

Title	Doped colloidal InAs nanocrystals in the single ionized dopant limit
Authors	Biaye, Moussa;Amit, Yorai;Gradkowski, Kamil;Turek, Natalia;Godey, Sylvie;Makoudi, Younes;Deresmes, Dominique;Tadjine, Athmane;Delerue, Christophe;Banin, Uri;Mélin, Thierry
Publication date	2019-05-16
Original Citation	Biaye, M., Amit, Y., Gradkowski, K., Turek, N., Godey, S., Makoudi, Y., Deresmes, D., Tadjine, A., Delerue, C., Banin, U. and Mélin, T. (2019) 'Doped Colloidal InAs Nanocrystals in the Single Ionized Dopant Limit', The Journal of Physical Chemistry C, 123 (23), pp. 14803-14812. doi: 10.1021/acs.jpcc.9b02576
Type of publication	Article (peer-reviewed)
Link to publisher's version	<a href="https://pubs.acs.org/doi/10.1021/acs.jpcc.9b02576">https://pubs.acs.org/doi/10.1021/acs.jpcc.9b02576</a> - <a href="https://pubs.acs.org/doi/10.1021/acs.jpcc.9b02576">10.1021/acs.jpcc.9b02576</a>
Rights	© 2019 American Chemical Society. This document is the Accepted Manuscript version of a Published Work that appeared in final form in The Journal of Physical Chemistry C, © American Chemical Society after peer review and technical editing by the publisher. To access the final edited and published work see <a href="https://pubs.acs.org/doi/10.1021/acs.jpcc.9b02576">https://pubs.acs.org/doi/10.1021/acs.jpcc.9b02576</a>
Download date	2025-02-08 22:29:30
Item downloaded from	<a href="https://hdl.handle.net/10468/8402">https://hdl.handle.net/10468/8402</a>



# UCC

**University College Cork, Ireland**  
Coláiste na hOllscoile Corcaigh

## Doped Colloidal InAs Nanocrystals in the Single Ionized Dopant Limit

Moussa Biaye, Yorai Amit, Kamil Gradkowski, Uri Banin, Natalia Turek, Sylvie Godey, Younes Makoudi, Dominique Deresmes, Athmane Tadjine, Christophe Delerue, and Thierry Mélin

*J. Phys. Chem. C*, **Just Accepted Manuscript** • DOI: 10.1021/acs.jpcc.9b02576 • Publication Date (Web): 16 May 2019

Downloaded from <http://pubs.acs.org> on May 21, 2019

### Just Accepted

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.



# Doped Colloidal InAs Nanocrystals in the Single Ionized Dopant Limit

*Moussa Biaye<sup>1</sup>, Yorai Amit<sup>2</sup>, Kamil Gradkowski<sup>2,†</sup>, Uri Banin<sup>2</sup>, Natalia Turek<sup>1</sup>, Sylvie Godey<sup>1</sup>,  
Younes Makoudi<sup>1,‡</sup>, Dominique Deresmes<sup>1</sup>, Athmane Tadjine<sup>1</sup>, Christophe Delerue<sup>1</sup>, Thierry  
Mélin<sup>1,\*</sup>*

(1) Institute of Electronics Microelectronics and Nanotechnology, University of Lille and Centre National de la Recherche Scientifique, IEMN-CNRS UMR 8520, Avenue Poincaré CS 60069, 59652 Villeneuve d'Ascq Cedex, France.

(2) Institute of Chemistry, Hebrew University, Jerusalem 91904, Israel ; Center for Nanoscience and Nanotechnology, Hebrew University, Jerusalem 91904, Israel.

\* corresponding author : [thierry.melin@iemn.fr](mailto:thierry.melin@iemn.fr)

† present address: Photonic Packaging Group, Tyndall National Institute, Lee Maltings Complex, Cork T12R5CP, Ireland

‡ present address: Institut FEMTO-ST, CNRS, Université Bourgogne Franche-Comté, 15B Avenue des Montboucons, F-25030 Besançon Cedex, France.

1  
2  
3 ABSTRACT  
4  
5

6 We investigate the electronic properties of individual n-type (Cu) doped and p-type (Ag) doped  
7 InAs colloidal nanocrystals (NCs) in the 2-8 nm size range from their charge transfers towards a  
8 highly oriented pyrolytic graphite (HOPG) substrate, using ultra-high vacuum Kelvin probe force  
9 microscopy (KPFM) with elementary charge sensitivity at 300K. The NC active dopant  
10 concentration is measured as  $N_D = 8.10^{20} \text{ cm}^{-3}$  and  $N_A > 5.10^{20} \text{ cm}^{-3}$  for n- and p-type doping,  
11 respectively. The electrostatic equilibrium between the NC and the HOPG reference substrate is  
12 investigated, and reveals an enhancement of the Fermi level mismatch between the NCs and the  
13 HOPG substrate at reduced NC sizes, both for n- and p-type doping. It also shows, for n-type  
14 doped NCs with smallest sizes ( $\sim 2$  nm), the existence of a full depletion regime, in which smallest  
15 NCs contain single ionized dopants. Results are compared with self-consistent tight-binding  
16 calculations of the electronic structure of InAs NCs including hydrogenoid impurities and the  
17 presence of a host substrate, in the case of n-type doped NCs. The observed enhancement of the  
18 NC-HOPG Fermi-level mismatch can be understood by considering a size-dependent electrostatic  
19 contribution attributed to dipolar effects at the NC-ligand interface. The estimated surface dipole  
20 density equals a few Debye/nm<sup>2</sup>, and is increased at smallest NC sizes, which follows the  
21 enhancement of ligand densities at small NC sizes previously reported for metallic or  
22 semiconducting NCs. The results put forward the role played by the NC-ligand interface  
23 electrostatics for electronic applications.  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

## INTRODUCTION

Doped semiconductor nanocrystals (NCs)<sup>1,2</sup> are the subject of intensive research due to their potential applications in electronics or optoelectronics. They enable *e.g.* to fabricate semiconductor nanomaterials incorporating magnetic impurities<sup>1</sup>, to synthesize nanostructures for photovoltaic applications<sup>3</sup>, or to design plasmonic nanomaterials due to the large achievable doping concentration up to a few percent<sup>4-8</sup>. The synthesis of doped NCs is now available for a variety of materials. It includes non-colloidal NCs grown by physical methods such as Indium Tin Oxide<sup>4</sup>, ZnO<sup>5</sup>, or Si<sup>6-8</sup>, but also NCs grown by colloidal chemistry such as CdSe<sup>9</sup>, ZnS<sup>10</sup>, or InAs<sup>11,12</sup>. The large concentration of impurities required to dope individual NCs with a few nm size has nonetheless raised fundamental questions such as the dopant solubility and the NC self-purification<sup>13</sup>. The control of doping processes as well as the structural and electrical characterization of dopants in NCs are still open fields of investigation<sup>13-16</sup>.

In this Article, we focus on colloidal InAs NCs doped by diffusion<sup>11</sup>. This system offers a unique test bench to study electronic doping issues in colloidal systems, since both n-type (Cu) doping and p-type (Ag) doping can be achieved for InAs NCs, as qualitatively evidenced from optical and scanning tunneling spectroscopy (STS) experiments<sup>11</sup>. n-type and p-type dopings are however different in their essence, since Cu behaves as an interstitial dopant with high solubility in InAs<sup>15</sup>, while Ag incorporates as a substituent of In with a finite low solubility limit, as evidenced from a recent structural work<sup>16</sup>. A strong need exists to characterize the active electronic doping of such colloidal NCs beyond structural considerations, and beyond early optical or STS experiments. This includes the accurate assessment of the NC active electronic doping level, which is of primary interest for electronic applications. It also includes the understanding of the electronic structure of

1  
2 doped NCs, which may be strongly affected by the presence of dopants<sup>11</sup>, and is insufficiently  
3 understood in link with experiments.  
4  
5

