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High Pressure Induced in Situ Solid-State Phase Transformation of Nonepitaxial Grown Metal@Semiconductor Nanocrystals

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Supporting Information

ABSTRACT: Considering the large lattice mismatch induced interface strain between nonepitaxial grown monocrystalline semiconductor shell and metal core, we studied the solid-state phase transformation of such nonepitaxial grown Au@CdS core/ shell NCs under high pressure in this paper. Consistent with HRTEM characterizations, the high resolution Raman spectra and synchrotron angle-dispersive X-ray diffraction (ADXRD) spectra evolution were utilized to investigate the hydrostatic pressure (0-24 GPa) induced gradual phase transformation. Due to the strong lattice interactions between Au core and CdS shell, the different behavior and improved stability under high pressure appeared compared to single quantum dots (QDs).

etal/semiconductor hybrid nanocrystals (NCs) under large lattice mismatch, in particular the case of monocrystalline semiconductor shell coated on metal core, are newly emerging nanomaterials with improved plasmonexciton coupling and stronger light-matter-spin interactions.¹⁻³ The Zamkov group has reported the enhanced lifetime of excitons in such nonepitaxial Au@CdS core/shell NCs due to the lower defect density in the heterointerface and the plasmon enhancement effect.⁴ For achieving wide solid-state applications, it is important to investigate construction stability and phase transformation of these nonepitaxial grown core/shell NCs under some special conditions, such as high pressure.^{5–13} For example, Chen et al. reported that pressure driving quantum-dot-Au into heteronanostructure super lattice.¹ Core/shell structures have maximum heterointerconnection between metal and semiconductor and therefore exhibit great capabilities for electrics,¹⁵ magnetics,¹⁶ photocatalysis,¹⁷ and biosensors technologies.^{18,19} Due to the semiconductor phase transformation and heterointerface effect driven by high pressure, it is significant to study such core/shell NCs phase



transformation under high pressure which is useful to design and fabricate high pressure detectors.

In the past decades, the phase transformation of quantum dots (QDs) under high pressure has drawn extensive research interest. For example, the Alivisatos group has reported the phase transformation of CdS and CdSe QDs under high pressure and the dependence of their luminescence properties on the crystal phase transformation.²⁰ Ouyang and his coworkers have investigated the spin coherence dynamics in solid CdSe QDs under high pressure.³ Some simulations studies were also carried out for probing into the mechanism of phase transformation of CdSe ODs.^{9,21,22} For example, Zahn has performed molecular dynamics simulation to illustrate the pathway of CdSe phase transformation from wurtzite type to rocksalt type.⁸ To the best of our knowledge, these is no work investigating phase transformation behaviors of hybrid metal@

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Figure 1. (A) Schematic of high pressure treatment; (B) the XRD pattern of Au@CdS core/shell nanocrystals before (top) and after (bottom) high treatments; (C and D) LRTEM of Au@CdS core/shell NCs before (C) and after (D) high pressure treatment; (E and F) HRTEM images Au@CdS core/shell NCs before (E) and after (F) high pressure treatment.

semiconductor NCs under hydrostatic high pressure, in particular the case of core/shell with large lattice mismatch. The insights into the *in situ* phase transformation and interface evolution of such nanostructures under high pressure are highly desirable for broadening their applications in solid state devices.

By use of the synchrotron angle-dispersive X-ray diffraction (ADXRD) and high resolution Raman characterization techniques, the *in situ* phase transformation such hybrid NCs under high pressure is explored in the case of nonepitaxial Au@CdS core/shell structure. It offers a unique opportunity to

explore various fundamental properties and interactions in solids with large lattice mismatch. $^{23-25}$

The symmetric Au@CdS core/shell NCs were prepared according to our previously reported nonepitaxial growth strategy¹ and then was placed in diamond anvil cell for high pressure treatment (Figure 1A). The ADXRD pattern (Figure 1B) showed the CdS shell transformed from the wurtzite phase into the rocksalt phase under 24.2 GPa while the Au core remained in the face center cubic (FCC) phase after high pressure treatment. The corresponding low-resolution transmission electron microscopy (LRTEM) images demonstrated

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Figure 2. (A and B) ADXRD pattern of Au@CdS core/shell depending on pressure: pressuring directly (A); hydrostatic pressure (B); (C and D) Raman spectrum (C) and Raman shift depending on pressure (D) of Au@CdS NCs.

the well-defined Au@CdS core/shell heterostructure and clear tightly connection interface (Figure 1, parts C and D). The CdS shell was also confirmed by high-resolution transmission electron microscope (HRTEM) characterization. The lattice distance of 0.35 nm was assigned to the (100) facets of wurtzite CdS (w-CdS). After high pressure treatment, the lattice distances were measured as 0.29 and 0.34 nm respectively, assigning to the facets (200) and (111) of rocksalt CdS (r-CdS). The electron diffraction pattern (Figure S1) further confirmed that the CdS shell was assigned to rocksalt phase. Meanwhile, CdS shell before and after high pressure were confirmed as single crystalline. Following the reported calculation method,¹ The lattice mismatch between Au core and a w-CdS or r-CdS shell was obtained and presented in Table S1. The lattice mismatch between Au core and r-CdS shell was found smaller and the reduced interface strain was beneficial for stabilizing the core/shell structure.^{1'} Therefore, the high pressure drove the phase transformation of CdS shell and the reducing of interface strain stabilized the core/shell structure.

