BNL-113435-2017-JA

Reversed Nanoscale Kirkendall Effect in Au-InAs Hybrid Nanoparticles

**Jing Liu, Yorai Amit, Yuanyuan Li,
Anna M. Plonka, Sanjit Ghose, Lihua Zhang,
Eric A. Stach, Uri Banin, and Anatoly I. Frenkel**

Submitted to Chemistry of Materials

October 2016

Center for Functional Nanomaterials

Brookhaven National Laboratory

**U.S. Department of Energy
USDOE Office of Science (SC),
Basic Energy Sciences (SC-22)**

Notice: This manuscript has been authored by employees of Brookhaven Science Associates, LLC under Contract No. DE-SC0012704 with the U.S. Department of Energy. The publisher by accepting the manuscript for publication acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or any third party's use or the results of such use of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Reversed Nanoscale Kirkendall Effect in Au-InAs Hybrid Nanoparticles

Jing Liu^{1,‡}, Yorai Amit^{2,3,‡}, Yuanyuan Li¹, Anna M. Plonka¹, Sanjit Ghose⁴, Lihua Zhang⁵, Eric A. Stach⁵, Uri Banin^{2,3,*} and Anatoly I. Frenkel^{1,6,*}

¹Department of Physics, Yeshiva University, New York, New York 10016, United States

²The Institute of Chemistry and ³The Center for Nanoscience and Nanotechnology, Hebrew University, Jerusalem 91904, Israel.

⁴National Synchrotron Light Source II, Brookhaven National Laboratory, Upton, New York 11973, United States

⁵Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York 11973, United States

⁶ Department of Materials Science and Chemical Engineering, Stony Brook University, Stony Brook, New York 11794, United States

ABSTRACT

Metal-semiconductor hybrid nanoparticles (NPs) offer interesting synergistic properties, leading to unique behaviors that have already been exploited in photocatalysis, electrical, and optoelectronic applications. A fundamental aspect in the synthesis of metal-semiconductor hybrid NPs is the possible diffusion of the metal species through the semiconductor lattice. The importance of understanding and controlling the co-diffusion of different constituents is demonstrated in the synthesis of various hollow structured NPs via the Kirkendall effect. Here, we used a post-synthesis, room-temperature reaction between AuCl₃ and InAs nanocrystals (NCs) to form metal-semiconductor core-shell hybrid NPs, through the “reverse Kirkendall effect”. In the presented system the diffusion rate of the inward diffusing specie (Au) is faster than that of the outward diffusion specie (InAs), which results in the formation of a crystalline metallic Au core surrounded by an amorphous, oxidized InAs shell containing nanoscale voids.

We used time-resolved (TR) x-ray absorption fine-structure (XAFS) spectroscopy to monitor the diffusion process and found that both the size of the Au core and the extent of the disorder of the InAs shell depend strongly on the Au-to-NC ratio. We have determined, based on multi-element fit analysis, that Au diffuses into the NC via the kick-out mechanism, substituting for In host atoms: this compromises the structural stability of the lattice and triggers the formation of In-O bonds. These bonds were used as markers to follow the diffusion process and indicate the extent of degradation of the NC lattice. Time-resolved x-ray diffraction (XRD) was used to measure the changes in crystal structures of InAs and the nanoscale Au phases. By combining the results of XAFS, XRD and electron microscopy, we correlated the changes in the local structure around Au, As and In atoms, and the changes in the overall InAs crystal structure. This correlative analysis revealed co-dependency of different structural consequences when introducing Au into the InAs NCs. This study of diffusion effects in nanocrystals therefore has relevance to powerful concepts in solid-state nanochemistry related to processes of cation exchange, doping reactions, and diffusion mechanisms.

1. INTRODUCTION

Colloidal semiconductor nanocrystals (NCs), also known as quantum dots (QDs), have attracted significant attention due to their unique size dependent optoelectronic properties^{1,2}. Synthetic routes already offer high control over the size, composition and shape of colloidal nanocrystals, leading to the demonstration of various geometries³⁻⁷ and heterostructures⁸⁻¹⁰ through, wet-chemistry methods. Nowadays, there is a growing interest in the synthesis of hybrid nanoparticles (NPs), which combine disparate materials onto a single system and often yield interesting synergistic properties.¹¹⁻¹⁵ Hybrid metal-semiconductor NCs were first presented by the growth of metal islands onto ZnO nanostructures,¹⁶ or TiO₂.¹⁷⁻¹⁹ However, these reports had limited control over the size and location of the metal component. High control over the growth of the metal domain was first presented by achieving anisotropic selective growth of gold tips on CdSe^{20,21} and CdS²² nanorods to obtain a well-defined system with specific regions for the metal and semiconductor phases. A technique that was later expanded to other systems²³⁻²⁷, and different synthetic routes, such as synthesizing the semiconductor component in the presence of the preformed metal structure,^{28,29} and through cation exchange reactions.³⁰ The emerging synergistic properties of such metal-semiconductor NPs were studied, showing enhanced light

absorption,²⁸ altered photoluminescence,³¹ exciton-plasmon interactions,^{32,33} and superior photo-induced charge separation,^{34,35} which leads to their use in photocatalysis,^{34,36-38} electrical^{28,39} and optoelectronic applications.^{40,41} Therefore, rational design of hybrid nanostructures is an important task, requiring fundamental understanding of the underlying nanoscale reaction and diffusion mechanisms.

A fundamental effect that may accompany the formation of a hybrid metal-semiconductor interface is the possibility of diffusion of metals into the semiconductor lattice. One extensively studied process of diffusion of two materials across the nanoparticle surface is known as the nanoscale Kirkendall effect.^{42,43} There, an atomic species A with the lower diffusion rate enters the nanocrystal slower than the B species diffusing from the nanocrystal outward. As a result, voids are formed in B, providing an interesting avenue for making hollow nanocrystals. Many examples of such mechanisms were reported for the synthesis of hollow NPs including CoS and CoO,⁴² ZnS,⁴⁴ PbS,⁴⁵ AuPt,⁴⁶ AlN,⁴⁷ and other metal oxides.⁴⁸⁻⁵⁰ The opposite case, in which the outward species diffuses faster than the inner material, has been much less studied and was reported only for Pb and O where the inward flow of oxygen ions is faster than the outward flow of Pb species resulting in a solid PbO structure rather than a hollow one⁴⁸. This “reversed nanoscale Kirkendall effect”, if generalized to two solid materials, presents an intriguing new phenomenon and, possibly, a new way to synthesize unique nanoscale core-shell structures.

For both of the above effects an essential question is the mechanism by which the diffusion of metals through the semiconductor nanocrystal lattice occurs. In general, diffusion of impurities can occur on the surface, through a hopping mechanism⁵¹⁻⁵⁴ or by an atomic exchange process.⁵⁴⁻⁵⁷ Or, they can diffuse into the lattice via substitutional or interstitial mechanisms.⁵⁸⁻⁶¹ However, diffusion in bulk semiconductors usually involves both interstitial and substitutional processes, and the two most prominent mechanisms are the Frank-Turnbull^{58,59,62,63} and kick-out mechanisms.^{58,59,62,64} The former occurs when an impurity diffuses interstitially through the lattice until an exchange event occurs and the impurity substitutes for a vacancy. In the latter, the impurity, which resides on an interstitial site, exchanges a lattice host atom by a kick-out action that results in the host atom occupying an interstitial site. This is an extensively studied topic in bulk semiconductors due to its significance in doped materials.^{58,65} However, there have been

few studies that reported the diffusion of impurities in nanostructured materials. Mokari *et. al.* reported on the solid-state diffusion of gold in InAs NCs at room-temperature, which resulted in a Au-InAs core-shell nanoparticle.⁶⁶

In that work, pre-synthesized InAs NCs were reacted with gold(III) chloride in the presence of a reducing agent (dodecylamine) to yield islands of metallic gold on the surface of the NCs. Interestingly, imaging the Au-InAs hybrids after a period of 24 hours, during which the sample was kept as a dry solid on the transmission electron microscopy (TEM) grid, revealed that the metal islands diffused from the surface of the NC to form a metal core surrounded by an amorphous InAs shell. X-ray diffraction (XRD) analysis indicated that the Au phase is compatible with bulk Au, the InAs crystal structure disappeared, and a weak signal of In_2O_3 was detected. A similar observation was made by Franchini *et. al.* for PbTe NCs.⁶⁷ Here, reacting pre-synthesized PbTe NCs with AuCl_3 in solution, at moderate temperatures (60-90 °C), also resulted in a core-shell structure where the gold is located in the center of an amorphous PbTe nanoparticle. The formation of such structures was explained by the fast diffusion of Au(0) species inward, balanced by Pb^{2+} and Te^{2-} diffusion outward. Spatially resolved energy-dispersive x-ray (EDX) analysis determined that the core consists of Au only, whereas the shell is a mixture of Pb, Te, and Au. However, both studies lack the ability to identify the mechanism through which the Au diffuses in the semiconductor lattice.

Recently, we employed advanced x-ray absorption spectroscopy techniques to study the local structure of Ag and Cu doped InAs NCs, employing a similar synthetic route as presented above.⁶⁸⁻⁷⁰ Interestingly, we found that reacting InAs NCs with a wide range of Cu concentrations, at room temperature, results in a purely interstitial doping scheme, up to a very high level of Cu incorporation, without evidence of the formation of a metal structure.⁶⁸ For Ag doped InAs, however, we identified two regions that depended on the ratio between the number of Ag species in the reaction vessel to the number of InAs NCs. Ag was found to initially behave as a substitutional dopant and, only above a threshold concentration, metal structures were formed on the InAs NC surface, yielding hybrid Ag-InAs nanoparticles.⁶⁹ In neither case did we observe the phenomena of metal agglomeration within the NC lattice, nor did we observe any changes in the local structure surrounding the impurity atoms, even after extended periods of time.