6  
7  
8 We investigate for this purpose in this Article n-type (Cu-doped) and p-type (Ag-doped) colloidal  
9 individual InAs NCs as a function of their size, in the ~2-8 nm size range. To characterize the NC  
10 doping, we use Kelvin Probe Force Microscopy (KPFM) experiments in ultra-high vacuum,  
11 enabling the measurement of the charge transfer between doped NCs and a highly oriented  
12 pyrolytic graphite (HOPG) reference substrate, with a charge sensitivity better than a single  
13 elementary charge, at room temperature. We observe for Cu-doped InAs NCs of different sizes a  
14 transition from a partial ionization regime towards a full depletion regime at smallest NC sizes.  
15 The ionization charge of fully depleted NCs is solely limited by the number of electrically active  
16 dopants, which enables to measure the NC active doping level (active donor and acceptor  
17 concentrations  $N_D$  and  $N_A$ ) at  $N_D=8.10^{20} \text{ cm}^{-3}$  and  $N_A > 5.10^{20} \text{ cm}^{-3}$  for Cu or Ag doping,  
18 respectively. The combined KPFM characterization of n-type and p-type doped NCs also provides  
19 a spectroscopy of the Fermi level mismatch between the NC and the reference HOPG substrate, as  
20 a function of the NC size and doping type, which is not achievable by other techniques. The  
21 analysis reveals an enhancement of the NC-HOPG Fermi level mismatch at reduced NC sizes,  
22 which is compared to self-consistent tight-binding calculations of the InAs NC electronic structure  
23 including hydrogenoid impurities and substrate, in the case of n-type doped NCs. These results are  
24 only understood provided a size-dependent electrostatic contribution be introduced, which is  
25 attributed to dipolar effects at the NC-ligand interface. The estimated surface dipole density equals  
26 ~0.2 C/m, and is increased by a factor of ~3-4 at the smallest NC sizes, which corresponds to the  
27 enhancement of ligand densities at small NC sizes previously reported for metallic or  
28 semiconducting NCs. These results put forward the important role played by the electrostatics at  
29 the NC-ligand interface, in combination with doping.  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

1  
2  
3 METHODS  
4

5  
6 *Nanocrystal synthesis.* The detailed NC synthesis can be found in previous work<sup>11,15</sup>. Pre-  
7 synthesized colloidal InAs NCs with dodecylamine / didodecyl-dimethylammonium bromide  
8 (DDA/DDAB) ligands have been doped by diffusion of metal impurities at room temperature using  
9 a toluene solution containing metal salts (CuCl<sub>2</sub> and AgNO<sub>3</sub>). Cu doping was used for n-type  
10 doping<sup>11</sup> with a Cu concentration of about 1500 Cu atoms / NC in solution during the doping  
11 procedure for a 5 nm size NC. The number of Cu atoms incorporated in NCs has been estimated  
12 from inductively coupled plasma atomic emission spectroscopy<sup>15</sup> and corresponds to about 465  
13 Cu atoms / NC for a 5 nm diameter NC. Ag has been used for p-type doping, with a concentration  
14 of about 1660 Ag atoms / NC in solution for a 5 nm NC size, corresponding to about 170 Ag atoms  
15 / NC, however present both as dopants or clusters at the NC surface due to the finite solubility of  
16 Ag in InAs<sup>16</sup>.  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30

31  
32 *Sample preparation.* Doped NCs dispersed in toluene have been stored under nitrogen in an  
33 oxygen-free (<1 ppm) environment. NCs have been deposited by drop casting from diluted toluene  
34 NC dispersions onto freshly cleaved highly-oriented pyrolytic graphite (HOPG) substrates (SPI  
35 Supplies) and transferred within a few minutes in a sealed container to the load-locks of the ultra-  
36 high vacuum atomic force microscopes used in this work (VT AFM/STM, Scienta Omicron, or JT  
37 AFM/STM, SPECS). Both set-ups have a base pressure in the 10<sup>-10</sup> mbar range. We took a special  
38 care in experiments to obtain a clear phase separation between the bare HOPG substrate (used as  
39 a reference for Kelvin probe measurements<sup>17</sup>) and the excess ligand layer deposited together with  
40 the NCs. This was achieved by a mild sample temperature annealing in ultra-high vacuum (UHV)  
41 (T<140°C for 15 min) as illustrated in the Supporting Information (Figure S1 and S2).  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

1  
2  
3 *Atomic force microscopy.* Two atomic force microscopy set-ups were used in this work. The main  
4 set-up is an optical-beam AFM (VT AFM/STM, Scienta Omicron) using conventional metal-  
5 plated cantilevers (EFM PPP, Nanosensors) with resonance frequency  $f_0$  of about 70 kHz and  
6 spring constant in the 1-3 N/m range. The oscillation amplitude of the cantilever (typical peak-to-  
7 peak oscillation amplitude  $A_{pp}=20$  nm) has been carefully calibrated using the technique derived  
8 from the work of F. Giessibl<sup>18</sup>. The minimum distance between the lowest turning point of the tip  
9 oscillation and the substrate critically depends on the cantilever frequency shift detuning  $\Delta f$ . We  
10 used here mostly low frequency detunings ( $\Delta f=-5$  Hz, corresponding to minimum tip-substrate  
11 distances in the 4-5nm range) to record simultaneous Kelvin probe and nc-AFM images while  
12 avoiding any role of short-range forces in Kelvin probe data used in a subsequent quantitative  
13 analysis. The role of  $\Delta f$  on nc-AFM topography images (in particular, on the measurement of a  
14 “true” NC height) is discussed in the core of our manuscript. This issue has been addressed by  
15 using a stiff-probe atomic force microscope (JT AFM/STM, SPECS) operating at low temperatures  
16 (in this work,  $T=77$ K). This set-up is based on a length-extensional quartz resonator (see e.g. Ref.<sup>19</sup>  
17 for high-resolution imaging on Silicon) with stiffness of about  $5 \cdot 10^5$  N/m and oscillation amplitude  
18  $A_{pp}=400$ pm. The sensors were used with a positive frequency shift detuning ( $\Delta f=+1$ Hz) to  
19 intentionally obtain nc-AFM topography images with significant repulsive force gradients (short  
20 range) contributions, for sake of comparison with optical-beam AFM topography images.  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43

44  
45 *Kelvin probe force microscopy.* Kelvin probe images have been recorded from the optical beam  
46 AFM (VT AFM/STM, Scienta Omicron) using Frequency Modulation (FM) KPFM or Amplitude  
47 Modulation (AM) KPFM. The two techniques differ since FM-KPFM (resp. AM-KPFM) is  
48 sensitive to electrical force gradients (resp. forces). Both techniques vary in their implementations,  
49 sensibilities, lateral resolutions and potential artifacts<sup>20</sup>. When measurements are conducted in the  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60



1  
2 regime of long-range electrostatic forces, both techniques can be analyzed quantitatively using  
3 conventional numerical electrostatic simulations<sup>21-23</sup>. FM-KPFM images are recorded by applying  
4 a low-frequency ac modulation (typically  $f_{\text{mod}} = 300\text{Hz}$ ,  $V_{\text{ac}} = 200\text{ mV}$ ) to the cantilever bias and  
5 compensating the ac cantilever frequency shift of the first flexural mode as a function of the tip dc  
6 potential. AM-KPFM images are recorded by electrically exciting the cantilever at its second  
7 flexural mode (typ.  $f_{\text{mod}} = 6.2 f_0$ ,  $V_{\text{ac}} = 200\text{ mV}$ ) and nullifying the induced ac cantilever oscillation  
8 amplitude as a function of the tip dc potential.  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18

19 *Transmission Electron Microscopy.* TEM measurements were performed using a Tecnai T12 G2  
20 Spirit and Tecnai F20 G2. All size statistics are analyzed using the "Scion image" program.  
21  
22  
23  
24

25 *Electrostatic numerical simulations.* Numerical simulations enable to extract the actual  
26 electrostatic potential of individual ionized NCs from experimental KPFM signals, which suffer  
27 from averaging mechanisms due to stray capacitances and tip oscillation. Numerical simulations  
28 have been implemented using COMSOL as a Poisson solver according to the developments of  
29 Ref.<sup>21</sup> and can be obtained either in AM-KPFM<sup>22</sup> or FM-KPFM modes<sup>23</sup>. A dielectric description  
30 of the NCs is used for the simulations, considering the substrate as metallic and the NCs as an InAs  
31 semiconducting core (with relative dielectric constant  $\epsilon_{\text{InAs}}=15.1$ ) surrounded by a ligand shell  
32 considered as a dielectric material with  $\epsilon_{\text{ligands}}=2.6$ . The thickness of the ligand layer is taken as  
33 0.35 nm as from comparative AFM and TEM measurements. The result of the simulations is used,  
34 in practice, as a tool to transform raw experimental KPFM data into local electrostatic potentials,  
35 and to estimate the NC ionization charge assuming a charge distribution model (e.g. core charge  
36 or junction model)<sup>24</sup>.  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52

