Visualization of the depletion layer is a significant a guideline for the material design of gas sensors. We attempted to measure the potential barrier at the interface of core–shell microspheres composed of $p$-$MgO/n$-$MgFe_2O_4/Fe_2O_3$ from the inside out by means of Kelvin probe force microscopy (KPFM) as a first step to visualizing enlargement of the depletion layer. As determined by high-angle annular dark-field scanning transmission electron microscopy, ca. 70% of the microspheres were hollow with a wall thickness of ca. 200 nm. Elemental mapping revealed that the hollow particles were composed of ca. 20 nm of MgO, ca. 80 nm of MgFe$_2$O$_4$, and ca. 100 nm of Fe$_2$O$_3$. A difference of 0.2 V at the $p$-$MgO/n$-$MgFe_2O_4$ interface was clarified by KPFM measurements of the hollow particles, suggesting that this difference depends on the formation of a $p$-$n$ junction. The potential barrier enlarged by the formation of a $p$-$n$ junction was considered to increase the resistance in air ($R_a$), since the $R_a$ of the core–shell hollow microspheres was higher than that of MgO, Fe$_2$O$_3$, MgO–Fe$_2$O$_3$, and MgO/MgFe$_2$O$_4$/Fe$_2$O$_3$ particles with irregular shapes. Measurement of the potential barrier height by KPFM is a promising potential approach to tuning the gas sensitivity of oxide semiconductors.

The detection of various gases is important for constructing safety nets in today’s society. For example, one type of well-known detection technology is monitoring systems for gas leaks and flammable gases such as methane that originates from coal oil complexes. Oxide semiconductors are used for these gas detection methods, wherein the presence of a gas is detected based on a change in resistance caused by the electrical interaction between gas molecules and the oxide semiconductor. For gas detection with oxide semiconductors, a linear relationship between the change in electrical resistance and gas concentration is assumed as a rule of thumb. According to assumption, increasing the amount of adsorbed oxygen is key to enhancing the sensor response to gas, or gas sensitivity. Adsorbed oxygen is generated when oxygen in the air takes electrons from the surface of the oxide semiconductor and adsorbs to the surface as negatively charged species (adsorbed oxygen: O$^-$, O$_2^-$). At the same time, a space charge layer (depletion layer) with a low carrier concentration forms from the surface of the oxide inward. Controlling this depletion layer could allow for tuning of the gas sensitivity.

Oxide semiconductor sensors using a change in a depletion layer enlarged by formation of a $p$-$n$ junction can be categorized following: the enlargement of depletion layer originates only from $p$-$n$ junction that from sulfurization on the surface of $p$-type oxide. Especially, latter contains electronic sensitizing by sulfurization, as shown in Table 1. Among the former, the morphology of $n$-TiO$_2$/p-CuO nanowires was effective to enhance sensor response to 1 ppm CO as one of reductant gases when the wall thickness of TiO$_2$ shell was 60 nm. This result was supported by the experimental fact that its base resistance in air was highest in the wall thickness from 0 to 100 nm. If there is correlation data between the combination of $p$-$n$ junction and the enlargement of depletion layer, the sensor with high sensing performance could be designed by selecting the optimal combination of $p$-$n$ junctions without try and errors of experiments.

As a first step toward this goal, this study visualized the increase in the depletion layer due to $p$–$n$ junction formation by measuring the barrier height at the grain boundary from the local surface potential near the grain boundary using a Kelvin probe force microscope (KPFM). The first visualization of the depletion layer is the measurement of the surface potential of the silicon $p$–$n$ junction by KPFM. After that, it was reported that the barrier height at the grain boundary of polycrystalline silicon was measured by using KPFM, and the potential...
barrier height changed depending on the grain boundary character. As a recent visualization technique of the depletion layer, when the forward bias and the reverse bias were applied to the operating semiconductor material (GaAs), the change of the depletion layer width of only 1 nm was measured. Besides, the electron beam induced current (EBIC) realized a visualization of the depletion layer by two-dimensional mapping. However, advanced thinning technique is required to visualize the depletion layer by above techniques.