In this work, we present a study of the structural evolution of InAs NCs during the addition, and solid-state diffusion of Au atoms. We employed time-resolved (TR) x-ray absorption fine-structure (XAFS) spectroscopy in conjunction with scanning transmission electron microscopy/ electron energy loss spectroscopy (STEM/EELS) and TR XRD to investigate the real-time Au diffusion process in 5nm InAs NCs. Analysis of this system by XAFS is much more challenging compared to other doped systems because of the proximity of As K-edge (11867 eV) and Au L₃-edge (11919 eV). In the case of extended x-ray absorption fine structure (EXAFS) signals that originate from the two nearby absorption edges, both the lower energy and the higher energy element EXAFS signals overlap at the higher energy edge region. This presents a particular challenge to the analysis of this system where As, the lower energy edge element, is part of the host structure, and Au, the higher energy element, is the impurity. Hence, for structural analysis of both the impurity and the host it is necessary to separate their contribution in EXAFS. Here, this was achieved through the use of EXAFS data analysis methods developed by us earlier for this particular purpose.⁷¹ We studied the effect of the Au concentration, in terms of the Au-to-NC ratio in the reaction solution, on the diffusion rate and the resulting structure of the Au phase, as well as the structural degradation of the InAs lattice. We found that there is a strong driving force for Au diffusion through the NC lattice, resulting in a core metallic structure inside the NC. This occurs even at low Au/NC ratios, where no evidence of metallic structures on the NC surface are observed. We monitored the structural evolution from the viewpoint of both host (In, As) atoms by analyzing their K-edge XAFS data, and impurity (Au) atoms, by analyzing their L₂ and L₃-edge XAFS data. From the host side, the rate of the structural degradation strongly depends on the Au/NC ratio, whereas the Au signal shows much slower changes. The degradation of the NC lattice is accompanied by the formation of In-O bonds, which act as a marker for investigating the process of Au incorporation and diffusion through the lattice.

As a whole, a multi-modal investigation of this complex system reveals features of a reversed nanoscale Kirkendall effect in which the flux of Au through the InAs NC lattice is faster than the reverse flux of In. The process is enabled by a “kick out” type mechanism, in which Au substitutes for In in the InAs structure. The final hybrid structure contains a nano-crystalline fcc Au core, surrounded by an InAs shell that is disordered and porous. Increasing the Au/InAs NC

ratios leads to both large Au cores and more substantial disorder in the InAs shell that surrounds that core. This eventually becomes a large, amorphous shell at large Au/InAs NC ratios. The reversed nanoscale Kirkendall effect observed and studied in this Au-InAs system, may also provide an additional route to the synthesis of nanocrystal core and amorphous/disordered shell structures of other pairs of materials, thus enriching the library of colloidal nanoscale building blocks.

2. EXPERIMENTAL

2.1 Synthesis

Colloidal InAs NCs were synthesized following a well-established wet-chemical synthesis.⁷² Precursor solutions containing (TMS)₃As (tris(trimethylsilyl)arsine) and InCl₃ (indium(III) chloride) were prepared in a nitrogen glovebox and kept under inert conditions throughout the reaction. A solution of distilled trioctylphosphine (TOP) was evacuated for 30 min and heated to 300 °C. The nucleation solution (2:1 In:As) was rapidly injected, and the solution temperature was lowered to 260 °C. The growth solution (1.2:1 In:As) was gradually introduced to the solution, allowing particle growth until the desired size was reached. Narrow size distributions were further achieved through size selective precipitation performed in a glovebox by adding methanol to the NC dispersion and filtering the solution through a 0.2 µm polyamide membrane filter.

Hybrid InAs-Au nanoparticles were obtained via a room temperature solution-phase reported reaction previously.^{66,70} Briefly, a gold(III) chloride solution was prepared by dissolving 10 mg (0.033 mmol) of the metal salt (AuCl₃), 75 mg (0.16 mmol) of didodecyldimethylammonium bromide DDAB, and 180 mg (0.95 mmol) of dodecylamine DDA in 10 mL of anhydrous toluene. Calculated amounts (v/v) of the impurity solution were added to a suspension of InAs NCs, according to the desired Au/NC ratio, while stirring. The Au concentrations were ranged from 8×10^{-6} mol to 8×10^{-5} mol for a solution of 1.6×10^{-8} mol of 5nm (in diameter) InAs NCs. These values are reported below as the Au/NC ratio in solution, ranging from 500 to 5000, respectively.

The reaction was performed under inert conditions in a glovebox, and terminated after 5 min by adding methanol and isolating the Au-InAs NCs through precipitation.

2.2 Electron microscopy

Scanning Transmission Electron Microscope (STEM) measurements were performed using the Hitachi HD2700C operated at 200 kV at the Center for Functional Nanomaterials in Brookhaven National Laboratory. The spatial resolution for imaging was about 1.0 Å. The probe current was in the 50–100 pA range. The STEM images were taken using a high angle annular dark field (HAADF) detector. The frequency distribution of Au core diameters in the sample of the Au to NC ratio of 1000 was measured over 135 InAs NCs. Elemental line scans with a step size of 1.4 Å were made with a high-resolution electron energy loss spectroscopy (EELS) detector (Gatan Enfina-ER). We extracted the Au and As EELS signal from the EELS spectrum using a power-law background model and an integration window in advance of the Au N- and As M-edges.

2.3 X-ray absorption spectroscopy experiment

Time-resolved In K-edge, As K-edge, Au L₃-edge and Au L₂-edge XAFS measurements were taken from Au-InAs samples with 1000 and 2000 Au/NC ratios. These samples were dissolved in toluene and sealed in a custom-made liquid cell, and were measured at the Advanced Photon Source (APS) 5BM-D beamline. The In and As K-edge of InAs control samples were collected at the APS 5BM-D beamline as well. The time-resolved In K-edge of solid Au-InAs samples with 500, 1000, 2000, 3000 and 5000 Au/NC ratios were collected at the SSRL BL2-2 beamline. These samples were spread on Kapton tape and mounted in a sample chamber. The samples were prepared under inert conditions in a glovebox. All samples were sealed in the glovebox prior to their transfer to the beamline, where they were kept under inert conditions during the measurement. The experiments were performed in transmission mode. From 3 to 6 scans were taken for each edge to improve the signal-to-noise ratio in data.

2.4 XAFS data analysis

XAFS data processing and analysis were done using the Athena and Artemis software within the IFEFFIT package^{73,74} For the In K-edge data we used a linear combination analysis method (*vide infra*) for XANES data and theoretical fitting for EXAFS data. To fit the In K-edge EXAFS data, we accounted for two contributions, In-As and In-O, which represents a bond between In and a low Z element, as discussed in greater detail below.

A recent strategy for deconvoluting the overlapping absorption edges⁷¹ was applied to the As K- and Au L₃-edge data. Specifically, the As-In contribution to the Au L₃-edge EXAFS from the lower energy As K-edge was taken into account. The scaling factor used to normalize the Au L₃-edge EXAFS was defined as $\frac{\Delta\mu_{0,As}}{\Delta\mu_{0,Au}}$, where $\Delta\mu_{0,As}$ and $\Delta\mu_{0,Au}$ represent the jumps in the absorption coefficients at corresponding absorption thresholds (E_0). The edge step ($\Delta\mu$) is defined as the vertical difference between the pre-edge and post-edge lines at the edge energy E_0 (SI Fig. 1). The correction to the photoelectron energy origin for the As K-edge EXAFS, that is 52 eV lower in energy than the nominal value of Au L₃-edge, is no longer a single adjustable parameter, as in conventional EXAFS analysis. It is now defined with respect to the Au L₃-edge energy as: $\Delta E_{0,As} - (52 + \Delta E_{0,Au})$. For the Au L₃-edge analysis, As-In paths contributes to the Au L₃-edge EXAFS data, and thus we performed fits for the In K-edge and Au L₃-edge simultaneously for the Au-InAs (1000 Au/NC) sample, by constraining the parameters of In-As pairs (bond lengths and their disorders) to be the same, as measured from each edge. The paths included in the fitting were the Au-As, Au-Au and As-In pairs for Au L₃ edge, and In-O and In-As pairs for In K-edge.

For the Au L₂-edge analysis, theoretical FEFF6 fits were performed simultaneously for all time dependent EXAFS data with the same Au concentration. The value of the amplitude reduction factor, S_0^2 , was obtained from the fitting of Au foil to 0.993 ± 0.051 and fixed to 0.993 in the fits. The photoelectron paths connecting the Au-As and Au-Au nearest neighboring pairs were included to the theoretical EXAFS signal with the same energy shift (ΔE_0) and individually varied coordination number (N), bonding distance correction (ΔR) and its means square disorder, or Debye-Waller factor (σ^2).

The results obtained for the Au L₃-edge and Au L₂-edge were found to be in qualitative agreement with each other, as explained in greater detail below. This agreement validates our data analysis procedure used for the Au L₃-edge analysis that overlaps with the As K-edge.

2.5 X-ray diffraction

X-ray diffraction data were collected at the XPD beamline of the National Synchrotron Light Source-II, Brookhaven National Laboratory, using a monochromatic beam with an incident energy of 42 KeV (corresponding to the wavelength of 0.2952 Å). Diffraction data were collected in transmission mode with an amorphous silicon-based flat panel 2D detector (PerkinElmer) mounted orthogonal to and centered on the beam path, and were reduced to 1D profiles using the Fit2D software. The sample-to-detector distances and tilts of the detector relative to the beam were refined using a LaB6 powder standard. Noticeable artifacts in the images such as the beam stop or dead pixels were masked. Due to the small particle size and low concentration of particles in the samples, the diffraction peaks are very broad and are too weak to perform any quantitative analysis using existing structure refinement methods. However, qualitative comparison of the diffraction peaks from InAs and Au provides clear indication of inter diffusion of the two-phase components, as discussed in greater detail below. The ratio between InAs (220) and Au (111) reflection intensity was estimated based on the maximum height of the peaks. Before estimating the height, each pattern was background corrected and normalized with baseline-scattered intensity.

RESULTS AND DISCUSSION

Synthesis of Au-InAs hybrid nanoparticles

Colloidal InAs NCs were synthesized using a well-established synthesis process,⁷² followed by a size selective precipitation to obtain narrow size distributions. The pre-synthesized InAs NCs were reacted with Au by mixing a suspension of InAs NCs in toluene with a gold(III) chloride solution containing the metal salt (AuCl₃), DDAB to stabilize the metal salt in the organic solution, and DDA, which acts as a reducing agent. Different Au concentrations were used in the reaction.

As seen in Figure 1, approximately 1 hour after the reaction of the 500 Au/NC ratio, no metallic features were observed on the NC surface. Increasing the ratio to 1000 Au/NC reveals higher contrast regions on the NC surface, indicating the formation of small Au clusters. After 36 hours, both samples reveal the formation of a higher contrast core material (Au) surrounded by a lower contrast shell material (InAs). The size of the Au core is larger for larger Au to NC ratio, as seen both in the TEM images (Figure 1) and HAADF STEM images (Figure 2). Formation of the Au core is confirmed by quantitative STEM/EELS analysis (Figure 2d-f). STEM images of the pure InAs NCs reveal clear lattice fringes (Figure 2a), while in the hybrid Au-InAs NPs lattice fringes were observed in the Au core (Fig 2c, inset), but no fringes were observed in the InAs shell. This is a clear indication of disordering of the InAs structure due to Au incorporation in the InAs.