53 *Tight binding numerical simulations.* The electronic structure of pristine InAs NCs was calculated  
54 using a tight-binding approach in which each In or As atom is represented by 20 atomic orbitals  
55  
56  
57  
58  
59  
60

1 including spin degeneracy. We used the  $sp^3d^5s^*$  model of Ref.<sup>25</sup>. The surface of the NCs is  
2  
3 passivated by pseudo-hydrogen atoms. Doped NCs are described assuming that each dopant  
4  
5 behaves as a hydrogenoid impurity characterized by a point charge  $+e$  placed at an interstitial  
6  
7 position plus an extra electron that fills the conduction states. The impurities are placed at random  
8  
9 positions excluding surface sites. The total potential coming from the fixed charges and the  
10  
11 electrons is added to tight-binding Hamiltonian<sup>26</sup>. The electronic states and the potential are solved  
12  
13 self-consistently in a Hartree-like approach<sup>27</sup>. In the case of free-standing doped NCs, the Fermi  
14  
15 level is determined by the number of electrons (impurities) occupying the conduction states. In the  
16  
17 case of NCs in equilibrium with a metal (here HOPG), the Fermi level is imposed by the metal  
18  
19 substrate and the number of electrons is considered as a variable that can take fractional values. In  
20  
21 that case, the total potential also includes the effect of the metal substrate described using the  
22  
23 image-charge method. The electronic states, the potential and the NC charge are obtained using a  
24  
25 self-consistent iterative procedure.  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35

## 36 RESULTS

37  
38

39 To probe the charge transfers from the NCs to their environment, we use HOPG as a reference  
40  
41 host substrate, since this material has a stable work function ( $\chi_{\text{HOPG}} = 4.5 \text{ eV}^{28}$ ) almost insensitive  
42  
43 to contamination in ambient air or vacuum<sup>28</sup>. The sample is prepared by NC drop casting from  
44  
45 colloidal dispersions in anhydrous toluene<sup>11</sup> onto freshly cleaved HOPG. Samples are immediately  
46  
47 loaded into ultra-high vacuum, followed by a mild sample annealing to improve the excess ligand  
48  
49 layer ordering, if required. Non-Contact Atomic Force Microscopy (nc-AFM) and Kelvin Probe  
50  
51 Force Microscopy (KFPM) experiments are then carried out (see Methods).  
52  
53  
54  
55  
56  
57  
58  
59  
60

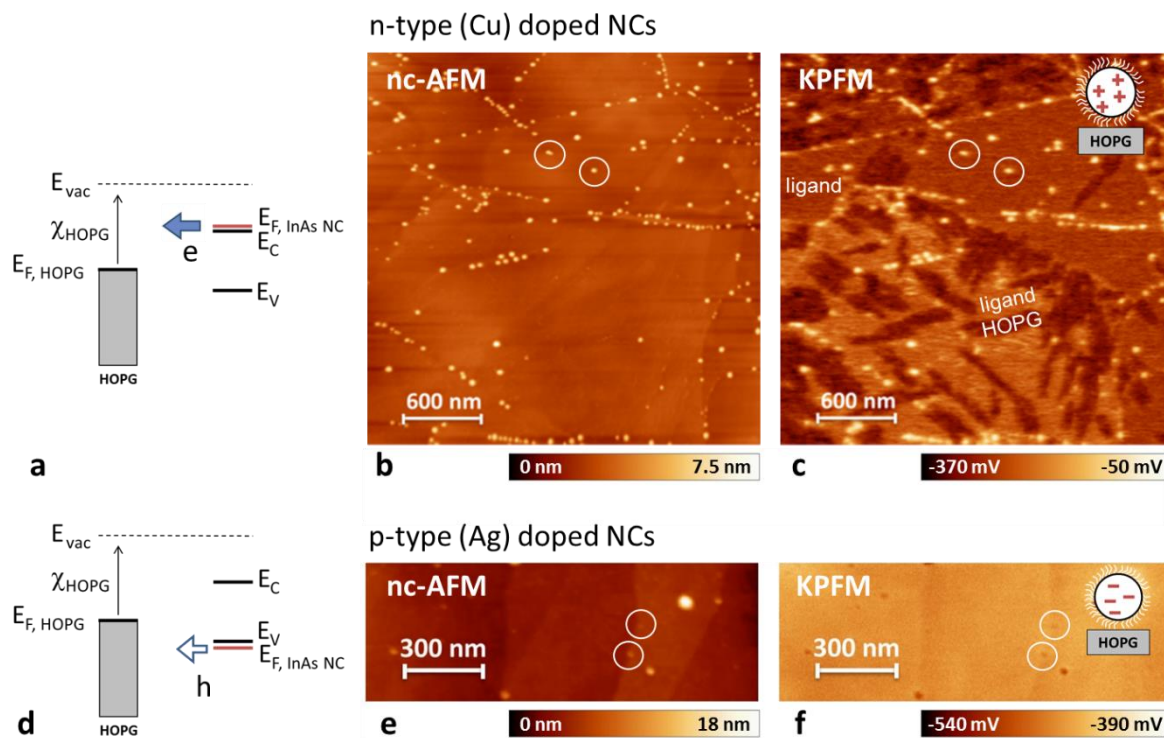


Figure 1: a) Energy diagram of HOPG (with work function  $\chi_{\text{HOPG}}$ ) and a highly n-type doped NC represented by its conduction and valence band ground levels  $E_c$  and  $E_v$ , and a Fermi level  $E_{F, \text{InAs NC}}$  (we choose  $E_{F, \text{InAs NC}} > E_c$  for simplicity). The vacuum level is  $E_{\text{vac}}$ . The arrow indicates the NC ionization process, in which the NCs become partially depleted and free electrons are transferred to HOPG, leaving the NC positively charged. b) nc-AFM image of Cu-doped NCs on HOPG, recorded with a cantilever with resonance frequency  $f_0 \sim 70$  kHz, stiffness  $k \sim 3$  N/m, and with a frequency shift detuning setpoint  $\Delta f = -5$  Hz and a peak-to-peak oscillation amplitude  $A_{\text{pp}} = 20$  nm. c) Simultaneously recorded frequency modulation KPFM image (electrostatic modulation frequency  $f_{\text{ac}} = 300$  Hz and amplitude  $V_{\text{ac}} = 200$  mV). The regulated KPFM dc bias is applied at the tip. Bright features correspond to positively charged NCs. d) Similar diagram as in a) for p-doped NCs. e) and f) nc-AFM and amplitude modulation KPFM images. Individual NCs are highlighted (the brighter features in the nc-AFM image correspond to agglomerated NCs). Dark features in the KPFM image correspond to negatively charged NCs. Scanning conditions are identical to b) and c) except for the use of an amplitude-modulation KPFM mode (modulation frequency  $f_{\text{ac}} \sim 6.2 f_0 \sim 420$  kHz).