In order to investigate the pressure-induced CdS shell phase transformation, the synchrotron ADXRD patterns evolution and Raman spectra of Au@CdS core/shell NCs (Figure 2) were recorded as a function of pressure. The ADXRD with directly pressure was performed at the 4W2 beamline of the

Beijing Synchrotron Radiation Facility. A small ruby piece was used to determine the pressure according to the ruby fluorescence. Figure 2A, S2, and S3 showed detailed diffraction peaks evolution, crystal phase transformation, lattice space of main facets, and the corresponding lattice alteration. As presented in Figure 2A, the CdS shell remained as wurtzite phase even when the pressure was raised up to 5.0 GPa which was higher than phase transformation pressure for reported bulk CdS (3.4 GPa).²⁶ The w-CdS shell transformed into the r-CdS phase until the pressure was up to 7.48 GPa. The more details were discovered by using hydrostatic pressure characterization (Figure 2B) with silicone oil as pressure medium. The characterization was performed at the beamline 16-BM-D of the High Pressure Collaborative Access Team at Advanced Photon Source, Argonne National Laboratory, and the pressure was determined by the ruby fluorescence spectra. The phase transformation of CdS shell occurred when the hydrostatic pressure was increased to be around 6.6 GPa. Figures 2B and S4 clearly revealed that between ~6.6 and 9.4 GPa, two phases of CdS coexisted and w-CdS transformed to r-CdS completely at a pressure of 9.4 GPa. Along with the crystal phase transformation, the unit cell volume of Au core and CdS shell also obviously varied (Figure S4). Higher than 6.6 GPa, the r-CdS appeared accompanied by a remarkable decrease in unit cell volume. In the range of 6.6 to 9.4 GPa, the



Figure 3. (A and B) Schematic of interface of FCC-Au and CdS: (A) w-CdS; (B) r-CdS for first principle calculation. (C) Stress in Gpa versus strain in % for both Au/w-CdS and Au/r-CdS interface models under compression strain. The strain direction is perpendicular to the interface (along the Z direction).

unit cell volume did not vary much because of the coexistence of wurtzite and rocksalt phases. Furthermore, the lattice parameters were smaller than the bulk CdS (a = b = 4.14092 Å, c = 6.7198 Å,) and became smaller as pressure rising (see Table S2). Over 9.4 GPa, r-CdS became dominant and kept unchanged even at 24.4 GPa (Figure 2B). From wurtzite phase to rocksalt phase, previous simulation work showed that wurtzite phase (4-fold coordinated CdS) transits into a middle phase (5-fold coordinated CdS), then into rocksalt (6-fold coordinated CdS).^{3,7} Different from bulk CdS and CdS QDs, the CdS shell on Au support as fabricated in our research only showed diffraction peaks assignable to the wurtzite and rocksalt phases with no other peaks arising from an intermediated phase. Such difference was presumably caused not only due to the Au core effect but also to the strong crystalline interactions between Au core and CdS shell. Besides that, it was found that the rocksalt phase was preserved when the pressure was reduced back to 1 bar (Figure 2A and S4), coincident with the fact that rocksalt phase was more stable in thermodynamics.,⁷²² Although the Au core kept as FCC phase, its lattice parameter and unit cell volume became smaller with pressure increment, as shown in Figure 2B. On the interface between Au core and CdS shell, decreasing of unit cell volume under increased pressure shortened the interatomic distance and led to dynamically enhanced interface strain. Interface strain also became larger as the distance of Au core and CdS shell shorten. Figure 3 showed the simulation of interface strain increment by DFT, depending on the compressive distance of Au core and CdS shell. As shown in parts A and B of Figure 3, the interface was designed by employing facet (111) of FCC Au and facet (0001) of w-CdS to simulate the Au@w-CdS core/shell NCs while facet (111) of FCC Au and facet (001) of r-CdS were employed for simulating the metal/ semiconductor interface of Au@r-CdS core/shell NCs. Figure 3C presented pressure on the interface depending on the strain Au core and CdS shell, and the interface strain rose sharply between 0.35 and 0.40 lattice strain. It might be attribute to the larger lattice mismatch of w-CdS shell and Au core, driving the phase transformation to reduce the interface strain. Therefore, the comprehensive effects enforced the phase transformation of single crystalline CdS shell and phase transformation made

the Au@CdS more stable because rocksalt phase CdS produced weaker interface strain.