Figure 1. TEM images of (a) As-synthesized 5 nm InAs NCs, (b) InAs NPs 1 hour after reaction with 500 Au atoms per NC (in solution), (c) InAs NPs 1 hour after reaction with 1000 Au atoms per NC, (d) InAs NPs 36 hours after reaction with 500 Au atoms per NC, and (e) InAs NPs 36 hours after reaction with 1000 Au atoms per NC. Schematic of the diffusion process of Au into the core of the InAs NCs is shown in the bottom left.

Figure 2. High angle annular dark field STEM images of as synthesized 5 nm InAs NCs (a) and Au-InAs NPs (after about a week after reaction of 1000 (b) and 4000 (c) Au atoms per NC). Atomically resolved fringes in Au core are seen in the inset (6.6 by 7.2 nm) in c). Images b) and c) share the same scale bar. The EELS line-scan profiles (d) at Au N- and As M- edges (e,f) of single Au-InAs NPs, taken about a week after reaction of 1000 Au atoms per NC.

XAFS data and analysis

To monitor structural changes in both the host (InAs) and the Au phases, XAFS data were measured at different aging times and at different Au/NC ratios. TR XAFS was measured at the In K-edge to monitor the changes in the average electronic and local structure of In atoms in the Au-InAs system, during the solid-state diffusion process. The In K-edge TR XANES data measured for different Au/NC ratios are plotted in Figure 3a-e. The intensity of the In K-edge main peak, corresponding to the 1s-5p electronic transition, increases with the introduction of Au

into the system (for any given time) and also changes over time (for any given dopant concentration), indicating a change in the electronic properties of In atoms.

Figure 3. Time-resolved XANES data at In K-edge of Au-InAs NPs, with nominal Au/NC ratios shown in the top right, (a)-(e), and InAs control samples (f). The Au-InAs NPs were reacted with 500, 1000, 2000, 3000 and 5000 Au atoms per NC, respectively. The aging time is defined as the time elapsed after the synthesis.

We note the existence of isosbestic points in the x-ray absorption near edge structure (XANES) spectra for all Au/NC ratios, which is an indication of the presence of only two distinctly different states of In, mixed in different fractions, that can change with time and with the Au/NC ratio. The first state corresponds to the starting InAs NC structure and the second, as we explain in greater detail below, to the disordered In-O structure.

As a control, we measured the as-synthesized InAs samples exposed to ambient atmospheric conditions (for a period of three days), or upon exposing the NCs to the ligand solution without the metal salt (Figure 3f). These control changes exhibited almost no changes

compared to the Au-doped InAs NCs of the same sizes showing a series of structural and electronic evolutions with time and Au concentrations.

The Fourier transform magnitudes of the k -weighted In K-edge TR EXAFS signals are shown in Figure 4a-e. The representative In K-edge k^2 -weighted $\chi(k)$ data are shown in Figure S3a-b. The main peak for pure InAs NCs at around 2.2 Å is due to the As atoms that surround each In atom in the lattice. For Au-InAs NPs samples, the intensity of this peak decreases with time, while a low-R peak appears and grows in intensity over time, in a qualitative agreement with the trend shown in Figure 3a-e for the In K-edge XANES data. In the quantitative data analysis, various binding species were considered as a possible origin of this new emerging peak, including In-Au, In-N, and In-O. In-Au bonding was found to be improbable due to the short bond length, and the fitting failed when this bonding was included. While we cannot distinguish between In-N (originating, possibly, from the ligand) and In-O, it is unlikely that the contributions from In-N bonds would change as much over time in the solid-state, whereas an evolution of an In-O peak is more reasonable if we consider the presence of an oxygen moiety near the sample. However, it is noteworthy that the resulting oxide phase does not appear in the control samples (Figure 4f), in agreement with the stability of their XANES spectra (Figure 3f). Hence, the evolution of the observed In-low Z peak is directly connected to the reaction of the Au atoms with the InAs NCs. In what follows, we will use the formation of the In-O peak as a marker of the decomposition of the InAs lattice in response to the diffusion of Au atoms. As a summary of the In K-edge XANES and EXAFS data, we conclude, qualitatively, that the amount of disorder in the InAs NC structure correlates with the Au/NC ratio, namely, the greater the latter, the more disordered is the former.

Figure 4. Fourier transform magnitudes of k -weighted In K-edge EXAFS data (a)-(e) of Au-InAs NPs with representative Au/NC ratios and InAs control samples (f). The Au-InAs NPs were reacted with 500, 1000, 2000, 3000 and 5000 Au atoms per NC, respectively. The aging time is defined as the time elapsed after the synthesis.

The TR XAFS data for Au-InAs NPs with 1000 and 2000 Au/NC ratios, measured at the As-K and Au L_3 -edge, are shown in Figure 5, and at the Au L_2 -edge in Figure 6 (more time resolved XAFS data at Au L_2 -edge are shown in Figure S4). The representative Au $L_{2,3}$ -edge k^2 -weighted $\chi(k)$ data are shown in Figure S3c-d. In the Au L_3 -edge XANES data (Figure 1a,b), the metallic Au feature is observed for all spectra with reduced oscillations compared to the bulk, as expected for nano-sized gold.⁷⁵ The As K-edge EXAFS is included in the extracted Au L_3 -edge EXAFS, due to the proximity of their absorption energies, as discussed in the Experimental section (SFigure S2). As seen in Figure 5c,d, the very strong contributions from As-In bonding can be identified at ~ 2 Å along with the Au-As and/or Au-Au contributions at longer distances. Therefore, the contribution from As K-edge EXAFS, namely, As-In first nearest neighbor contribution, was considered in the fitting of the Au L_3 -edge EXAFS, in addition to the Au-As and Au-Au contributions. This is in contrast to the Au L_2 -edge data (Figure 6) that contain only Au-Au and Au-As contributions. Although the two sets of data measured from the Au L_3 and L_2

Figure 5. Time-resolved XANES data at the Au L_3 -edge ((a) and (b)) and FT magnitudes of k^2 -weighted EXAFS data ((c) and (d)) of Au-InAs NPs with 1000 and 2000 Au/NC in reaction, respectively.

edges contain similar information, both of them are important for successful analysis of low and high Au/NC ratios. Indeed, for low Au compositions, the As-In contribution dominates the Au L_3 -edge spectra (Figure 5c). That is an excellent edge, therefore, to measure As-In pairs but not good for the Au-As and Au-Au contributions that are weak and difficult to analyze. For the same compositions, Au L_2 -edge data can be used to recover the two latter contributions. For large Au/NC ratios, both Au L_3 and Au L_2 -edge data can be used interchangeably. We used both of them to compare their results for the EXAFS analysis of the Au-As and Au-Au contributions, as obtained for either edge at high values of Au/NC ratios. It is important to perform this

comparison in order to validate our procedure of the deconvolution of the EXAFS spectra of As K-edge and Au L₃-edges. If the procedure is correct, both sets of the results (for the Au L₂- and Au L₃-edges) should be similar, within the uncertainties.

The positions of the absorption edge and main features in the Au L₂-edge XANES regime of Au-InAs NPs (Figure 6a) are very similar to that of bulk Au, but with smaller oscillation amplitudes, which are typical for nano-scale gold particles, i.e., the same observation as the one just made for the Au L₃-edge (Figure 5a). The overall similarity with the bulk indicates that the Au atoms are already in an environment similar to that of the metal state in the system at early stages after the reaction (Figure S4), due to rapid nucleation of Au on the NC surface. The same conclusion can be made from Figure 5. R-space spectra of Au L₂-edge EXAFS (Figure 6b), show two different contributions. The double peak above 2 Å corresponds to the Au-Au contribution, while the lower-R peak (below 2 Å) corresponds to Au-As contribution. From the time-dependent data, shown in Figure 5 and Figure S4, we learn that Au nucleates relatively fast for both 1000 and 2000 Au/NC ratios because the metallic features set in already ca. 1h after the reaction.

Figure 6. XANES data at the Au L₂-edge (a) and Fourier transform magnitudes of k^2 -weighted EXAFS data (b) of Au-InAs NPs (reacted with 1000 and 2000 Au atoms per NC, respectively) at selected aging times, together with the data for Au foil.

Despite the fact that EXAFS analysis of the nearest neighbors environment of As atoms can be analyzed only from the Au L₃-edge, the As K-edge XANES region is sufficiently well separated from the Au L₃-edge for its separate examination. Figures S5 demonstrates that the intensity of the main peak of the As K-edge XANES region increases with time due to the diffusion of Au into the NC lattice for both 1000 and 2000 Au per NC ratios, demonstrating that the electronic properties of As atoms change similarly to those of In atoms. Specifically, both As and In edge shape changes are consistent with the transfer of electron density away from both atoms, as possible, e.g., when As-O and In-O bonds are formed. Such a common trend is expected because, as demonstrated from the In edge data, Au diffusion leads to the breaking of In-As bonds. Hence, both In and As edge data will be affected. In validation of the role of Au in the In-As bond breaking, Figure S6 shows no visible changes in As K-edge XANES and EXAFS behaviors in the pure InAs NC sample exposed to air for three days, or upon exposing the NCs to the ligand solution without the metal salt. Figures 3f and 4f conveyed the same information, as seen from the In K-edge.

Results of analysis of the TR EXAFS data of Au-InAs NPs collected at the Au L₂-edge provide quantitative information on the behavior of the Au species. It is confirmed, from the analysis of EXAFS at the Au L₂-edge of 1000 and 2000 Au/NC samples that the Au region forms very rapidly, within ca. 1h from the reaction (Figure S7). Only the Au-Au and Au-As contributions were used in fitting the data (Figures S7 and S8, and Tables S1 and S2). The Fourier transform parameters used in fitting are shown in Table S4. As shown in Table S1 and S2, the coordination number (CN) of Au-Au pairs obtained from the fitting is about 6.5 ± 1.4 for the 1000 Au/NC ratio and 8.4 ± 0.8 for 2000 Au/NC ratio at 2 hour after synthesis, and remains relatively stable, with only a small increase to about 7.1 ± 0.8 for the 1000 Au/NC ratio and 8.8 ± 0.9 for the 2000 Au/NC ratio, after about 20 hours. The Au-Au interatomic distance (SI Tables S1, 2) was found to be 2.81 Å, which is shorter than the value of bulk gold (2.88 Å). This finding is consistent with the finite size effect that is known to cause shorter Au-Au bond lengths in nano-sized structures compared to their bulk counterparts.⁷⁶⁻⁷⁸

EXAFS analysis demonstrated that Au exists in two forms in the InAs QD. In one form it is mixed in the InAs lattice, forming Au-As pairs, and in the other it forms Au metallic phase.