1  
2  
3 *Qualitative evidence for n- and p-type doping in KPFM experiments.* The expected charge  
4 transfers from doped NCs are illustrated in Figure 1 in the case of n-type (Cu) and p-type (Ag)  
5 doped NCs. The Fermi levels for doped NCs in the inset of Figure 1 are placed for sake of  
6 simplicity beyond the conduction and valence band onsets as expected for degenerately doped bulk  
7 materials—this point will be specifically discussed hereafter based on tight-binding calculations.  
8  
9 Assuming that the HOPG Fermi level falls within the NC band-gap before charge transfer, NC  
10 dopants are expected to ionize and transfer free electrons (resp. holes) towards the HOPG substrate  
11 (arrows in Figure 1 a and d) for n-type (resp. p-type) doping. This process leaves the NCs partially  
12 depleted, which corresponds to a positive (resp. negative) charging for the n-doped (resp. p-doped)  
13 NCs on the HOPG substrate. This picture qualitatively matches with KPFM experiments shown  
14 in Figure 1. KPFM images here correspond to maps of the sample electrostatic potential, since we  
15 chose to apply the regulated dc compensation bias to the AFM tip (see Methods). KPFM images  
16 of doped NCs are shown in Figure 1c and f, for n-type and p-type doped NCs, respectively. They  
17 exhibit bright features (positive NC charging) and dark features (negative NC charging),  
18 respectively. This observation agrees with the energy diagrams in Figure 1a and d. Such a charge  
19 transfer mechanism has been observed experimentally for n-doped hydrogen-passivated Si NCs<sup>21</sup>.  
20  
21 Both n- and p-type NC doping have however not been observed for Si NCs due to difficulties in  
22 reaching an effective doping for p-type NCs<sup>21,24</sup>. Additional features observed in the KPFM image  
23 in Figure 1c correspond to the presence of an excess sub-monolayer of ligands on the HOPG  
24 substrate (Figures S1 and S2).  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

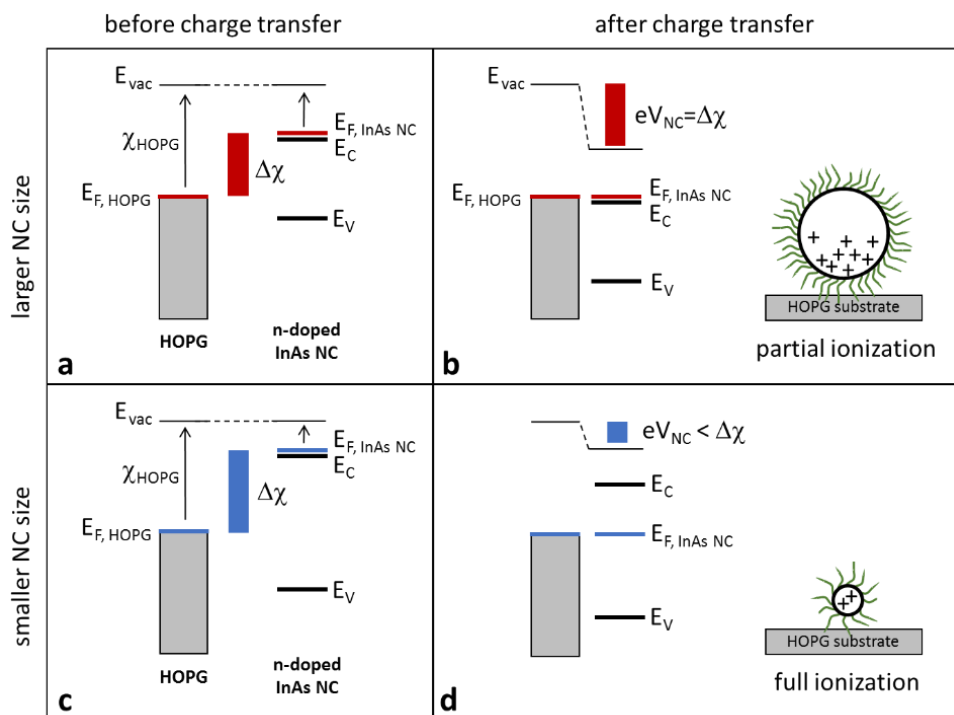


Figure 2: a) Energy diagram of HOPG (with work function  $\chi_{HOPG}$ ) and a n-type doped NC with conduction and valence band ground levels  $E_C$  and  $E_V$ , and Fermi level  $E_{F,InAs NC}$  (choosing  $E_{F,InAs NC} > E_C$ ). b) Energy diagram at equilibrium after charge transfer in the partial ionization (depletion) limit. The NC electrostatic potential  $V_{NC}$  compensates for the Fermi level mismatch  $\Delta\chi = E_{F,InAs NC} - E_{F,HOPG}$  (in red) prior to charge transfer. A depleted junction forms at the NC/HOPG interface (see text). c) Same energy diagram as in a) but for a NC with smaller size and containing only a few dopants. An enhancement of the Fermi level mismatch  $\Delta\chi = E_{F,InAs NC} - E_{F,HOPG}$  is introduced, assuming in a simple picture an increase of the NC band-gap upon quantum confinement (see text for a discussion). d) Energy diagram after charge transfer drawn in the full ionization (depletion) limit, in which the NC electrostatic energy  $eV_{NC}$  (in blue) cannot reach and equilibrate the mismatch  $\Delta\chi$ , due to an insufficient number of dopants in the NC.

*Partial and full ionization (depletion) regimes.* We now focus on the charge state of ionized NCs. Energy diagrams drawn before and after charge transfer are described in Figure 2 in the case of n-doped NCs. Similar diagrams would apply for p-doped NCs, but are not represented. As depicted in Figure 2a and 2b, when the NCs contain enough dopants to account for  $\Delta\chi = E_{F,InAs NC} - E_{F,HOPG}$ ,

1  
2 which is the relevant case for large size NCs, an electrostatic equilibrium sets in and compensates  
3  
4 for the Fermi level mismatch prior to charge transfer between the doped NCs and the HOPG  
5  
6 substrate<sup>21,24</sup> ( $\Delta\chi$  is shown as a red bar in Figure 2a and b). In this situation, the NCs become only  
7  
8 *partially* ionized, and a depletion layer (junction) builds in at the interface with the substrate, as  
9  
10 previously analyzed in the case of n-doped Silicon NCs<sup>24</sup>. A second scenario may occur if the NCs  
11  
12 do not contain enough active dopants to ensure an electrostatic compensation of the Fermi level  
13  
14 mismatch  $\Delta\chi$  upon charge transfer. This situation leads to a full NC ionization (or depletion)  
15  
16 regime, in which the NC ionization charge equals the number of electrically active dopants in the  
17  
18 NCs. However, the NC electrostatic energy  $eV_{\text{NC}}$  remains less than  $\Delta\chi$  (see Figure 2 c and d). The  
19  
20 occurrence of such a scenario strongly depends on the NC size range (including quantum  
21  
22 confinement issues) and doping (including band tailing or filling issues). It will be discussed later  
23  
24 by comparison with self-consistent tight-binding calculations for doped NCs. The NC size required  
25  
26 to observe a full depletion regime can nonetheless be roughly estimated by noticing that for NCs  
27  
28 with a few nm size, both  $\Delta\chi$  and the electrostatic confinement energy of a NC carrying an  
29  
30 elementary charge fall in the eV range<sup>21,24,29</sup>. Thus, the full ionization scenario of Figure 2c and d  
31  
32 is expected for NCs containing single (or at most a few) active dopants. It corresponds to NCs with  
33  
34 sizes of a few nm, assuming a doping level in the  $10^{20} \text{ cm}^{-3}$  range. A crossover between the partial  
35  
36 ionization and the full depletion regimes as a function of the NC size has not been observed  
37  
38 experimentally in literature so far. Its signature would be here a reduction of the NC electrostatic  
39  
40 energy  $eV_{\text{NC}}$  (see Figure 2b and 2d) in the full depletion regime, due to the limitation of  $eV_{\text{NC}}$  by  
41  
42 the number of available dopants. The observation of such a transition (see below) also provides a  
43  
44 method to measure the concentration of electrically active dopants in NCs, since the NC depletion  
45  
46 charge exactly equals the number of electrically active dopants in the full depletion regime.  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

1  
2  
3 *Quantitative analysis of the KPFM data.* We performed a quantitative analysis of the NC charge  
4 state and electrostatic potentials based on combined nc-AFM and KPFM measurements. The  
5 analysis is carried out both for n-type (Cu) and p-type (Ag) doped NCs, as well as for intrinsic  
6 reference NCs (see Supporting Information), as a function of their size in the 2-8 nm size range,  
7 taking advantage of the nominal dispersion of the NC sizes as from NC solutions with average size  
8 of about 4-5 nm. Working beyond qualitative imaging requires extra experimental care to achieve  
9 a quantitative analysis of doping concentrations. One step consists in recording KPFM signals of  
10 individual NCs in the long-range electrostatic force field, in order to ensure a convenient  
11 quantitative analysis using a long-range electrostatics formalism<sup>22</sup>. Such a method has already been  
12 applied to the case of Si NCs<sup>21</sup>, or to nanoscale domains in organic donor acceptor photovoltaic  
13 blends<sup>23</sup>. Quantifying the doping concentration additionally requires measuring the NC size  
14 accurately, which is critical to determine the volume of small-size NCs. A drawback of using  
15 atomic force microscopy stems however from the fact that the recorded NC heights may not be  
16 correct in the long-range force regime. Such an issue has been reported for tapping mode imaging  
17 of NCs<sup>30</sup>. It was addressed in a more recent study using combined nc-AFM and KPFM on  
18 molecular layers<sup>31</sup>, demonstrating that correct height measurements can be recovered using this  
19 combined powerful approach (see Supporting Information Figure S3), while working with large  
20 frequency shift topography set-points in the short-range (dissipative) regime.