In this study, it is possible to form heterogeneous junctions by our simple process (Fig. 1) for preparation of core–shell micro hollow particles. The KPFM measurement sample can also be prepared with a simple method (embedding the particles in a conductive resin and polishing them).

In our previous research, we revealed that composite oxides of MgO–Fe₂O₃ respond to 10 ppb hydrogen sulfide. It was found that MgO acts as a p-type semiconductor and MgFe₂O₄ acts as an n-type semiconductor, thereby contributing to an increase in the depletion layer due to the p–n junction. In this study, KPFM measurements clarified the formation of p–n junctions in core–shell microspherical particles with Fe₂O₃ as the core and MgFe₂O₄ and MgO as the shells. In addition, microstructural observations indicated that the MgO shell behaves as a semiconductor.

The preparation of core–shell microspherical particles is depicted (Fig. 1). After chemically attaching OH groups to the surface of hematite (Fe₂O₃) particles obtained by thermal oxidation of magnetite (Fe₃O₄) at 800 °C for 3 h, the particles were immersed in a solution containing magnesium ions to precipitate Mg(OH)₂. By heat-treating (800 °C, 3 h), Mg(OH)₂ was dehydrated to MgO, and MgFe₂O₄ was formed at the interface between the Fe₂O₃ core and MgO shell.

### Table 1. Oxide semiconductor sensors using a change in a depletion layer enlarged by formation of a p–n junction. "/" denotes outside oxide/inside oxides, and "–" mixtures. The enlargement of depletion layer originates only from p–n junction is show in Refs., and that from sulfurization on the surface of p-type oxide in Refs.

| Materials   | Target gases | Operating temperature (°C) | Comparison of sensor response | p–n junction effect (Ratio of composite to pure in sensor response) | References |
|-------------|--------------|----------------------------|-------------------------------|---------------------------------------------------------------|------------|
| NiO/ZnO     | 100 ppm TEA  | 320                        | 78.4(ZnO)                     | 185.1 to 2.36                                                 | 7          |
| NiO/ZnO     | 100 ppm acetone | 330                    | < 7(ZnO), < 3(NiO)            | < 12 to 1.7(ZnO), < 4(NiO)                                   | 8          |
| NiO/ZnO     | 10 ppm H₂   | 200                        | n/a                          | 60%(S = ΔR/Ro × 100) to n/a                                  | 9          |
| NiO/SnO₂    | 10 ppm TEA  | 220                        | 14.5(SnO₂)                    | 48.6 to 3.35                                                 | 10         |
| CuO/ZnO     | 50 ppm ethanol | 240                      | ≥ 2.5(CuO)                    | 4.5 to 1.8                                                   | 11         |
| CuO/TiO₂    | 10 ppm H₂   | 200                        | 0.26(CuO), 0.88(TiO₂)         | 2(S = ΔI/ΔI₀) to 8(CuO), 2(TiO₂)                             | 12         |
| 107950039243000TiO₂/CuO | 1 ppm CO | 300                         | 1.1(CuO)                     | 7.14 to 6.5                                                  | 13         |
| SnO₂–CuO    | 1000 ppm ethanol | 150              | n/a                          | 84.7 to n/a                                                  | 14         |
| SnO₂/CuO    | 50 ppm HCHO | 250                        | ≥ 1.4(CuO)                    | ≥ 2.4 to 1.7                                                 | 15         |
| CuO–SnO₂    | 50 ppm H₂S  | 200                        | 7.8(SnO₂)                     | 35,000 to 4487                                               | 16         |
| CuO–SnO₂    | 200 ppm H₂S | ≥ 27                        | n/a                          | < 800 to n/a                                                 | 17         |
| CuO/In₂O₃   | 10 ppm H₂S  | 200                        | ≥ 60(CuO)                     | ≥ 120 to 2.0                                                 | 18         |
| 107635326162000CuO-ZnO | Hollow tubule | 50 ppm H₂S | 170 | n/a | < 65 to n/a | 19         |
| CuO/ZnO     | 100 ppm H₂S | 250                        | 10(ZnO), 1.3(CuO)             | < 60 to 6(ZnO), 46(CuO)                                     | 20         |
| CuO/ZnO     | 100 ppm H₂S | 250                        | 10(ZnO), 1.3(CuO)             | < 60 to 6(ZnO), 46(CuO)                                     | 20         |