Thus, the effective coordination number, ν_{AuAu} , which describes the Au-Au pairs with respect to the metal phase only, can be defined as:

$$\nu_{\text{AuAu}} = N_{\text{AuAu}} / \left(1 - \frac{N_{\text{AuAs}}}{4} \right), \quad (1)$$

where N_{AuAu} and N_{AuAs} are the apparent coordination numbers from the EXAFS fitting for the Au-Au and Au-As, respectively. Assuming a model in which Au atoms substitutes for In atoms in the InAs phase, for each Au atom there should be four As atoms at the nearest neighboring positions. Thus, $\frac{N_{\text{AuAs}}}{4}$ contains the fraction of all Au atoms in this substitutional location, and $(1 - \frac{N_{\text{AuAs}}}{4})$ is the fraction of Au atoms in the Au core. As shown in Tables S1 and S2, the Au-Au coordination number is relatively stable at about 6.7 for 1000 Au/NC ratio from 2 to 12 hours after synthesis, and increases above 8 after 22 hours. For comparing the size of the Au core inferred by EXAFS analysis with that imaged by STEM, the effective coordination number is a better quantity than the apparent coordination number (N), in analogy with other heterogeneous systems of this nature.^{79,80} Using Eq. (1), we calculated the effective average Au-Au coordination numbers for Au-InAs NPs (1000 and 2000 Au/NC) based on the Au L₂-edge fitting results for which the largest values were 8.5 and 9.5, respectively. For the purpose of estimating the Au core size from the effective coordination numbers, we adopt regular cuboctahedral cluster models. The model clusters that correspond to those coordination numbers contain 147 (the CN is 8.98) and 309 (the CN is 9.63) Au atoms, respectively, and are ca. 1.7 nm and 2.2 nm in size.⁸¹ The so obtained size of the Au core for the 1000 Au/NC sample is in good agreement with the 1.5 nm value measured by STEM imaging (Figure 2 and Figure S2) and is consistent with the EELS line profile shown in Fig. 2. In addition, it is also consistent with the reduction of the Au-Au distance compared to the bulk Au foil (*vide supra*).

While the agreement between different probes (EXAFS and STEM) is very good, STEM images not only provide proof that the Au atoms nucleate, but also show directly that the stability of the NC scaffold is compromised upon the diffusion of Au at high Au/NC ratios. Whereas the InAs shell remains whole and the overall NP size does not seem to change for the 1000 Au/NC sample (Figure 2b), the 4000 Au/NC sample exhibits regions where the InAs shell breaks off the Au core (Figure 2c). Au diffusion at high concentrations thus has a destructive

effect on the NC lattice. A different view at the effects of Au diffusion on the structure of the InAs host is available through the coordination numbers of In-As and In-O bonds obtained from EXAFS analysis (Figure 7 and Table S3 and the Fourier transform parameters used in fitting are shown in Table S5). The coordination numbers of In-As pairs decrease with time and with Au concentration, while those of In-O pairs increase with time and Au/NC ratio, indicating the gradual breaking of In-As and forming of In-O bonds during Au diffusion. Figure 7 indicates also that the nucleation of Au occurs relatively fast during and after synthesis and the further growth of Au is relatively slow. Accordingly, the coordination number of Au-As is nearly unchanged during the measurements (Tables S1,S2).

Figure 7. Comparison of coordination numbers of (a) In-As and (b) In-O pairs in Au-InAs NPs for various Au/NC ratios as function of aging time (elapsed after the beginning of doping reaction) , obtained from the best fit of the time-resolved In K-edge EXAFS data.

We note that the Au-As distances (Tables S1,S2) are similar to the In-As ones, hence, the model of Au incorporation into the InAs lattice is substitutional, not the interstitial, which would have been characterized by extremely short Au-As distances as formation of In-Au nearest neighbors. The interstitial model, possessing such properties, was previously reported by us for Cu doped InAs NCs.⁶⁸ Hence, the kick-out, not the Frank-Turnbull mechanism is likely at play.

To identify the origin of the O species in the InAs NC we performed a series of control experiments. We measured the XANES and EXAFS of (i) as-synthesized InAs NCs, (ii) InAs

NCs that were exposed to atmospheric conditions for 72 hours, and (iii) InAs NCs that were reacted with the same precursor solution only without the metal salt (*i.e.* containing similar concentrations of DDA and DDAB). Results shown in Figures 3, 4 and S4 show little or no changes between these three samples. We thus conclude that the diffusion of Au into InAs NCs triggers the formation of In-O bonds. Considering that only In-O bonds are identified, we conjecture that the mechanism of diffusion involves the kick-out of In atoms by Au. Correspondingly, as the Au continues to diffuse to the center of the NC through the kick-out mechanism, the InAs NCs structure becomes amorphous.

XRD data and analysis

In addition to STEM data that provide statistical information about the effects of Au diffusion on different InAs NCs, and XAFS data, that characterize the local structure of Au, In and As atoms, we analyzed X-ray diffraction data that provide long range information on both the Au phase and InAs phase, and their relative changes with time and Au concentration. Thus, a combination of the three measurements will help to better understand the co-dependency of the different changes induced in InAs NCs upon Au diffusion.

Time resolved x-ray diffraction measurements of Au-InAs NPs were performed on the representative 1000 Au/NC sample. In Figure 8(a), the diffraction peaks corresponding to InAs and Au are identified. Both sets of diffraction peaks broaden and shift to higher 2-theta values compared to the corresponding bulk values, which is typical for nanoparticles due to their smaller lattice parameter, and is consistent with the EXAFS fitting result of the reduced Au-Au distance (Figure S7 and Tables S1 and S2). Noticeably, the diffraction peaks of In_2O_3 are absent, which is in line with the lack of long-range order in In-O interactions, though the In-O bonding was observed from EXAFS. Relative changes of Au and InAs crystalline volumes were studied for the 1000 Au/NC sample by using the relative changes in the InAs/Au peak intensities as a function of time. This ratio was found to monotonically decrease with time, implying the long-range order of InAs is reduced relative to the increase in Au ordering. Hence, the combination of EXAFS and XRD results demonstrates that the structural changes of InAs NCs occur at both short and long-range scales. In addition, the kinetics of growth of the Au phase (Figure 8a, inset), extracted from data in Figure S9, shows a two-step behavior, in qualitative agreement with the

data obtained from XAFS.

Figure 8. XRD patterns of (a) Au-InAs NPs with 1000 Au/NC ratio collected at 2 hours and 20 hours after synthesis; the inset showing the peak ratio between InAs (220) and Au (111) peaks (b) Au-InAs NPs with different Au/NP ratios, taken 2 days after synthesis.

Unifying discussion

Following the above presentation of the multiple data obtained by complementary STEM, XAFS and XRD experiments, we now attempt to unify these observations. XANES and EXAFS data provide information on the chemical, electronic and/or structural changes in the In, As and Au environments. We interpret the changes in the In environments in terms of the volume fractions of InAs NCs that remain unaffected by Au diffusion and the volume fractions of the In-O regions formed. The former quantity can be obtained by normalizing the In-As coordination numbers measured by EXAFS by four, which is the stoichiometric value of In-As coordination number. The volume fractions of the In-O regions can be estimated either by normalization of the In-O

coordination numbers by six, its stoichiometric value in the oxide, or from the linear combination analysis (LCA) of the In K-edge XANES data (as shown in Figure S10). The LCA was carried out for the TR XANES of representative Au/NC ratios shown in Figure 3. The XANES spectra of pure InAs NCs, and Au-InAs with 5000 Au/NC collected at 58 h (corresponding to the disordered final state), were used as two basis sets for the fitting.

Figure 9 shows the volume fractions of In-As and In-O regions for different Au/NC ratios, along with the cartoons illustrating the growth of the Au regions in the cores of the Au-InAs NPs. All data points correspond to the final states measured ca. 60 h after synthesis. The behavior of the In-O regions, independently analyzed by EXAFS and XANES, are in excellent agreement with each other.

Figure 9. (a) Relative amounts of InAs and In-O phases for Au-InAs NPs with different Au/NP ratios at 55 hours after synthesis, obtained from EXAFS analysis for InAs and In-O; (b) Schematics of proposed diffusion process for Au-InAs NPs.

As shown by XAFS, STEM and XRD, with the increase of the Au/InAs ratio, the Au core size increases and the extent of the disorder in the InAs phase increases. Formation of such crystalline metal core and disordered semiconductor shell is intriguing. Often, when two materials react and diffuse in nanocrystals, the nanoscale Kirkendall effect has been reported⁸² leading to formation of voids and, ultimately, to hollow nanoparticles. The conditions for the

Kirkendall effect are that the inward diffusing material diffuses slower than the outward diffusing material. But, what happens when the material diffusing inward has faster diffusion rate than the one diffusing outward? In this case the inward diffusing material can form a crystalline core. The outward diffusing materials, on the other hand, due to the difference in the diffusion rate, will end up in the shell and, may in principle, also contain voids. However, these voids can merge with the outer surface or be manifested as a porous shell. These details should depend on the dimensions of the nanoparticle, the metal/NC ratio and/or the difference of the diffusion rates.

The system presented herein is a case study for this reversed nanoscale Kirkendall effect. All our observations can be explained in this framework. The Au core/InAs shell structure was formed as a result of this mechanism. Considering that Au diffuses inward faster than In diffuses outward, a crystalline Au core is formed without hollow regions. On the other hand, the InAs shell is porous and disordered (Figure 2c, inset).

CONCLUSIONS

A study of the diffusion of Au atoms through the lattice of InAs NCs was carried out. XAFS measurements revealed that Au substitutes for *In* atom via a kick-out mechanism, whilst moving towards the center of the NC to form a metallic Au core. Both XAFS and XRD measurements indicate that both the size of the metallic core and the extent of the disorder in the shell strongly depend on the initial Au/NC ratio. While XAFS analysis reveals the formation of In-O bonds, XRD measurements do not reflect the formation of an In₂O₃ phase. Control experiments performed by either exposing the InAs NCs to ambient atmosphere or to the same ligand composition, revealed no formation of In-O bonds nor any changes to the InAs structure, thus directly linking between the observed changes and the diffusion of Au. The final Au-InAs core shell is comprised of a crystalline Au core and a disordered, porous shell, as directly observed by STEM. Considering the larger diffusion coefficient for Au in InAs⁸³ than for the self diffusion of InAs,⁸⁴ Au can be considered a fast diffuser in InAs and therefore, the formation of the above structure can be rationalized through a reversed Kirkendall-effect. This understanding can be used as a new way to synthesize unique nanoscale core-shell structures.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: anatoly.frenkel@yu.edu; uri.banin@mail.huji.ac.il.