21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45 *Procedure for NC size and KPFM measurements.* We worked here according to the conclusions  
46 of Ref.<sup>31</sup>. KPFM images have been recorded in the long-range force regime using a small cantilever  
47 frequency shift detuning  $\Delta f = -5$  Hz (measured NC average height  $\langle h \rangle = 4.5 \pm 0.1$  nm, see Figure  
48 S4). The NC correct heights have been recorded by using a larger frequency shift detuning  $\Delta f = -$   
49 18 Hz in the dissipative regime (measured NC height distribution  $\langle h \rangle = 5.13 \pm 0.1$  nm, see Figure  
50 S4 and Figure SI for a NC per NC comparison). We separately measured the NC height distribution  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

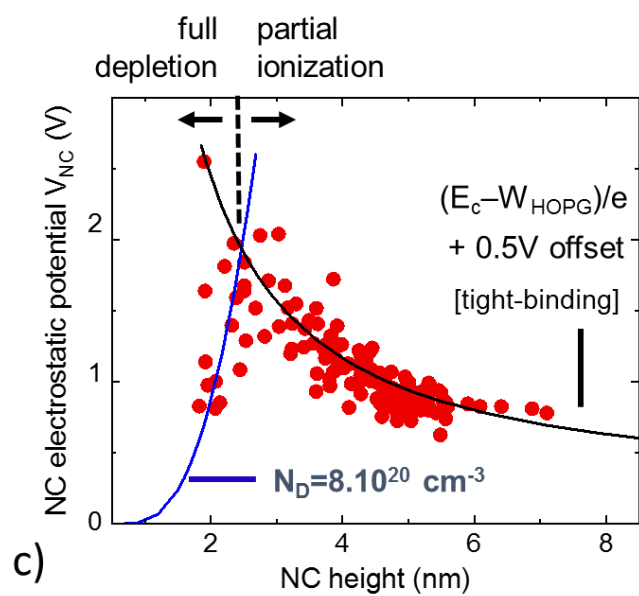
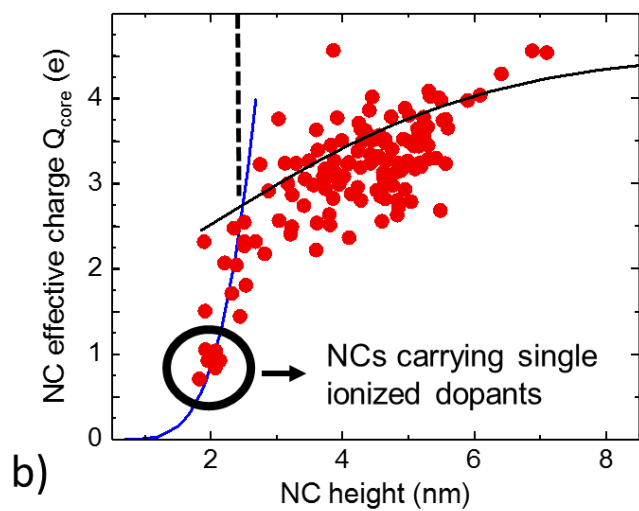
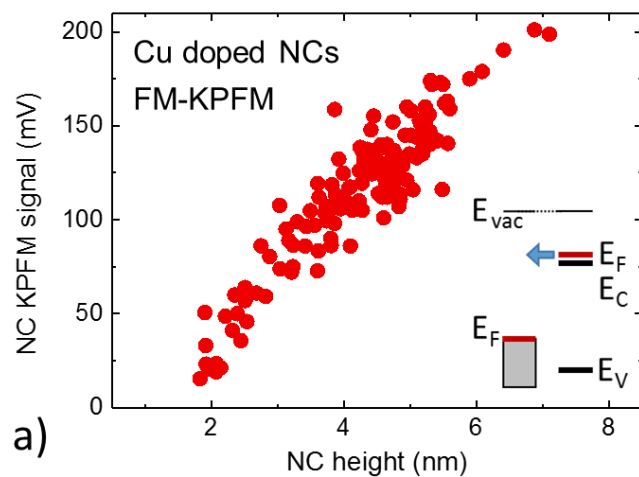
1  
2 using a stiff-probe AFM (SPECS JT AFM/STM) operated with a positive frequency detuning to  
3 ensure the use of repulsive short-range forces. The corresponding height statistics provides an  
4 average NC height  $\langle h \rangle = 5.2 \pm 0.2$  nm (see Figure S4). The error bar on the average height is due  
5 to the finite number of investigated NCs (here, 55 NCs imaged at low temperature). The measured  
6 distribution falls in agreement with data obtained at large  $\Delta f$  ( $\langle h \rangle = 5.13 \pm 0.1$  nm), but offset by  
7  $\Delta h = 0.7 \pm 0.1$  nm with respect to imaging at  $\Delta f = -5$  Hz (see Figure S4). This value of  $\Delta h$  was used  
8 to correct NC heights from nc-AFM images recorded at  $\Delta f = -5$  Hz. Only corrected heights have  
9 been used in the following.

10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22 *TEM imaging and estimation of the ligand layer thickness.* We finally compared the NC height  
23 measurements to size measurements obtained from transmission electron microscopy (TEM) on  
24 n-type (Cu) doped NCs from the same batch (see Methods). A TEM micrograph and a size  
25 statistics are shown in Figure S4. The average NC size (diameter) measured from TEM is smaller  
26 in comparison with AFM measurements, and equals  $\langle d \rangle = 4.5$  nm. This lower value is explained  
27 by the fact that TEM is not sensitive to the NCs ligand layer but only to the inorganic NC core. By  
28 comparison with nc-AFM data acquired in the dissipative regime ( $\langle h \rangle = 5.1 \pm 0.1$  nm for cantilever-  
29 based nc-AFM, and  $\langle h \rangle = 5.2 \pm 0.2$  nm for nc-AFM carried out with a stiff probe), we therefore  
30 estimate a ligand layer thickness of about 6 -8 Å. This value is smaller than the length of the  
31 individual ligand molecules in vacuum, which indicates the relaxation of ligands, as shown in  
32 previous work on semiconducting and metallic NCs<sup>32,33</sup>.

33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48 *Quantitative KPFM analysis of n-type (Cu) doped NCs.* We now focus on the quantitative analysis  
49 of the doped NC KPFM signals, starting with n-type (Cu) doped NCs. Raw NC KPFM signals are  
50 plotted in Figure 3a as a function of the NC corrected height, and show a gradual decrease of  
51 KPFM signals with reduced NC sizes. This feature is a priori counterintuitive—an enhancement of  
52  
53  
54  
55  
56  
57  
58  
59  
60



1  
2  $\Delta\chi$  with the NC quantum confinement would rather be expected in the picture of Figure 1. A  
3 straightforward explanation however comes from side-capacitance effects known to take place in  
4 KPFM experiments<sup>34</sup>, which lead to an averaging between the actual NC electrostatic potential  
5 and the substrate surface potential. The averaging process highly depends on the NC size, but also  
6 on the tip oscillation, as well as on the choice of the FM or AM KPFM imaging mode. KPFM  
7 signals can however be deconvoluted from side-capacitance effects using numerical simulations<sup>22</sup>  
8 (see Methods and Supporting Information Figure S6). Since the modelling is purely electrostatic,  
9 a NC dielectric description is used, based on measured values for the NC core and ligand thickness  
10 previously determined from nc-AFM and TEM experiments. A core charge model is used in order  
11 to describe the ionized dopants<sup>22</sup>, in which an effective charge  $Q_{\text{core}}$  is located at the NC center.  
12 Such a model is effective, and meant to account for the surface dipole generated by the ionized  
13 NC on the substrate, and, in practice, to derive the ionized NC electrostatic potential  $V_{\text{nc}}$  from  
14 experimental data. The actual amount of charge carried by the NC will however depend on the  
15 actual ionized dopant distribution within the NC, which may form a depleted junction at the NC-  
16 substrate interface in the partial ionization regime<sup>24</sup>. The core charge model is however well  
17 adapted in the full depletion regime, even though the dipole generated by the NC ionized charge  
18 (and thus the corresponding KPFM signal) still depends on the exact charge location within the  
19 NC in the few dopant limit. Hence, the experimental KPFM signal of a NC carrying a single  
20 ionized dopant will be “viewed” in the core charge analysis as a NC with a core charge  $Q_{\text{core}}$  in the  
21 0-2e range, depending on the dopant location, *i.e.* with the dopant located at the NC-substrate  
22 interface, or located at the NC top.  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60