Figure 1. Preparation of core–shell microspheres. The Fe₂O₃ cores were completely covered with MgO shells, and the interfacial MgFe₂O₄ phase was formed by heating at 800 °C for 3 h.
Results and discussion

The X-ray diffraction (XRD) pattern of the obtained core–shell microspherical particles is shown in Supplementary Fig. S1. All patterns were attributed to the Fe₂O₃ core and MgFe₂O₄ and MgO shells. Since the diffraction peaks of MgFe₂O₄ and MgO partially overlap, the abundance was estimated as follows from the relative peak intensity ratio in the ICDD database.

\[
\text{Abundance ratio} = \frac{\Sigma I(\text{MgFe}_2\text{O}_4)}{\Sigma I(\text{MgO})}
\]  

Figure 2. Microstructure of core–shell microspheres: (a) bright-field image obtained by inserting the object aperture into the center of diffraction spot, i.e., 000; (b) HAADF-STEM image; and elemental mapping images of (c) Mg-Kα, (d) Fe-Kα, and (e) O-Kα from the square area marked in (b).

According to Eq. (1), the abundance ratio of the sample after heat treatment (800 °C, 3 h) was approximately 1, indicating the presence of the same amounts of the MgFe₂O₄ and MgO shell constituents.

The secondary electron image of the core–shell microspherical particles and the MgKα, FeKα, and OKα mapping images are shown in Supplementary Fig. S2. The diameter of the core–shell microspherical particles was approximately 1 μm, and Mg and Fe existed in a spherical shape.

The microstructural observations of the core–shell microspherical particles are shown in Fig. 2. The typical bright-field image shows the presence of hollow spherical particles (Fig. 2a). The abundance of hollow particles was approximately 70%, as indicated by the high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) images (Fig. 2b-1,2). Figure 2c is enlarged view of the square area in Fig. 2b-2. Based on the elemental mapping of the shell of the hollow particles (Fig. 2d–f), the shell thickness was approximately 200 nm. It is suggested that approximately 100 nm of the inner shell is Fe₂O₃, approximately 80 nm of the outer shell is MgFe₂O₄, and approximately 20 nm of the outermost surface is MgO. From these observations, it is assumed that the core Fe₂O₃ diffused into the shell MgO to form interfacial MgFe₂O₄, while Mg(OH)₂ was dehydrated to MgO by the heat treatment (800 °C, 3 h).

The KPFM results for the core–shell micro hollow particles are shown in Fig. 3. Since the core–shell particles were mirror-polished after being embedded in a conductive resin, the resin penetrated the hollow particles. The potential barrier of Cu within the conductive resin was adopted as the background potential for measuring the potential barrier height. In Fig. 3, high potential barriers are shown in red, and low are in blue. Based on the line analysis of four potential barrier heights (Fig. 3A–H), the average change in the potential barrier in the shell was approximately 0.2 V. In all four lines, the potential barrier in the inner shell tended to be higher than that in the outer shell. This may reflect the result of p–n junction formation between the p-type MgO and n-type MgFe₂O₄. Thus far, in the field of gas sensors, although it has been suggested that a p–n junction will cause the depletion layer to expand, this phenomenon has yet to be visualized.

In general, MgO is considered an insulator because of its high band gap (7.8 eV). However, recent studies have reported that one-dimensional MgO monolayers consist of an aggregate of several nanometers of MgO...
(MgO microcrystals) with a band gap of 3.2 eV. Figure 4 shows a high-resolution TEM image of the MgO layer (approximately 20 nm) of the core–shell micro hollow particles in this study. The MgO layer consists of MgO microcrystals of several tens of nanometers, suggesting that the MgO layer in this study behaves as a semiconductor.

Supplementary Fig. S3 shows the temperature dependence of the electrical resistance in air (R_a) of spherical Fe_2O_3 particles, amorphous MgO particles, a mixture of both particles, and the core–shell micro hollow particles. The core–shell micro hollow particles showed high R_a values at all temperatures due to the p–n junction effect.