Authors Contributions

J.L and Y.A contributed equally to this work.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGEMENTS

The research leading to these results has received funding through the NSF-BSF International Collaboration in Chemistry program. J. L., Y.A., A.I.F., and U.B. acknowledge the support of this work by the NSF Grant No. CHE-1413937 and the BSF Grant No. 2013/610. U.B. thanks the Alfred and Erica Larisch Memorial Chair. This research used Hitachi 2700C of the Center for Functional Nanomaterials for STEM/EELS studies and X-rays from XPD beamline of the National Synchrotron Light Source II, both of which are U.S. Department of Energy (DOE) Office of Science User Facilities operated for the DOE Office of Science by Brookhaven National Laboratory under Contract No. DE-SC0012704.

Supporting Information Available: Figures for additional XAFS and XRD results; Fitting results of Au L₃, Au L₂ and In K-edge of InAs NPs. This material is available free of charge via the Internet at <http://pubs.acs.org>.

REFERENCES

1. Alivisatos, A. P., Perspectives on the Physical Chemistry of Semiconductor Nanocrystals. *J. Phys. Chem.* **1996**, 100, 13226-13239.
2. Brus, L. E., A Simple Model for the Ionization Potential, Electron Affinity, and Aqueous Redox Potentials of Small Semiconductor Crystallites. *J. Chem. Phys.* **1983**, 79, 5566-5571.
3. Peng, X.; Manna, L.; Yang, W.; Wickham, J.; Scher, E.; Kadavanich, A.; Alivisatos, A. P., Shape Control of CdSe Nanocrystals. *Nature* **2000**, 404, 59-61.
4. Lu, W.; Fang, J.; Ding, Y.; Wang, Z. L., Formation of PbSe Nanocrystals: A Growth toward Nanocubes. *J. Phys. Chem. B* **2005**, 109, 19219-19222.
5. Jin, R.; Cao, Y.; Mirkin, C. A.; Kelly, K. L.; Schatz, G. C.; Zheng, J. G., Photoinduced Conversion of Silver Nanospheres to Nanoprisms. *Science* **2001**, 294, 1901-1903.
6. Caswell, K. K.; Bender, C. M.; Murphy, C. J., Seedless, Surfactantless Wet Chemical Synthesis of Silver Nanowires. *Nano. Lett.* **2003**, 3, 667-669.
7. Jen-La Plante, I.; Mokari, T., Harnessing Thermal Expansion Mismatch to Form Hollow Nanoparticles. *Small* **2013**, 9, 56-60.
8. Talapin, D. V.; Nelson, J. H.; Shevchenko, E. V.; Aloni, S.; Sadtler, B.; Alivisatos, A. P., Seeded Growth of Highly Luminescent CdsSe/CdS Nanoheterostructures with Rod and Tetrapod Morphologies. *Nano. Lett.* **2007**, 7, 2951-2959.
9. Rivest, J. B.; Swisher, S. L.; Fong, L.-K.; Zheng, H.; Alivisatos, A. P., Assembled Monolayer Nanorod Heterojunctions. *ACS Nano* **2011**, 5, 3811-3816.
10. Sitt, A.; Salant, A.; Menagen, G.; Banin, U., Highly Emissive Nano Rod-in-Rod Heterostructures with Strong Linear Polarization. *Nano. Lett.* **2011**, 11, 2054-2060.

11. Costi, R.; Saunders, A. E.; Banin, U., Colloidal Hybrid Nanostructures: A New Type of Functional Materials. *Angew. Chem., Int. Ed.* **2010**, 49, 4878-4897.
12. Banin, U.; Ben-Shahar, Y.; Vinokurov, K., Hybrid Semiconductor–Metal Nanoparticles: From Architecture to Function. *Chem. Mater.* **2014**, 26, 97-110.
13. Pescaglini, A.; Iacopino, D., Metal Nanoparticle-Semiconductor Nanowire Hybrid Nanostructures for Plasmon-Enhanced Optoelectronics and Sensing. *J. Mater. Chem. C* **2015**, 3, 11785-11800.
14. Liu, H.; Feng, Y.; Chen, D.; Li, C.; Cui, P.; Yang, J., Noble Metal-Based Composite Nanomaterials Fabricated Via Solution-Based Approaches. *J. Mater. Chem. A* **2015**, 3, 3182-3223.
15. Yuhas, B. D.; Habas, S. E.; Fakra, S. C.; Mokari, T., Probing Compositional Variation within Hybrid Nanostructures. *ACS Nano* **2009**, 3, 3369-3376.
16. Wood, A.; Giersig, M.; Mulvaney, P., Fermi Level Equilibration in Quantum Dot–Metal Nanojunctions. *J. Phys. Chem. B* **2001**, 105, 8810-8815.
17. Subramanian, V.; Wolf, E. E.; Kamat, P. V., Green Emission to Probe Photoinduced Charging Events in ZnO–Au Nanoparticles. Charge Distribution and Fermi-Level Equilibration. *J. Phys. Chem. B* **2003**, 107, 7479-7485.
18. Subramanian, V.; Wolf, E. E.; Kamat, P. V., Catalysis with TiO₂/Gold Nanocomposites. Effect of Metal Particle Size on the Fermi Level Equilibration. *J. Am. Chem. Soc.* **2004**, 126, 4943-4950.
19. Hirakawa, T.; Kamat, P. V., Charge Separation and Catalytic Activity of Ag@TiO₂ Core–Shell Composite Clusters under UV–Irradiation. *J. Am. Chem. Soc.* **2005**, 127, 3928-3934.

20. Mokari, T.; Rothenberg, E.; Popov, I.; Costi, R.; Banin, U., Selective Growth of Metal Tips onto Semiconductor Quantum Rods and Tetrapods. *Science* **2004**, 304, 1787-1790.
21. Mokari, T.; Sztrum, C. G.; Salant, A.; Rabani, E.; Banin, U., Formation of Asymmetric One-Sided Metal-Tipped Semiconductor Nanocrystal Dots and Rods. *Nat. Mater.* **2005**, 4, 855-863.
22. Saunders, A. E.; Popov, I.; Banin, U., Synthesis of Hybrid CdS–Au Colloidal Nanostructures. *J. Phys. Chem. B* **2006**, 110, 25421-25429.
23. Yang, J.; Elim, H. I.; Zhang, Q.; Lee, J. Y.; Ji, W., Rational Synthesis, Self-Assembly, and Optical Properties of PbS–Au Heterogeneous Nanostructures Via Preferential Deposition. *J. Am. Chem. Soc.* **2006**, 128, 11921-11926.
24. Menagen, G.; Mocatta, D.; Salant, A.; Popov, I.; Dorfs, D.; Banin, U., Selective Gold Growth on CdSe Seeded CdS Nanorods. *Chem. Mater.* **2008**, 20, 6900-6902.
25. Khalavka, Y.; Sönnichsen, C., Growth of Gold Tips onto Hyperbranched CdTe Nanostructures. *Adv. Mater.* **2008**, 20, 588-591.
26. Yang, J.; Ying, J. Y., Nanocomposites of Ag₂S and Noble Metals. *Angew. Chem., Int. Ed.* **2011**, 50, 4637-4643.
27. Li, P.; Wei, Z.; Wu, T.; Peng, Q.; Li, Y., Au–ZnO Hybrid Nanopyramids and Their Photocatalytic Properties. *J. Am. Chem. Soc.* **2011**, 133, 5660-5663.
28. Lee, J.-S.; Shevchenko, E. V.; Talapin, D. V., Au–PbS Core–Shell Nanocrystals: Plasmonic Absorption Enhancement and Electrical Doping Via Intra-Particle Charge Transfer. *J. Am. Chem. Soc.* **2008**, 130, 9673-9675.
29. Yang, J.; Ying, J. Y., Room-Temperature Synthesis of Nanocrystalline Ag₂S and Its Nanocomposites with Gold. *Chem. Commun.* **2009**, 3187-3189.

30. Manzi, A.; Simon, T.; Sonnleitner, C.; Döblinger, M.; Wyrwich, R.; Stern, O.; Stolarczyk, J. K.; Feldmann, J., Light-Induced Cation Exchange for Copper Sulfide Based CO₂ Reduction. *J. Am. Chem. Soc.* **2015**, 137, 14007-14010.
31. Chen, W.-T.; Yang, T.-T.; Hsu, Y.-J., Au-CdS Core–Shell Nanocrystals with Controllable Shell Thickness and Photoinduced Charge Separation Property. *Chem. Mater.* **2008**, 20, 7204-7206.
32. Li, M.; Yu, X.-F.; Liang, S.; Peng, X.-N.; Yang, Z.-J.; Wang, Y.-L.; Wang, Q.-Q., Synthesis of Au–CdS Core–Shell Hetero-Nanorods with Efficient Exciton–Plasmon Interactions. *Adv. Funct. Mater.* **2011**, 21, 1788-1794.
33. Achermann, M., Exciton–Plasmon Interactions in Metal–Semiconductor Nanostructures. *J. Phys. Chem. Lett.* **2010**, 1, 2837-2843.
34. Costi, R.; Saunders, A. E.; Elmalem, E.; Salant, A.; Banin, U., Visible Light-Induced Charge Retention and Photocatalysis with Hybrid CdSe–Au Nanodumbbells. *Nano. Lett.* **2008**, 8, 637-641.
35. Costi, R.; Cohen, G.; Salant, A.; Rabani, E.; Banin, U., Electrostatic Force Microscopy Study of Single Au–CdSe Hybrid Nanodumbbells: Evidence for Light-Induced Charge Separation. *Nano. Lett.* **2009**, 9, 2031-2039.
36. Elmalem, E.; Saunders, A. E.; Costi, R.; Salant, A.; Banin, U., Growth of Photocatalytic CdSe–Pt Nanorods and Nanonets. *Adv. Mater.* **2008**, 20, 4312-4317.
37. Ben-Shahar, Y.; Scotognella, F.; Waiskopf, N.; Kriegel, I.; Dal Conte, S.; Cerullo, G.; Banin, U., Effect of Surface Coating on the Photocatalytic Function of Hybrid CdS–Au Nanorods. *Small* **2015**, 11, 462-471.