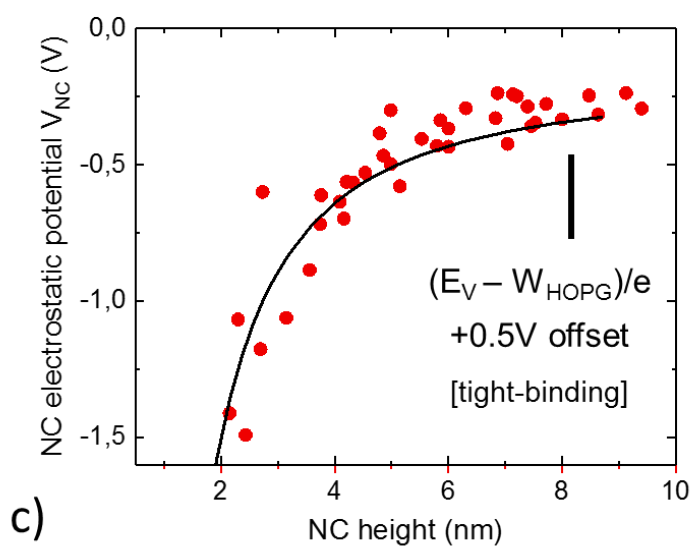
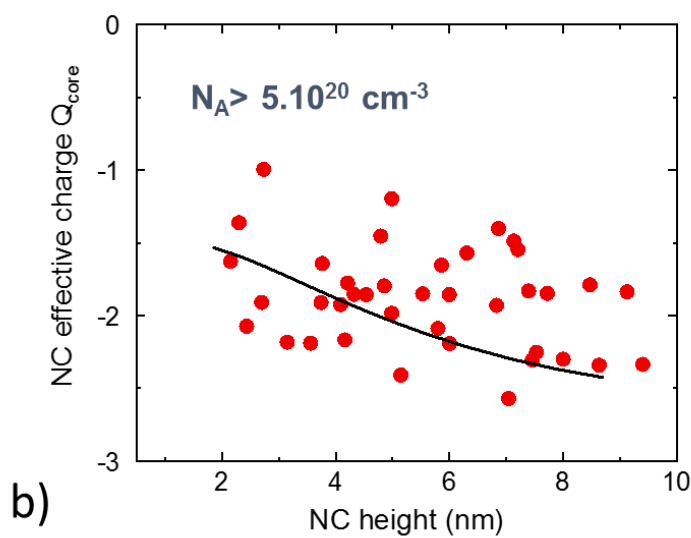
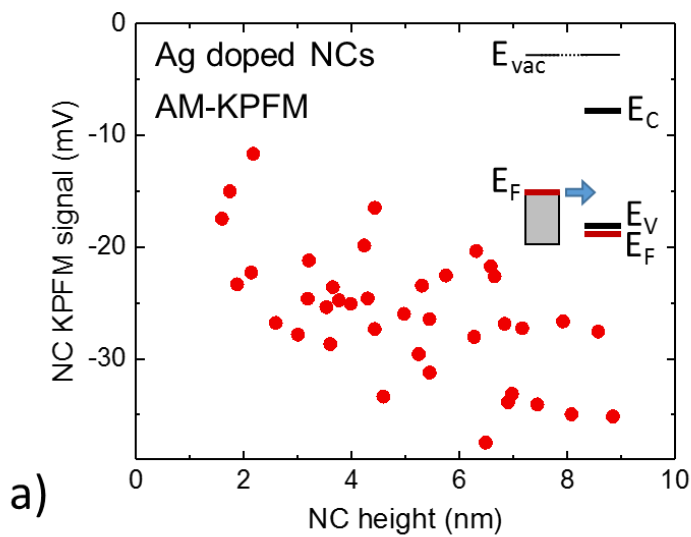
1  
2 Figure 3: a) FM-KPFM contrast of individual n-type (Cu) doped NCs plotted as a function of their corrected  
3 height. The inset shows the energy diagram prior to charge transfer. b) NC effective core charge calculated  
4 from a). The blue continuous line is a fit to data in the full depletion regime, leading to a doping  
5 concentration  $N_D=8.10^{20} \text{ cm}^{-3}$  (see text). The black continuous line corresponds to the line fitted in c). The  
6 core charge values of smallest NCs (highlighted points) correspond to the single ionized dopant limit. c)  
7 NC electrostatic potential calculated from a). The black continuous line describes, as a guide to the eye, the  
8 evolution of the NC conduction band  $E_c$  with respect to the HOPG Fermi level for undoped NCs, with a  
9 phenomenological 0.5 eV offset (see text). The blue continuous lines corresponds to the line fitted in b).  
10 The sharp potential drop at small NC size is attributed to the crossover towards the full depletion.  
11  
12

13  
14  
15  
16  
17  
18  
19  
20  
21  
22 The NC core charge  $Q_{\text{core}}$  and the electrostatic potential  $V_{\text{NC}}$  extracted from raw KPFM signals are  
23 shown in Figure 3b and 3c, respectively. No adjustable parameter was introduced in the analysis.  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
The NC electrostatic potential is increased as the NC size is reduced (black continuous line in  
Figure 3c), which corresponds to an enhancement of the Fermi-level mismatch between the doped  
NCs and the reference HOPG substrate. A first explanation stems from quantum confinement  
effects, which push towards higher energy the onset of the conduction band levels for undoped  
NCs. Assuming in a naïve view that the NC Fermi level follows the conduction band of the  
undoped NCs due to degenerate doping, this provides a tentative prediction of the Fermi-level  
mismatch between the doped NCs and the reference HOPG substrate. This effect is represented by  
the black line in Figure 3c as a guide to the eye from the tight-binding calculation of undoped InAs  
NC conduction band levels<sup>29</sup>, introducing an electrostatic potential offset of 0.5 eV. However,  
other effects such as band filling or tailing<sup>11</sup>, or electrostatic effects at the NC-ligand interface have  
to be considered. They will be discussed in the following, based on tight-binding calculations for  
doped NCs, and will discard the simple quantum confinement picture taken at this stage.

1  
2 A striking effect occurs additionally at smallest NC size (typically below 2 nm), with the  
3  
4 observation of a sharp decrease in the NC electrostatic potential  $V_{\text{NC}}$ . We attribute this transition  
5  
6 to the crossover between the partial ionization and full depletion regimes described in Figure 2. In  
7  
8 the full depletion regime, the NC electrostatic potential  $V_{\text{NC}}$  is equal to the product of the NC  
9  
10 average charge and of the electrostatic potential of a NC carrying an elementary charge (see  
11  
12 Supporting Information Figure S6). We use this property to estimate the NC doping from a fit of  
13  
14 the electrostatic data of Figure 3b and 3c at small NC size, taking as a rough approximation a  
15  
16 continuous charge model as a function of the NC size. The values of  $V_{\text{NC}}$  at small NC size are well  
17  
18 accounted for using an active dopant concentration  $N_{\text{D}} \sim 8 \cdot 10^{20} \text{ cm}^{-3}$  (blue line in Figure 3b). The  
19  
20 agreement is further supported by examining the NC effective core charge in Figure 3b. At small  
21  
22 NC size, the NC core charge  $Q_{\text{core}}$  falls in the range 0-2e, as expected for NCs carrying single  
23  
24 ionized dopants. In particular, for NC sizes around 2 nm, the  $Q_{\text{core}}$  values correspond to elementary  
25  
26 charges (see highlighted points). The agreement is even more striking that no adjustable parameter  
27  
28 has been used in the simulations. A comparative analysis of n-type (Cu) doped and (reference)  
29  
30 intrinsic InAs NCs is additionally provided in Figure S7 in the Supporting Information.  
31  
32  
33  
34  
35