The sensor response of MgO (Supplementary Fig. S3e) to 250 ppm at 3 ppm H_2S was added as Fig. S4. The sensor response (S = R_g/R_a) increased upon exposure to H_2S. Generally, in air, oxygen is adsorbed as a negative charge on the surface of an n-type oxide semiconductor (adsorbed oxygen: O^2-), and a depletion layer is formed from the surface to the inside. When the atmosphere is switched from air to reducing gas (H_2S), the adsorbed...
oxygen ($O^{2-}$) reacts with $H_2S$ [$H_2S + 3 O^{2-}$ (ad.) $\Rightarrow H_2O + SO_2 + 6e^-$], and the adsorbed oxygen electrons are depleted. By moving them to the layer, the depletion layer is reduced, leading to a reduction in electrical resistance. Since the behavior of the sensor response in Supplementary Fig. S4 showed an increase in resistance, the depletion layer is increasing. Therefore, it was considered that MgO behaved as p-type.

In order to investigate the cause of the difference in surface potential due to junction between oxides, the wave of surface potential in the same region as Fig. 3 was separated by Gaussian function. The width of depletion layer of each oxide was labelled as the full width half maximum (FWHM) in Fig. 5 in symbols of A1, A2, D1, and D2. Subsequently, the carrier concentration was calculated using the width. It was assumed that the dielectric constant of each oxide is proportional to the thickness of each oxide (MgO: 20 nm, MgFe$_2$O$_4$: 80 nm, Fe$_2$O$_3$: 100 nm), obtained from the HAADF-STEM image in Fig. 4. The dielectric constant of each region was calculated by distributing the dielectric constant of each oxide (MgO: 9.90$^{32}$, MgFe$_2$O$_4$: 154$^{128}$, Fe$_2$O$_3$: 65.9$^{99}$) based on the thickness of each oxide. The carrier concentration calculated using the dielectric constant of each region changed by the width of depletion layer at each region (Supplementary Table S1). Generally, the carrier concentration decreases as an enlargement of depletion layer width. The carrier concentration of MgO–MgFe$_2$O$_4$ (A1 and A2 of Supplementary Table S1) was higher than that of single crystal of MgO$^{30}$ (3.6 x 10$^{17}$ cm$^{-3}$) and much lower than that of polycrystal of MgFe$_2$O$_4$,$^{31}$ (2.5 x 10$^{22}$ cm$^{-3}$). This is evidence that depletion layer was enlarged by p–n junction formation between the p-type MgO and n-type MgFe$_2$O$_4$. In the carrier concentration of MgFe$_2$O$_4$–Fe$_2$O$_3$ (D1 and D2 of Supplementary Table S1), same tendency was confirmed even considering the carrier concentration of Fe$_2$O$_3$,$^{32}$ (1.6 x 10$^{19}$ cm$^{-3}$). This suggests that the enlargement of depletion layer by formation of p–n junction could affect the carrier concentration of n–n junction (MgFe$_2$O$_4$–Fe$_2$O$_3$). From above discussion, it is considered that the KPFM measurement results of this study were effective to characterize electrically the core–shell microsphere particles.

**Conclusion**

The MgO/MgFe$_2$O$_4$/Fe$_2$O$_3$ core–shell microsphere particles were prepared by heat treating core–shell microsphere particles with Fe$_2$O$_3$ as the core and MgO as the shell. Approximately 70% of the obtained spherical particles were hollow in structure and comprised, from the outside in, approximately 20 nm of MgO, 80 nm of MgFe$_2$O$_4$, and 100 nm of Fe$_2$O$_3$ from the outer shell. As determined by KPFM measurements of the hollow particles, the difference in potential barrier height at the interface between MgO and MgFe$_2$O$_4$ was approximately 0.2 V. This difference was reflected in the measured $R_t$ values, suggesting that it was due to the formation of a p–n junction between p-type MgO and n-type MgFe$_2$O$_4$. In the development of gas sensors, measuring the potential barrier height with KPFM may lead to tunable gas sensitivity. As one of recent our results, the potential barrier height of jointing interface between p-type CuO (Eg: 1.4 eV) and n-type SnO$_2$ (Eg: 3.7 eV) was higher than that of CuO and SnO$_2$. The sensitivity to detection gases could be tuned by selecting combination of p-type and n-type oxides among many oxide semiconductors with different bandgap, based on the magnitude in the resultant potential barrier height by the formation of p–n junction. The estimation of carrier concentration based on the surface potential of each junction of oxides measured by KPFM was clarified to be quite effective for depletion engineering of gas sensing materials.