38. Ben-Shahar, Y.; Scotognella, F.; Kriegel, I.; Moretti, L.; Cerullo, G.; Rabani, E.; Banin, U., Optimal Metal Domain Size for Photocatalysis with Hybrid Semiconductor-Metal Nanorods. *Nat. Commun.* **2016**, *7*.
39. Lavieville, R.; Zhang, Y.; Casu, A.; Genovese, A.; Manna, L.; Di Fabrizio, E.; Krahne, R., Charge Transport in Nanoscale “All-Inorganic” Networks of Semiconductor Nanorods Linked by Metal Domains. *ACS Nano* **2012**, *6*, 2940-2947.
40. Hyun, J. K.; Lauhon, L. J., Spatially Resolved Plasmonically Enhanced Photocurrent from Au Nanoparticles on a Si Nanowire. *Nano. Lett.* **2011**, *11*, 2731-2734.
41. Pescaglini, A.; Martín, A.; Cammi, D.; Juska, G.; Ronning, C.; Pelucchi, E.; Iacopino, D., Hot-Electron Injection in Au Nanorod–ZnO Nanowire Hybrid Device for Near-Infrared Photodetection. *Nano. Lett.* **2014**, *14*, 6202-6209.
42. Yin, Y.; Rioux, R. M.; Erdonmez, C. K.; Hughes, S.; Somorjai, G. A.; Alivisatos, A. P., Formation of Hollow Nanocrystals through the Nanoscale Kirkendall Effect. *Science* **2004**, *304*, 711-714.
43. Cabot, A.; Smith, R. K.; Yin, Y.; Zheng, H.; Reinhard, B. M.; Liu, H.; Alivisatos, A. P., Sulfidation of Cadmium at the Nanoscale. *ACS Nano* **2008**, *2*, 1452-1458.
44. Shao, H.-F.; Qian, X.-F.; Zhu, Z.-K., The Synthesis of ZnS Hollow Nanospheres with Nanoporous Shell. *J. Solid State Chem.* **2005**, *178*, 3522-3528.
45. Wang, Y.; Cai, L.; Xia, Y., Monodisperse Spherical Colloids of Pb and Their Use as Chemical Templates to Produce Hollow Particles. *Adv. Mater.* **2005**, *17*, 473-477.
46. Liang, H.-P.; Guo, Y.-G.; Zhang, H.-M.; Hu, J.-S.; Wan, L.-J.; Bai, C.-L., Controllable AuPt Bimetallic Hollow Nanostructures. *Chem. Commun.* **2004**, 1496-1497.

47. Zheng, J.; Song, X.; Zhang, Y.; Li, Y.; Li, X.; Pu, Y., Nanosized Aluminum Nitride Hollow Spheres Formed through a Self-Templating Solid–Gas Interface Reaction. *J. Solid State Chem.* **2007**, 180, 276-283.
48. Wang, C. M.; Baer, D. R.; Thomas, L. E.; Amonette, J. E.; Antony, J.; Qiang, Y.; Duscher, G., Void Formation During Early Stages of Passivation: Initial Oxidation of Iron Nanoparticles at Room Temperature. *J. Appl. Phys.* **2005**, 98, 094308.
49. Nakamura, R.; Lee, J. G.; Tokozakura, D.; Mori, H.; Nakajima, H., Formation of Hollow ZnO through Low-Temperature Oxidation of Zn Nanoparticles. *Mater. Lett.* **2007**, 61, 1060-1063.
50. Nakamura, R.; Tokozakura, D.; Nakajima, H.; Lee, J.-G.; Mori, H., Hollow Oxide Formation by Oxidation of Al and Cu Nanoparticles. *J. Appl. Phys.* **2007**, 101, 074303.
51. Kellogg, G. L., Field Ion Microscope Studies of Single-Atom Surface Diffusion and Cluster Nucleation on Metal Surfaces. *Surf. Sci. Rep.* **1994**, 21, 1-88.
52. Tsong, T. T., Quantitative Investigations of Atomic Processes on Metal Surfaces at Atomic Resolution. *Prog. Surf. Sci.* **1980**, 10, 165-248.
53. Zhang, Z.; Lagally, M. G., Atomistic Processes in the Early Stages of Thin-Film Growth. *Science* **1997**, 276, 377-383.
54. Tsong, T. T., Mechanisms of Surface Diffusion. *Prog. Surf. Sci.* **2001**, 67, 235-248.
55. Kellogg, G. L.; Feibelman, P. J., Surface Self-Diffusion on Pt(001) by an Atomic Exchange Mechanism. *Phys. Rev. Lett.* **1990**, 64, 3143-3146.
56. Chen, C.; Tsong, T. T., Displacement Distribution and Atomic Jump Direction in Diffusion of Ir Atoms on the Ir(001) Surface. *Phys. Rev. Lett.* **1990**, 64, 3147-3150.

57. Tsong, T. T.; Chen, C.-L., Atomic Replacement and Vacancy Formation and Annihilation on Iridium Surfaces. *Nature* **1992**, 355, 328-331.
58. Willoughby, A. F. W., Atomic Diffusion in Semiconductors. *Rep. Prog. Phys.* **1978**, 41, 1665.
59. Tuck, B., *Introduction to Diffusion in Semiconductors*. Peter Peregrinus: Stevenage, 1974.
60. Dunlap, W. C., Diffusion of Impurities in Germanium. *Phys. Rev.* **1954**, 94, 1531-1540.
61. Weisberg, L. R.; Blanc, J., Diffusion with Interstitial-Substitutional Equilibrium. Zinc in GaAs. *Phys. Rev.* **1963**, 131, 1548-1552.
62. Myers, H. P., *Introductory Solid State Physics*. Gothenburg: 1981.
63. Frank, F. C.; Turnbull, D., Mechanism of Diffusion of Copper in Germanium. *Phys. Rev.* **1956**, 104, 617-618.
64. Aleksandrov, O. V.; Krivoruchko, A. A., Out-Diffusion of Impurity Via the Kick-out Mechanism During Gettering. *Semiconductors* **2007**, 41, 1048-1055.
65. Gosele, U. M., Fast Diffusion in Semiconductors. *Ann. Rev. Mater. Sci.* **1988**, 18, 257-282.
66. Mokari, T.; Aharoni, A.; Popov, I.; Banin, U., Diffusion of Gold into InAs Nanocrystals. *Angew. Chem., Int. Ed.* **2006**, 45, 8001-8005.
67. Franchini, I. R.; Bertoni, G.; Falqui, A.; Giannini, C.; Wang, L. W.; Manna, L., Colloidal PbTe-Au Nanocrystal Heterostructures. *J. Mater. Chem.* **2010**, 20, 1357-1366.
68. Amit, Y.; Eshet, H.; Faust, A.; Patllola, A.; Rabani, E.; Banin, U.; Frenkel, A. I., Unraveling the Impurity Location and Binding in Heavily Doped Semiconductor Nanocrystals: The Case of Cu in InAs Nanocrystals. *J. Phys. Chem. C* **2013**, 117, 13688-13696.

69. Amit, Y.; Li, Y.; Frenkel, A. I.; Banin, U., From Impurity Doping to Metallic Growth in Diffusion Doping: Properties and Structure of Silver-Doped InAs Nanocrystals. *ACS Nano* **2015**, 9, 10790-10800.
70. Mocatta, D.; Cohen, G.; Schattner, J.; Millo, O.; Rabani, E.; Banin, U., Heavily Doped Semiconductor Nanocrystal Quantum Dots. *Science* **2011**, 332, 77-81.
71. Menard, L. D.; Wang, Q.; Kang, J. H.; Sealey, A. J.; Girolami, G. S.; Teng, X.; Frenkel, A. I.; Nuzzo, R. G., Structural Characterization of Bimetallic Nanomaterials with Overlapping X-ray Absorption Edges. *Phys. Rev. B* **2009**, 80, 064111.
72. Cao; Banin, U., Growth and Properties of Semiconductor Core/Shell Nanocrystals with InAs Cores. *J. Am. Chem. Soc.* **2000**, 122, 9692-9702.
73. Ravel, B.; Newville, M., Athena, Artemis, Hephaestus: Data Analysis for X-ray Absorption Spectroscopy Using IFEFFIT. *J. Synchrotron Radiat.* **2005**, 12, 537-541.
74. Newville, M., Ifeffit : Interactive XAFS Analysis and FEFF Fitting. *J. Synchrotron Radiat.* **2001**, 8, 322-324.
75. Frenkel, A. I.; Cason, M. W.; Elsen, A.; Jung, U.; Small, M. W.; Nuzzo, R. G.; Vila, F. D.; Rehr, J. J.; Stach, E. A.; Yang, J. C., Critical Review: Effects of Complex Interactions on Structure and Dynamics of Supported Metal Catalysts. *J. Vac. Sci. Technol. A* **2014**, 32, 020801.
76. Frenkel, A. I.; Hills, C. W.; Nuzzo, R. G., A View from the Inside: Complexity in the Atomic Scale Ordering of Supported Metal Nanoparticles. *J. Phys. Chem. B* **2001**, 105, 12689-12703.
77. Frenkel, A. I.; Nemzer, S.; Pister, I.; Soussan, L.; Harris, T.; Sun, Y.; Rafailovich, M. H., Size-Controlled Synthesis and Characterization of Thiol-Stabilized Gold Nanoparticles. *J. Chem. Phys.* **2005**, 123, 184701.

78. Sanchez, S. I.; Menard, L. D.; Bram, A.; Kang, J. H.; Small, M. W.; Nuzzo, R. G.; Frenkel, A. I., The Emergence of Nonbulk Properties in Supported Metal Clusters: Negative Thermal Expansion and Atomic Disorder in Pt Nanoclusters Supported on γ -Al₂O₃. *J. Am. Chem. Soc.* **2009**, 131, 7040-7054.
79. Sun, Y.; Frenkel, A. I.; Isseroff, R.; Shonbrun, C.; Forman, M.; Shin, K.; Koga, T.; White, H.; Zhang, L.; Zhu, Y.; Rafailovich, M. H.; Sokolov, J. C., Characterization of Palladium Nanoparticles by Using X-ray Reflectivity, EXAFS, and Electron Microscopy. *Langmuir* **2006**, 22, 807-816.
80. Frenkel, A., Solving the 3D Structure of Metal Nanoparticles. *Z. Kristallogr.* **2007**, 222, 605-611.
81. Glasner, D.; Frenkel, A. I., Geometrical Characteristics of Regular Polyhedra: Application to EXAFS Studies of Nanoclusters. *AIP Conf. Proc.* **2007**, 882, 746-748.
82. Wang, W.; Dahl, M.; Yin, Y., Hollow Nanocrystals through the Nanoscale Kirkendall Effect. *Chem. Mater.* **2013**, 25, 1179-1189.
83. Indium Arsenide (InAs), Vibrational Modes of Impurities. in *Impurities and Defects in Group IV Elements, IV-IV and III-V Compounds. Part B: Group IV-IV and III-V Compounds.*, Madelung, O.; Rössler, U.; Schulz, M., Eds. Springer Berlin Heidelberg: Berlin, Heidelberg, 2003; pp 1-2.
84. Kato, H.; Yokozawa, M.; Kohara, R.; Okabayashi, Y.; Takayanagi, S., Self-Diffusion in InAs Crystals. *Solid-State Electron.* **1969**, 12, 137-139.