36  
37  
38 *Quantitative KPFM analysis of p-type (Ag) doped NCs.* We now switch to the case of p-type (Ag)  
39  
40 doped NCs. Care has to be taken because of the finite solubility limit of Ag in InAs. Ag atoms  
41  
42 indeed incorporate as dopants at the NC surface in the so-called “doping regime”, but also tend to  
43  
44 form surface clusters in the “growth region” beyond the solubility limit<sup>16</sup>. The number of Ag  
45  
46 dopants introduced in NCs in the doping regime also stays at most constant as a function of the  
47  
48 NC size<sup>16</sup>. This would correspond to a strong reduction of the doping concentration  $N_{\text{A}}$  with  
49  
50 increased NC size, but this effect is a priori “transparent” in KPFM experiments, provided the NCs  
51  
52 contain enough dopants to ensure an equilibrium in the partial ionization regime, as in Figure 2a.  
53  
54  
55  
56  
57  
58  
59  
60

1  
2 We applied to p-type (Ag) doped NCs the same analysis of experimental data as for n-type (Cu)  
3 doped NCs, however keeping in mind that an estimation of the NC doping level  $N_A$  should only  
4 be valid for NCs with smallest sizes, and not through the full NC size range. Experimental KPFM  
5 signals for p-type (Ag) doped NCs are shown in Figure 4a. Data have been here recorded in the  
6 amplitude modulation (AM) KPFM mode. The NC electrostatic potential is shown in Figure 4c,  
7 and has been derived from data from Figure 4a by taking into account an additional side  
8 capacitance effect associated with the cantilever itself in the AM-KPFM mode<sup>22,34</sup>, (capacitance  
9 gradient of  $2.4 \cdot 10^{-11}$  F/m for the cantilevers used in this work, as determined from a numerical  
10 simulation). This contribution was included in the formalism of Ref.<sup>22</sup>, in order to calculate the  
11 values of  $V_{NC}$  and  $Q_{core}$  from raw AM-KPFM data. As seen in Figure 4c, the NC electrostatic  
12 potential is enhanced while reducing the NC size. The values for the mismatch between the NC  
13 valence band  $E_V$  and the HOPG substrate Fermi level for undoped NCs are also shown as a guide  
14 to the eye (continuous black line) as derived from tight-binding calculations for undoped NCs<sup>29</sup>.  
15 This includes a phenomenological electrostatic offset of +0.5 V, as in the case of Cu-doped NCs.  
16 The main difference with n-type NCs is that no sharp decrease in the values of  $V_{NC}$  is observed at  
17 small NC size, indicating that the full depletion regime is not reached for p-type doped NCs. This  
18 point agrees with the values for the effective core charge  $Q_{core}$  shown (Figure 4b) which do not  
19 clearly fall in the  $[0-2e]$  range as for n-type doped NCs in Figure 3b. The apparent absence of a  
20 cross-over towards a full depletion regime for p-type (Ag) doped NCs may be due a larger acceptor  
21 density as compared to the n-type (Cu) doped NC samples, or potentially due to double acceptor  
22 configuration for Ag dopants in InAs, as originally put forward in substitutional doping scenario<sup>11</sup>.  
23 Only a minimum doping level  $N_A > \sim 5 \cdot 10^{20} - 10^{21} \text{ cm}^{-3}$  can therefore be estimated from the KPFM  
24 analysis of Figure 4b.  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60



1  
2 Figure 4: a) Experimental AM-KPFM contrast of individual p-type (Ag) doped NCs plotted as a function  
3 of the NC corrected height. The inset schematics shows the energy diagram prior to charge transfer. b) NC  
4 effective core charge  $Q_{\text{core}}$  calculated from data plotted in a). The black continuous line corresponds to the  
5 model used in c). A dopant concentration  $N_A > 5 \cdot 10^{20} \text{ cm}^{-3}$  can be estimated from the ionization charge of  
6 NCs with smallest sizes (see text). c) NC electrostatic potential calculated from data shown in a). The black  
7 line describes the evolution of the NC valence band  $E_V$  with respect to the HOPG Fermi level upon quantum  
8 confinement for undoped NCs (see text). A phenomenological 0.5 eV offset is introduced as in Figure 3.

9  
10  
11  
12  
13  
14  
15  
16  
17  
18 *Comparison with tight-binding calculations of n-type doped NCs.* We now focus on the  
19 comparison between experimental results and tight-binding calculations of doped InAs NCs. p-  
20 type (Ag) doped NCs are discarded from the analysis due to their specific structural doping issues  
21 (surface doping and dopant clustering)<sup>16</sup>. We only deal with n-type (Cu) doped InAs NCs, for  
22 which interstitial hydrogenoid dopants randomly distributed in the NC volume are considered (see  
23 Methods). The effect of dopants on the electronic structure of InAs NCs is illustrated in Figure 5a  
24 and b for an InAs NC with an InAs core effective diameter of about 2.4 nm either undoped (Figure  
25 5a), or doped with four dopants (Figure 5b, dopant concentration  $N_D \sim 6 \cdot 10^{20} \text{ cm}^{-3}$ ). The reference  
26 for energies in Figure 5a and b corresponds to the valence band of bulk InAs. As described in  
27 Ref.<sup>11</sup>, the introduction of dopants generates electronic states below the conduction levels of  
28 undoped NCs, *i.e.* band tailing, this effect being balanced by the population of the conduction  
29 electronic states, *i.e.* band-filling. Here, due to spin degeneracy, two electronic levels are populated  
30 while four NC dopants have been introduced. The NC Fermi-level is indicated in red in Figure 5b.  
31 It has an energy close to – but below – the first conduction level of the undoped NC in Figure 5a.  
32 This observation already breaks the simple picture used in the simplified energy diagrams of  
33 Figure 1 and Figure 2, although the donor concentration (here,  $N_D \sim 6 \cdot 10^{20} \text{ cm}^{-3}$ ) is by far beyond  
34 the degenerate limit for bulk InAs, of conduction band effective density of states  $N_C < 10^{17} \text{ cm}^{-3}$ .

1  
2 Another change in the electronic structure stems from the ionization process when the NCs are not  
3 considered in vacuum (as in Figure 5a and b), but rather brought in contact with an electron  
4 reservoir, as experimentally achieved in KPFM experiments. Removing an electron from a NC in  
5 a charge transfer process indeed changes the NC energy level filling, but it also introduces an  
6 additional electrostatic potential energy, which alters in return the NC electronic level structure.  
7 In order to describe this issue, the tight-binding calculations for doped NCs have been inserted in  
8 a self-consistent calculation ensuring the NC equilibrium with a metal substrate positioned  $3.5 \text{ \AA}$   
9 below the NC (this distance corresponds to the effective ligand thickness as determined from  
10 experiments). In this process, a NC gets ionized until its Fermi level equilibrates with the substrate  
11 reference Fermi level. The electronic structure of the doped NC used in Figure 5b is shown in  
12 Figure 5c, when brought in equilibrium with the substrate (an electrostatic offset of  $+0.75 \text{ eV}$  has  
13 been introduced here). The energy reference in Figure 5c is the Fermi level of the metal substrate.  
14 In this example, the ionization charge carried by the NC is  $\sim +2e$ , as illustrated by the Fermi level  
15 which accounts for the filling of only one NC conduction level, as compared to the two populated  
16 levels in Figure 5b prior to charge transfer. The change in the NC electronic structure upon charge  
17 transfer is also visible, for instance from the energies of the first confined conduction band levels,  
18 or from the NC apparent band-gap. This point attests to the need for a self-consistent approach to  
19 calculate the electronic structure of doped NCs for the interpretation of KPFM experiments.  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43

44 We show in Figure 5 the results of the self-consistent tight binding calculations for the NC  
45 electrostatic potential (Figure 5d) and for the NC ionization charge (Figure 5e). Expected charge  
46 transfers are first predicted using nominal parameters for the electronic structure of InAs  
47 nanocrystals (using a  $4.9 \text{ eV}$  affinity value for bulk InAs) in equilibrium with the HOPG substrate  
48 (with work function  $\chi_{\text{HOPG}} = 4.5 \text{ eV}$ ).  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60