**Methods**

Core–shell microspherical particle synthesis. Magnetite (Fe$_3$O$_4$) spherical particles with the diameter of ca. 1 μm were obtained by dissolving iron oxyhydroxide in a solvent (ethylene glycol and 9 wt% H$_2$O) and hydrothermally treating it at 200 °C for 24 h in an autoclave, as described in our previously published work.$^{33}$ An Fe$_3$O$_4$ spherical powder with a particle size of 1 μm was then obtained by heat-treating (800 °C, 3 h). The Fe$_3$O$_4$ spherical particles were immersed in a 6 mol/L sodium hydroxide aqueous solution (alkalization). Subsequently, the alkalized Fe$_3$O$_4$ spherical particles were dissolved in an aqueous magnesium acetate (Mg(CH$_3$COO)$_2$) solution and stirred for 30 min. At this time, the molar ratio of Fe:Mg was 4:6. The obtained suspension was centrifuged (5000 rpm, 3 min) and heat-treated (800 °C, 3 h) to obtain core–shell microspherical particles.

Sample for HAADF-STEM observation. The powder sample was dissolved in 10 mL of ethanol to 1 wt%, and a suspension was obtained through ultrasonication. The obtained suspension was dropped onto a Cu...
grid with a collodion film and dried to obtain the sample for TEM observation at 200 kV (TECNAI-F20, FEI, Japan). The core–shell microspherical particles were characterized by elemental mapping using an Si detector to detect characteristic X-rays (Mg-Kα: 1.253 keV; Fe-Kα: 6.389 keV; O-Kα: 0.525 keV).

**Sample for KPFM measurement.** As a first step, a conductive resin (Technovit 5000, Kulzer, Germany) were prepared, which is composed of the mixture of powder (90 wt% Cu and 10 wt% benzoyl peroxide) and liquid (organic compounds: C₅H₈O₂, C₁₂H₁₈O₄, C₁₄H₂₂O₆). The mixing weight ratio of powder to liquid is 2:1. The liquid was put in the half of the powder in a hard paper cup and mixed thoroughly. Continuously, the second half of powder was poured in the cup after mixed for 40 s. After that, the mixture of the core–shell microspherical particles and the conductive resin were poured into a mold and cured to obtain the polishing sample. Parallel polishing (#1500, #2000, #2400, #4000) using water-resistant abrasive paper and buffing (diamond slurry: 3 μm, 0.25 μm) afforded the observation sample for KPFM with a mirror surface. The final shape of the sample was a disc of 10 mm diameter and 1 mm thickness. Then, the sample was attached to the sample holder, which is stainless steel disk of 15 mm diameter and 1 mm thickness by carbon tape, and the lower surface of the holder was directly connected to the stage of KPFM (SPM-9700HT, Shimadzu, Japan).

**KPFM measurement conditions.** The Kelvin Probe Force Microscopy (SPM-9700HT, Shimazu, Japan) was used for visualization of potential barrier height at the joining interface of MgO/MgFe₂O₄/Fe₂O₃ core–shell microsphere particles. The surface potential (in reality, the contact potential difference between the probe and sample) was measured by applying an alternating voltage between the probe and sample while vibrating the conductive probe at 0.1 Hz for square area of 2 μm × 2 μm and detecting the vibration of the cantilever at 74 kHz for KPFM mode due to electrostatic force. In this study, the sample was scanned with tapping mode by Pt–Ir coated Si cantilever with a curvature radius of tip, R ≤ 25 nm, resonance frequency, f₀ = 75 kHz, force constant, kₚ = 2.8 N/m (EFM-20, NanoWorld, Switzerland). The measurement was conducted with following conditions: scanning speed, 0.1 Hz; resolution, 256 × 256 pixels. The spatial resolution of this device is 0.2 nm. It is noted that the spatial resolution of this device is 0.2 nm.

