupled through the O 2p holes.[4c] This p–d exchange-like p–p coupling interactions result long-range magnetic coupling. Furthermore, in organic ligand (alkanethiol or alkylamine)-passivated ZnO nanoclust systems, similar effect has been predicted.[4f] In this case, N or S atoms of the ligands bind to the Zn site with the accompanying hybridization between Zn 4s orbitals with N 2p or S 3p orbitals. As a result, the redistribution of charges between Zn and O atoms result in a magnetic system where the p electrons in O and N, and 3p electrons in S sites are spin polarized. In the current ZnO/ZnS core/shell system, the surface Zn sites of core ZnO NPs must bind to S atom of ZnS shell through the shell formation. Although the Zn–S bonds are limited to the interfaces between ZnO core and ZnS shell, the situation is not very different from the above systems. Hence, the spin polarization of p electrons in O and S sites through the p–p coupling interactions could be predicted also in the current system.

In summary, ZnO/ZnS core/shell NPs were successfully synthesized. We showed the ferromagnetism appeared at the ZnO–ZnS interfaces. This ferromagnetism could be attributed to p–p coupling interactions between S 3p and O 2p electrons. Although the origin of the interface ferromagnetism in the current system is not completely clear and further investigations will be needed, our present findings possibly open up a new way to introduce magnetism in semiconductor-based spintronics devices.

This work was supported by a Grant-in-Aid for Scientific Research in Priority Areas "Photochromism (No. 471)" from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of the Japanese Government.

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