Table of Contents Figure (TOC)

Formation of Au-InAs nanoparticles via reverse nanoscale Kirkendall effect

Supporting Information of

Reversed Nanoscale Kirkendall Effect in Au-InAs Hybrid Nanoparticles

Jing Liu^{1,‡}, Yorai Amit^{2,3,‡}, Yuanyuan Li¹, Anna M. Plonka¹, Sanjit Ghose⁴, Lihua Zhang⁵, Eric A. Stach⁵, Uri Banin^{2,3,*} and Anatoly I. Frenkel^{1,6,*}

¹Department of Physics, Yeshiva University, New York, New York 10016, United States

²The Institute of Chemistry and ³The Center for Nanoscience and Nanotechnology, Hebrew University, Jerusalem 91904, Israel.

⁴National Synchrotron Light Source II, Brookhaven National Laboratory, Upton, New York 11973, United States

⁵Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York 11973, United States

⁶Department of Materials Science and Chemical Engineering, Stony Brook University, Stony Brook, New York 11794, United States

Table of Contents:	Page
1. Edge step determination process of for Au L ₃ -edge analysis (Figure S1).	S2
2. Frequency distribution of diameters of Au nanoparticles from STEM (Figure S2).	S3
3. Additional EXAFS results (Figures S3-S6).	S4-S7
4. Additional EXAFS fitting results (Figures S7-S8).	S8-S9
5. Additional XRD data (Figure S9).	S10
6. Linear combination analysis results of XANES (Figure S10).	S11
7. Fitting results of Au L ₃ , Au L ₂ and In K-edge of Au-InAs NPs (Tables S1-S3).	S12-S16
8. Details of Fourier transform parameters used in fitting (Tables S4-S5).	S17-S18

Figure S1. An example of the pre- and post- edge lines, and the edge step determination process for Au L₃-edge EXAFS analysis.

Figure S2. Frequency distribution of diameters of Au nanoparticles located in the core of the InAs NCs (see Figure 2b in the main text) for the Au/NC ratio of 1000 after about a week of reaction of Au with NCs.

Figure S3. (a) Time resolved In K-edge k^2 -weighted $\chi(k)$ data for the Au-InAs NPs with 1000 Au/NC ratio; (b) In K-edge k^2 -weighted $\chi(k)$ data for the Au-InAs NPs with various Au/NC ratios; (c) The Au L_3 -edge k^2 -weighted $\chi(k)$ data for the Au-InAs NPs with 1000 and 2000 Au/NC ratios collected 1 hour and 22 hours after the reaction; (d) The Au L_2 -edge k^2 -weighted $\chi(k)$ data for the Au-InAs NPs with 1000 and 2000 Au/NC ratios collected at selected aging times.

Figure S4. Time-resolved XANES data at the Au L_2 -edge ((a) and (b)) and FT magnitudes of k^2 -weighted EXAFS data ((c) and (d)) of InAs NCs reacted with 1000 and 2000 Au atoms per NC, respectively.

Figure S5. The TR XANES at As K-edge of (a) Au-InAs NPs with 1000 Au atoms per NC and (b) with 2000 Au atoms per NC, compared with the spectrum of pure InAs NCs.

Figure S6. As K-edge XANES (a) and FT magnitudes of k^2 -weighted EXAFS data (b) of InAs NCs control samples.

Figure S7. The coordination numbers (a) and bonding distance (b) of Au-As and Au-Au pairs obtained from the best fitting results of Au L₂-edge and Au L₃-edge TR EXAFS data of Au-InAs NPs (1000 Au/NC).

Figure S8. Best fitting curves (red lines) for As K/Au L₃-edge and In K-edge Fourier transform magnitudes of k^2 -weighted TR EXAFS of Au-InAs NPs (1000 Au/NC) (black lines), obtained by multiple data set fitting.

Figure S9. XRD patterns of (a) InAs NCs reacted with 1000 Au/NC starting from 2 hours until 20 hours after synthesis with interval of two hours.

Figure S10. Results of linear combination analysis of time-resolved XANES data for In K-edge of Au-InAs NPs with different Au/NC ratios. The numbers near each curve indicate the Au/NC ratio. The data are calculated relative to those in Au-InAs NPs with 5000 Au/NC, measured 58h after synthesis.

Table S1. Best fits results of the structural parameters of the Au-Au and Au-As nearest neighbor pairs obtained from Au L₂-edge TR EXAFS of Au-InAs NPs with 1000 and 2000 Au/NC ratios.

Sample	bond	N	R (Å)	σ^2 (Å ²)	S ₀ ²
Au foil	Au-Au	12	2.870 ± 0.003	0.008 ± 0.000	0.993 ± 0.051
Au1000, 3h	Au-Au	6.5 ± 1.4	2.803 ± 0.013	0.015 ± 0.003	0.993
	Au-As	0.5 ± 0.2	2.426 ± 0.026	0.004 ± 0.003	
Au1000, 9h	Au-Au	6.5 ± 1.1	2.809 ± 0.011	0.016 ± 0.002	0.993
	Au-As	0.4 ± 0.2	2.462 ± 0.026	0.004 ± 0.003	
Au1000, 23h	Au-Au	7.1 ± 0.8	2.805 ± 0.010	0.015 ± 0.002	0.993
	Au-As	0.6 ± 0.3	2.454 ± 0.023	0.004 ± 0.003	
Au1000, 31h	Au-Au	6.7 ± 1.1	2.807 ± 0.011	0.015 ± 0.002	0.993
	Au-As	0.4 ± 0.2	2.462 ± 0.026	0.004 ± 0.003	
Au2000, 2h	Au-Au	8.4 ± 0.8	2.827 ± 0.005	0.013 ± 0.001	0.993
	Au-As	0.3 ± 0.1	2.482 ± 0.024	0.003 ± 0.003	
Au2000, 6h	Au-Au	8.3 ± 0.7	2.827 ± 0.005	0.013 ± 0.001	0.993
	Au-As	0.3 ± 0.1	2.472 ± 0.023	0.003 ± 0.003	
Au2000, 16h	Au-Au	8.8 ± 0.9	2.827 ± 0.006	0.013 ± 0.001	0.993
	Au-As	0.3 ± 0.2	2.484 ± 0.025	0.003 ± 0.003	
Au2000, 21h	Au-Au	8.8 ± 1.0	2.825 ± 0.006	0.013 ± 0.001	0.993
	Au-As	0.3 ± 0.2	2.471 ± 0.025	0.003 ± 0.003	

The ΔE_0 obtained from the fitting of Au foil is 2.0 ± 0.4 eV.

The ΔE_0 for Au-Au and Au-As pairs are constrained to be the same respectively during the fitting. The values obtained for different Au/NC ratios from fitting are:

1000 Au/NC: ΔE_0 (Au-Au) = -1.3 ± 0.5 eV; ΔE_0 (Au-As) = -2.3 ± 5.0 eV

2000 Au/NC: ΔE_0 (Au-Au) = -0.6 ± 0.3 eV; ΔE_0 (Au-As) = 1.8 ± 5.4 eV

Table S2. Best fits results of the structural parameter of the As-In, Au-Au, Au-As, In-O and In-As pairs obtained from via multiple data set fitting of As K/Au L₃-edge and In K-edge EXAFS of Au-InAs NPs (1000 Au/NC).

Sample	bond	N	R (Å)	σ^2 (Å ²)	ΔE_o (eV)	S_0^2
InAs	As-In	4	2.618 ± 0.004	0.004 ± 0.001	3.6 ± 0.7	0.816 ± 0.076
	In-As	4	2.620 ± 0.005	0.005 ± 0.001	4.9 ± 1.3	0.952 ± 0.090
Au foil	Au-Au	12	2.864 ± 0.004	0.008 ± 0.001	3.0 ± 0.5	0.839 ± 0.062
Au1000, 1h	As-In	2.4 ± 0.6	2.619 ± 0.005	0.006 ± 0.001	2.2 ± 2.7	0.816
	Au-Au	6.7 ± 1.7	2.769 ± 0.016	0.013 ± 0.002	2.8 ± 1.4	0.839
	Au-As	0.8 ± 0.4	2.497 ± 0.014	0.002 ± 0.002	2.8 ± 1.4	0.839
	In-O	1.8 ± 0.6	2.156 ± 0.035	0.014 ± 0.006	4.0 ± 3.0	0.952
	In-As	3.8 ± 0.3	2.619 ± 0.005	0.006 ± 0.001	4.8 ± 1.1	0.952
Au1000, 6h	As-In	2.1 ± 0.9	2.618 ± 0.008	0.005 ± 0.001	3.8 ± 3.4	0.816
	Au-Au	6.7 ± 2.3	2.797 ± 0.023	0.015 ± 0.003	4.0 ± 2.1	0.839
	Au-As	1.1 ± 0.5	2.518 ± 0.022	0.003 ± 0.002	4.0 ± 2.1	0.839
	In-O	2.1 ± 0.7	2.148 ± 0.004	0.011 ± 0.006	5.5 ± 3.5	0.952
	In-As	3.1 ± 0.5	2.618 ± 0.008	0.005 ± 0.001	4.5 ± 1.9	0.952
Au1000, 12h	As-In	2.5 ± 0.8	2.614 ± 0.009	0.006 ± 0.001	2.4 ± 3.5	0.816
	Au-Au	6.6 ± 2.3	2.790 ± 0.024	0.014 ± 0.003	3.7 ± 2.0	0.839
	Au-As	0.8 ± 0.5	2.513 ± 0.018	0.002 ± 0.003	3.7 ± 2.0	0.839
	In-O	2.4 ± 0.6	2.156 ± 0.030	0.011 ± 0.005	6.7 ± 2.6	0.952
	In-As	3.1 ± 0.5	2.614 ± 0.009	0.006 ± 0.001	3.9 ± 2.1	0.952
Au1000, 22h	As-In	2.7 ± 1.1	2.614 ± 0.012	0.006 ± 0.002	-2.3 ± 5.6	0.816
	Au-Au	8.9 ± 2.8	2.783 ± 0.023	0.015 ± 0.003	3.4 ± 1.9	0.839
	Au-As	1.2 ± 0.7	2.510 ± 0.020	0.003 ± 0.002	3.4 ± 1.9	0.839
	In-O	3.3 ± 0.5	2.133 ± 0.016	0.009 ± 0.003	5.4 ± 1.4	0.952
	In-As	2.4 ± 0.5	2.614 ± 0.009	0.006 ± 0.002	3.2 ± 2.5	0.952
Au1000, 30h	As-In	2.1 ± 1.2	2.579 ± 0.026	0.004 ± 0.002	1.6 ± 4.6	0.816
	Au-Au	8.2 ± 2.6	2.810 ± 0.031	0.017 ± 0.004	4.1 ± 1.9	0.839
	Au-As	0.9 ± 1.2	2.570 ± 0.046	0.005 ± 0.010	4.1 ± 1.9	0.839

	In-O	3.2 ± 0.7	2.119 ± 0.022	0.006 ± 0.003	5.4 ± 2.2	0.952
	In-As	1.8 ± 0.6	2.579 ± 0.026	0.004 ± 0.002	-2.6 ± 5.7	0.952

Table S3. Best fits results of the structural parameters of the In-O and In-As pairs obtained from via fitting of In K-edge EXAFS of Au-InAs NPs with different Au/NC ratios. For samples with 3000 and 5000 Au/NC ratios, only In-O pair is included in fitting.