**XRD measurement conditions.** Powder XRD (Ultima IV, RIGAKU, Japan) was used to identify the crystalline phase of the core–shell microspherical particles. The tube voltage, tube current, and scanning speed were 45 kV, 40 mA, and 4°/min, respectively.

**Sample for SEM observation.** Field emission scanning electron microscopy (JSM-7600F, JEOL, Japan) was used for morphological observations and elemental mapping of the core–shell microspherical particles. The accelerating voltage, working distance, and detection angle were 15 kV, 8 mm, and 15°, respectively.

**Sample for electrical resistance measurement.** An Au wire was fixed with Au paste to an Au interdigitated electrode (teeth number: 50, gap size: 5 μm) via ordinary ultraviolet exposure, and the solvent was volatilized by heat treatment (400 °C, 30 min). The sample for electrical resistance measurement was obtained by heat treatment for ohmic contact (400 °C, 30 min).

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**References**

1. Patel, P. Monitoring methane. *ACS Cent. Sci.* 3, 679–682 (2017).
2. Seiyama, T., Kato, A., Fujishi, K. & Nagatani, M. A new detector for gaseous components using semiconductive thin films. *Anal. Chem.* 34, 1502 (1962).
3. N. Taguchi, Japan Patent 45-38200 (1962).
4. Yamazoe, N., Fuchigami, J., Kishikawa, M. & Seiyama, T. Interactions of tin oxide surface with O₂, H₂O and H₂. *Surf. Sci.* 86, 335–344 (1979).
5. Xu, C., Takami, J., Miura, N. & Yamazoe, N. Grain size effects on gas sensitivity of porous SnO₂-based elements. *Sens. Actuators B* 3, 147–155 (1991).
6. Bielanski, A. & Haber, J. Oxygen in catalysts on transition metal oxides. *Catal. Rev. Sci. Eng.* 19, 1–41 (1979).
7. Jü. D. et al. Highly sensitive and selective triethylamine-sensing properties of nanosheets directly grown on ceramic tube by forming NiO/ZnO PN heterojunction. *Sens. Actuators B* 200, 288–296 (2014).
8. Liu, Y., Li, G., Mi, R., Deng, C. & Gao, P. An environment-benign method for the synthesis of p-NiO/n-ZnO heterostructure with high triethylamine-sensing properties of NiO/SnO₂ hollow sphere P–N heterojunction sensors. *Sens. Actuators B* 191, 537–544 (2014).
9. Lee, J. H., Kim, J. Y., Mirzaei, A., Kim, H. W. & Kim, S. S. Significant enhancement of hydrogen-sensing properties of ZnO nanofibers through NiO loading. *Nanomaterials* 8, 902 (2018).
10. Jü, D. et al. High triethylamine-sensing properties of NiO/SnO₂ hollow sphere P–N heterojunction sensors. *Sens. Actuators B* 215, 39–44 (2015).
11. Yin, M., Wang, F., Fan, H., Xu, L. & Liu, S. Heterojunction CuO@ZnO microcubes for superior p-type gas sensor application. *J. Alloys Compd.* 672, 374–379 (2016).
12. Alev, O., Şennik, E. & Oztürk, Z. Z. Improved gas sensing performance of p–copper oxide thin film/n–TiO₂ nanotubes heterostructure. *J. Alloys Compd.* 749, 221–228 (2018).
13. Lee, J.-H., Kim, J.-H. & Kim, S. S. CuO–TiO₂ p–n core–shell nanowires: Sensing mechanism and p/n sensing-type transition. *Appl. Surf. Sci.* 448, 489–497 (2018).
33. Abe, H., Naka, T., Sato, K., Suzuki, Y. & Nakano, M. Shape-controlled syntheses of magnetite microparticles and their magnetoresistance. Sens. Actuators B 290, 233–241 (2019).