The w-CdS shell phase transformation pressure was also confirmed by its Raman spectra. As reported by Xiong et al.,²⁷⁻²⁹ Raman characterization was more sensitive to detect the phase transformation and related crystal lattice vibrations. Herein, the Raman spectra evolution was collected to study the phase transformation of Au@CdS NCs depending on pressure. Figure 2C exhibited that the first order longitudinal optical mode (1LO) and the second order longitudinal optical mode (2LO) of w-CdS shell centered at 303.4 and 610.6 cm^{-1} , respectively. Comparing to the reported 1LO of bulk wurtzite CdS (306 cm⁻¹) and CdS QDs (297 cm⁻¹), 25,30 the blue Raman shift of w-CdS shell was attribute to the weak surface optical mode (SO) and the low confided affection. The strong coupling between Au core and CdS shell enlarged the size and reduced the intensity of SO of CdS phonon.^{25,30} As the pressure increased, the peak of the 1LO phonon of CdS shell blue-shifted and became weaker.³¹ With compression of unit cell, the strength of Cd-S bond became stronger and accordingly the vibration energy became larger, thus resulting in the blue shift of Raman peak. Meanwhile, the shortened Cd-S bond might limit the vibration of lattice and lead to the weakening of Raman peaks. During compressing, lattice parameters (a, b and c) of w-CdS changed in different degrees, leading to the obvious symmetry change and the drastically diminished Raman peak at a lower pressure (5.44 GPa).^{3,7} It was reported that the 1LO Raman shift of CdS rocksalt phase was optically forbidden and Raman inactive.³¹ Hence, during the period of the CdS shell transforming into the rocksalt phase, the point-group transited from T_d into O_h (Figures S4 and S5) resulting in the higher symmetry of crystal and Raman inactivity. Furthermore, Raman shift of w-CdS was reported linearly depending on pressure in both bulk and nanoscale.^{26,32} However, such a linear relationship was not observed for Au@ CdS NCs in our research (Figure 2D). This nonlinear relationship suggested the totally different lattice vibration behaviors in w-CdS shell because of the strong direct lattice interactions between Au core and single crystalline CdS shell. Additionally, the direct lattice interactions also gave the result that the CdS lattice on the interface of Au core and CdS shell



Figure 4. (A) ADXRD pattern of Au NCs depending on pressure and (B and C) the TEM images of Au before (B) and after (C) high pressure treatment. (D) XRD pattern of CdS NCs and (E and F) the TEM images before (E) and after (F) high pressure treatments.

was squeezed with higher pressure or strain compared with that on the surface of Au@CdS nanocrystals. The squeezed asymmetry of the CdS shell was absent from the case of CdS QDs or bulk case, and it might cause a nonlinear relationship of the Raman data depending on pressure. Hence, the Au core made the phase transformation of w-CdS into r-CdS more complex than that for pure CdS and hinted that this kind of nonepitaxial grown core/shell NCs could enable efficient plasmon-exciton coupling and tunable light-matter-spin interactions.

In order to confirm the mechanism, Au NCs, CdS NCs with similar size and were investigated by high pressure treatments. Just shown in Figure 4A and S8, (111) and (200) facets of FCC-Au were located at 15° and 17°, respectively, and the according diffraction peaks were weak before pressure treatment that might be attributed to the small size. Under high pressure, Au nanocrystals were joined together easily and the diffraction peak intensity became stronger. TEM images of Au NCs (Figure 4, parts B and C) before and after highpressure treatment revealed that Au NCs grown to around 10 nm from 5 nm under high pressure. The different increasing rate of (111) and (200) facets diffraction peaks might be because Au nanoparticles united with little facets selectivity. Parts D-F of Figure 4 revealed the phase transformation of CdS NCs under high pressure. The ADXRD pattern of CdS NCs (Figure 3A) showed that CdS NCs remained the wurtzite phase even under 7.1 GPa, which was much higher than that for the w-CdS shell and further confirmed that Au supports enhanced w-CdS shell phase transforming. The TEM images of CdS NCs (Figure 4, parts E and F) show that the sizes were closed before and after high pressure treatment, illustrating the dependence of phase transformation of each CdS NPs. Therefore, Au core enhanced the phase transformation of w-CdS shell was further confirmed and the single crystalline of w-CdS shell was important to remain the core/shell structure.

In summary, the phase transformation behaviors of nonepitaxial Au@CdS core/shell NCs solid under high pressure have been elaborately studied by combining the ADXRD and Raman characterization techniques. As pressure increased, the single crystalline CdS shell gradually transformed from the wurtzite phase into the rocksalt phase gradually, while the Au core remained as an FCC phase and the overall core/shell was well preserved. In particular, the nonlinear Raman shift versus pressure indicated that the synergistic effect from the presence of Au core lattice interaction and quantum size effect of CdS shell. Compared to the behaviors of CdS NCs and Au nanoparticles under high pressure, the different phase transformation and structure evolution performance in such Au@CdS NCs indicated its good stability and the strong lattice interactions between Au core and CdS shell. All these unprecedented features suggest that nonepitaxial grown core/ shell NCs have improved heterointerface and interactions which may open up new potential applications.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jp-clett.8b03057.

Experiment details, Tables S1 and S2, and Figures S1–S4 (PDF)

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Notes

The authors declare no competing financial interest.

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