Sample	bond	N	R (Å)	σ^2 (Å ²)	ΔE_o (eV)	S_0^2
InAs	In-As	4	2.617 ± 0.004	0.005 ± 0.000	5.6 ± 1.0	0.964 ± 0.073
Au500, 2.5h	In-O	0.8 ± 0.2	2.156 ± 0.019	0.005 ± 0.001	5.3 ± 1.1	0.964
	In-As	3.7 ± 0.3	2.617 ± 0.003	0.005 ± 0.001	5.6 ± 0.5	
Au500, 14h	In-O	1.1 ± 0.2	2.156 ± 0.015	0.005 ± 0.001	5.3 ± 1.1	0.964
	In-As	3.2 ± 0.4	2.617 ± 0.003	0.005 ± 0.001	5.6 ± 0.5	
Au500, 23h	In-O	1.2 ± 0.2	2.150 ± 0.013	0.005 ± 0.001	5.3 ± 1.1	0.964
	In-As	3.0 ± 0.3	2.616 ± 0.003	0.005 ± 0.001	5.6 ± 0.5	
Au500, 43h	In-O	1.5 ± 0.2	2.144 ± 0.012	0.005 ± 0.001	5.3 ± 1.1	0.964
	In-As	2.9 ± 0.3	2.618 ± 0.003	0.005 ± 0.001	5.6 ± 0.5	
Au500, 64h	In-O	1.6 ± 0.2	2.148 ± 0.010	0.005 ± 0.001	5.3 ± 1.1	0.964
	In-As	2.9 ± 0.2	2.620 ± 0.005	0.005 ± 0.001	5.6 ± 0.5	
Au1000, 4h	In-O	1.2 ± 0.2	2.145 ± 0.029	0.007 ± 0.001	5.5 ± 1.0	0.964
	In-As	3.3 ± 0.7	2.610 ± 0.007	0.005 ± 0.001	3.4 ± 1.4	
Au1000, 15h	In-O	2.3 ± 0.3	2.138 ± 0.014	0.007 ± 0.001	5.5 ± 1.0	0.964
	In-As	2.4 ± 0.6	2.610 ± 0.008	0.005 ± 0.001	3.4 ± 1.4	
Au1000, 33h	In-O	2.7 ± 0.3	2.140 ± 0.012	0.007 ± 0.001	5.5 ± 1.0	0.964
	In-As	2.1 ± 0.5	2.610 ± 0.007	0.005 ± 0.001	3.4 ± 1.4	
Au1000, 49h	In-O	2.9 ± 0.3	2.138 ± 0.010	0.007 ± 0.001	5.5 ± 1.0	0.964
	In-As	2.0 ± 0.4	2.609 ± 0.007	0.005 ± 0.002	3.4 ± 1.4	
Au1000, 65h	In-O	3.0 ± 0.3	2.141 ± 0.011	0.007 ± 0.001	5.5 ± 1.0	0.964
	In-As	1.4 ± 0.6	2.610 ± 0.009	0.004 ± 0.003	3.4 ± 1.4	
Au2000, 5h	In-O	2.7 ± 0.4	2.135 ± 0.014	0.006 ± 0.001	5.9 ± 0.7	0.964
	In-As	1.7 ± 0.7	2.591 ± 0.021	0.003 ± 0.002	-1.9 ± 4.7	
Au2000, 17h	In-O	3.4 ± 0.5	2.135 ± 0.014	0.006 ± 0.001	5.9 ± 0.7	0.964
	In-As	0.8 ± 0.4	2.602 ± 0.030	0.003 ± 0.002	-1.9 ± 4.7	
Au2000, 26h	In-O	4.2 ± 0.3	2.136 ± 0.013	0.006 ± 0.001	5.9 ± 0.7	0.964

	In-As	0.8 ± 0.3	2.599 ± 0.027	0.003 ± 0.002	-1.9 ± 4.7	
Au2000, 58h	In-O	4.4 ± 0.4	2.134 ± 0.008	0.006 ± 0.001	5.9 ± 0.7	0.964
	In-As	0.6 ± 0.3	2.608 ± 0.032	0.003 ± 0.002	-1.9 ± 4.7	
Au2000, 67h	In-O	4.4 ± 0.3	2.134 ± 0.007	0.006 ± 0.001	5.9 ± 0.7	0.964
	In-As	0.5 ± 0.2	2.589 ± 0.028	0.003 ± 0.002	-1.9 ± 4.7	
Au3000, 5h	In-O	3.6 ± 0.7	2.144 ± 0.022	0.006 ± 0.002	7.4 ± 0.9	0.964
Au3000, 15h	In-O	4.2 ± 0.8	2.151 ± 0.018	0.006 ± 0.002	7.4 ± 0.9	0.964
Au3000, 24h	In-O	4.5 ± 0.5	2.151 ± 0.011	0.006 ± 0.002	7.4 ± 0.9	0.964
Au3000, 32h	In-O	4.7 ± 0.8	2.148 ± 0.016	0.006 ± 0.002	7.4 ± 0.9	0.964
Au3000, 56h	In-O	4.9 ± 0.5	2.149 ± 0.010	0.006 ± 0.002	7.4 ± 0.9	0.964
Au5000, 6h	In-O	3.9 ± 0.9	2.167 ± 0.025	0.007 ± 0.002	7.9 ± 1.0	0.964
Au5000, 14h	In-O	4.7 ± 0.6	2.156 ± 0.013	0.007 ± 0.002	7.9 ± 1.0	0.964
Au5000, 25h	In-O	4.8 ± 0.6	2.157 ± 0.012	0.007 ± 0.002	7.9 ± 1.0	0.964
Au5000, 50h	In-O	5.0 ± 0.7	2.162 ± 0.013	0.007 ± 0.002	7.9 ± 1.0	0.964
Au5000, 58h	In-O	5.4 ± 0.8	2.159 ± 0.014	0.007 ± 0.002	7.9 ± 1.0	0.964

Table S4. Fourier transform parameters used in fitting of the Au L₂ EXAFS data of Au-InAs with 1000 and 2000 Au/NC ratios and fitting of the As K/Au L₃, In K-edge EXAFS data of Au-InAs NPs with 1000 Au/NC ratio.

Edge	Sample	k-range ($\text{\AA}^{-1}$)	r-range ($\text{\AA}$)	k-weighting	Δk ($\text{\AA}^{-1}$)
Au L ₂ -edge	Au foil	2.7-11.1	1.55-3.50	2	1
	Au1000, 3h	2.0-10.3	1.40-3.25	2	1
	Au1000, 9h	2.0-10.3	1.40-3.25	2	1
	Au1000, 23h	2.0-10.3	1.40-3.25	2	1
	Au1000, 31h	2.0-10.3	1.40-3.25	2	1
	Au2000, 2h	2.0-10.9	1.55-3.28	2	1
	Au2000, 6h	2.0-10.9	1.55-3.28	2	1
	Au2000, 16h	2.0-10.9	1.55-3.28	2	1
	Au2000, 21h	2.0-10.9	1.55-3.28	2	1
	Au foil	2.0-12.0	1.49-3.70	2	1
Au L ₃ -edge	Au1000, 1h	2.5-12.8	1.40-3.81	2	1
	Au1000, 6h	2.5-13.2	1.40-3.70	2	1
	Au1000, 12h	2.4-12.8	1.40-3.80	2	1
	Au1000, 22h	2.5-13.8	1.40-3.70	2	1
	Au1000, 30h	2.5-12.8	1.60-3.96	2	1
	Au foil	2.0-12.0	1.49-3.70	2	1
In K-edge	InAs	2.5-14.7	1.50-2.76	2	1
	Au1000, 1h	2.2-13.9	1.20-2.80	2	1
	Au1000, 6h	2.3-13.9	1.20-2.82	2	1
	Au1000, 12h	2.2-13.0	1.20-2.83	2	1
	Au1000, 22h	2.0-11.7	1.20-2.84	2	1
	Au1000, 30h	2.6-10.5	1.20-2.90	2	1

Table S5. Fourier transform parameters used in fitting of the In K-edge EXAFS data of Au-InAs NPs with 500,1000, 2000, 3000 and 5000 Au/NC ratios.

InAs	k-range ($\text{\AA}^{-1}$)	r-range ($\text{\AA}$)	k-weighting	Δk ($\text{\AA}^{-1}$)
Au500, 2.5h	2.6-12.0	1.20-2.76	2	2
Au500, 14h	2.6-11.0	1.46-2.78	2	2
Au500, 23h	2.6-11.8	1.40-3.00	2	2
Au500, 43h	2.6-11.6	1.34-2.72	2	2
Au500, 64h	2.6-12.0	1.20-2.80	2	2
Au1000, 4h	2.5-12.0	1.34-2.80	2	2
Au1000, 15h	2.5-12.0	1.20-2.80	2	2
Au1000, 33h	2.5-13.0	1.20-2.72	2	2
Au1000, 49h	2.5-11.5	1.20-2.82	2	2
Au1000, 65h	2.5-10.0	1.20-2.80	2	2
Au2000, 5h	2.3-11.2	1.20-2.80	2	2
Au2000, 17h	2.3-10.5	1.20-2.72	2	2
Au2000, 26h	2.2-9.5	1.20-2.72	2	2
Au2000, 58h	2.4-9.0	1.20-2.72	2	2
Au2000, 67h	2.4-10.0	1.20-2.72	2	2
Au3000, 5h	2.2-8.0	1.20-2.50	2	2
Au3000, 15h	2.2-9.0	1.20-2.35	2	2
Au3000, 24h	2.2-9.0	1.20-2.35	2	2
Au3000, 32h	2.2-9.0	1.20-2.35	2	2
Au3000, 56h	2.2-9.0	1.20-2.35	2	2
Au5000, 6h	2.3-8.8	1.20-2.38	2	2
Au5000, 14h	2.3-9.0	1.20-2.38	2	2
Au5000, 25h	2.3-9.0	1.20-2.38	2	2
Au5000, 50h	2.3-9.0	1.20-2.38	2	2
Au5000, 58h	2.3-9.0	1.20-2.38	2	2