15. Zhu, L.-Y. et al. Fabrication of heterostructured p-CuO/n-SnO2 core–shell nanowires for enhanced sensitive and selective formaldehyde detection. Sens. Actuators B 290, 118–125 (2018).

16. Maekawa, T., Tamaki, J., Miura, N. & Yamazoe, N. Sensing behavior of CuO-loaded SnO2 element for H2S detection. Chem. Lett. 20, 575–578 (1991).

17. Zhou, X., Cao, Q., Huang, H., Yang, P. & Hu, Y. Study on sensing mechanism of CuO–SnO2 gas sensors. Mater. Sci. Eng. B 99, 44–47 (2003).

18. Li, X. et al. Octahedral-like CuO/In2O3 mesocages with double-shell architectures: Rational preparation and application in hydrogen sulfide detection. ACS Appl. Mater. Interfaces 9, 44632–44640 (2017).

19. Na, H.-B. et al. A fast response/recovery ppb-level H2S gas sensor based on porous CuO/ZnO heterostructural tubule via confined effect of absorbent cotton. Sens. Actuators B 297, 126816 (2019).

20. Han, X. et al. Composition-controllable p-CuO/n-ZnO hollow nanofibers for high-performance H2S detection. Sens. Actuators B 285, 495–503 (2019).

21. Kikukawa, A., Hosaka, S. & Imura, R. Silicon pn junction imaging and characterizations using sensitivity enhanced Kelvin probe force microscopy. Appl. Phys. Lett. 66, 3510–3512 (1995).

22. Turekawa, S., Kido, K. & Watanabe, T. Measurements of potential barrier height of grain boundaries in polycrystalline silicon by Kelvin probe force microscopy. Philos. Mag. Lett. 85, 41–49 (2005).

23. Anada, S. et al. Precise measurement of electric potential, field, and charge density profiles across a biased GaAs p–n tunnel junction by in situ phase-shifting electron holography. J. Appl. Phys. 122, 225702 (2017).

24. Haney, P. M., Yoon, H. P., Gaury, B. & Zhizhein, N. B. Depletion region surface effects in electron beam induced current measurements. J. Appl. Phys. 120, 095702 (2016).

25. Hashishin, T. et al. Magnesium ferrite sensor for H2S detection. Sens. Mater. 28, 1229–1236 (2016).

26. Yin, D., Chen, C., Saito, M., Inoue, K. & Ikuhara, Y. Ceramic phases with one-dimensional long-range order. Nat. Mater. 18, 19–23 (2019).

27. Subramanian, M. A., Shannon, R. D., Chai, B. H. T., Abraham, M. M. & Wintersgill, M. C. Dielectric Constants of BeO, MgO, and MgFe2O4. J. Phys. Chem. of Solids 26, 1325–1341 (1965).

28. Pollard, J. H., Bowler, D. L. & Pomerantz, M. A. Electrical conductivity induced in Mgo by relativistic electron bombardment. J. Phys. Chem. Solids 225702 (1965).

29. Zaki, H. M. The influence of Zn ions substitution on the transport properties of Mg-ferrite. Phys. B Condens. Matter 404, 3356–3362 (2009).

30. Zhang, R. et al. Enhanced photoelectrochemical water oxidation performance of Fe3O4 nanorods array by S doping. ACS Sustain. Chem. Eng. 5, 7502–7506 (2017).

31. Abe, H., Naka, T., Sato, K., Suzuki, Y. & Nakano, M. Shape-controlled syntheses of magnetite microparticles and their magnetoelectrochemical properties. Int. J. Mol. Sci. 20, 3617 (2019).

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Author contributions

T.H. designed the research study, performed characterization of the samples, and wrote almost the paper. C.S. performed KPFM measurements, drew Fig. 3 and graphical abstract. Y.N. established the preparation technique of core–shell particles and wrote partially the paper. H.A. supported synthesizing magnetite sphere. M.M. advised always electronic behavior of core–shell particles and fine structure of core–shell particles. H.K. advised always about research direction of this study.

Competing interests

The authors declare no competing interests.

Additional information

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