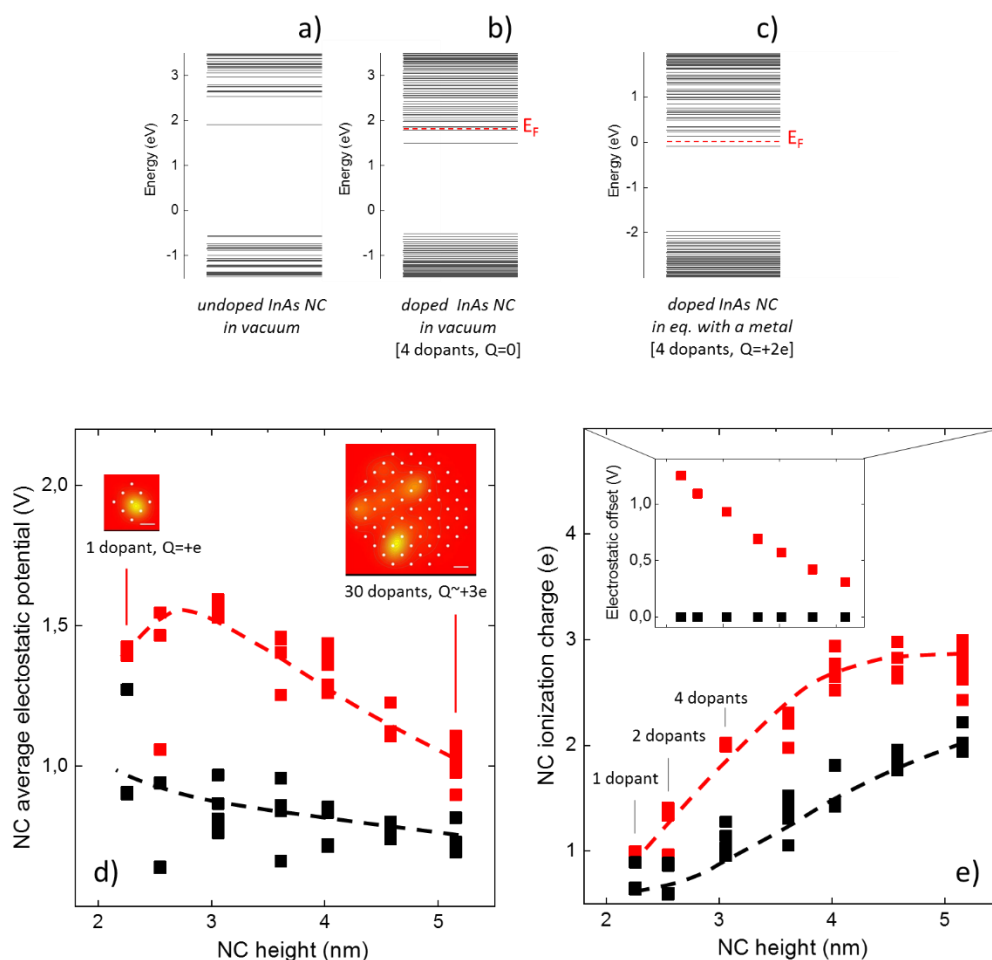


Figure 5: Tight-binding calculation of the electronic levels of an InAs NC with core diameter of about 2.4 nm (NC height of about 3.1 nm, including ligands) either a) undoped or b) doped with four hydrogenoid dopants ( $N_D=6 \cdot 10^{20} \text{ cm}^{-3}$ ). The reference for energies in a) and b) is the onset of the valence band of bulk InAs. c) Same calculation as in b) except that the NC is brought in equilibrium with a metal substrate (taken here as a reference for energies), and the NC electronic structure is calculated self-consistently. Here, the NC carries an ionization charge of  $\sim +2e$  (two electrons have been transferred to the metal substrate). The Fermi levels are indicated in b) and c) by a dashed red line. d) Calculated NC electrostatic potential and e) calculated NC ionization charge plotted as a function of the NC height. Black points refer to nominal self-consistent tight binding calculations, while red points additionally include the electrostatic offset shown in the inset of e) (see text). The inset in d) corresponds to cross sections of the ionized NC electrostatic potential maps for two NCs.

1  
2  
3 Calculation results (black points in Figure 5d and 5e) reveal weaker charge transfers than  
4 experimentally observed. This is obvious (i) from the values of the average NC electrostatic  
5 potential, which are much weaker in Figure 5d (black points) than values shown in Figure 3c; and  
6  
7 (ii) from the fact that the full depletion regime is *not* reached for NCs with smaller sizes in Figure  
8  
9 5e (black points), as compared with the experimental results shown in Figure 3b. Charge transfers  
10  
11 therefore appear to be experimentally higher than theoretical predictions. To account for this, we  
12  
13 introduce in the calculations an electrostatic contribution to the NC electrostatic potential as a  
14  
15 phenomenological supplementary parameter. This contribution is introduced as a rigid shift of the  
16  
17 NC energy levels prior to the self-consistent procedure. It is equivalent in its principle to the +0.5  
18  
19 V electrostatic offset used in the analysis of the electrostatic potential of ionized NCs in Figure 3  
20  
21 and 4, except that the offset is now introduced in the self-consistent tight-binding calculations  
22  
23 developed for *doped* NCs. We speculate that the offset originates in the electrostatics of the NC-  
24  
25 ligand interface, which has been discarded so far in our analysis. This hypothesis agrees with the  
26  
27 fact that excess ligands deposited on the HOPG surface exhibit electrostatic features in KPFM  
28  
29 images (Figure 1c), which is consistent with a dipolar character. Assuming an interface dipole of  
30  
31 magnitude  $\sim 1$  Debye per ligand, a 0.5 V electrostatic offset is reached for a surface ligand density  
32  
33 of a few  $\text{nm}^{-2}$ , which is a typical value for ligand densities<sup>33, 35, 36</sup>. This corresponds to a dipole  
34  
35 density of  $\sim 0.2$  C/m (here, with dipoles oriented towards the outside of the NCs). We show in  
36  
37 Figure 5d and Figure 5e the results of self-consistent tight-binding calculations for doped InAs  
38  
39 NCs, introducing the size dependent electrostatic offset shown in the inset of Figure 5e (red points).  
40  
41 The offset has been chosen to reproduce the experimental enhancement of the NC electrostatic  
42  
43 potential with reduced NC sizes observed in Figure 3b. An illustration of the NC ionized dopant  
44  
45 distribution is shown in the inset of Figure 5d for two NCs, revealing the distribution of ionized  
46  
47 dopants in the NCs. The NC average electrostatic potential derived from the self-consistent tight-  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

1  
2 binding calculations is shown in Figure 5d (red points) and now reproduces data of Figure 3b,  
3  
4 when taking into account the electrostatic offset. It exhibits, as in Figure 3c, a drop at smallest NC  
5  
6 size, which suggests that a full ionization regime is achieved, as in Figure 3. This is confirmed by  
7  
8 the plot of the NC ionization charge shown in Figure 5e (red points), showing that smallest NCs -  
9  
10 which carry single dopants - also carry a +1e ionization charge, and are thus in the full ionization  
11  
12 limit. The introduction of a size-dependent electrostatic offset therefore enables a full agreement  
13  
14 with the experimental data. Its dependence on the NC size can be attributed to the increase of the  
15  
16 ligand surface densities at small NC size. This effect has already been put forward in the case of  
17  
18 gold NCs<sup>35</sup> and more recently in the case of semiconductor NCs<sup>36</sup> and originates in a favored steric  
19  
20 configuration and/or enhanced defect ratios at small NC radii. Such an enhancement reaches a  
21  
22 factor 3 for Au NCs<sup>35</sup> in a size range similar to our work. This enhancement of ligand densities  
23  
24 agrees with the values for the electrostatic potential offset introduced in the calculations and shown  
25  
26 in Figure 5e (inset), ranging from ~ 0.3V at large NC size, and reaching ~ 1 V for the smallest NC  
27  
28 size. Our analysis therefore highlights the impact of the electrostatic properties of the ligands onto  
29  
30 the electronic properties of doped NCs, an effect which has not been studied in detail thus far.  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40

## 41 CONCLUSION

42  
43  
44 In conclusion, we have investigated the doping properties of n- and p-type InAs colloidal  
45  
46 nanocrystals from KPFM experiments operated in ultra-high vacuum with single charge sensitivity  
47  
48 at room temperature. The analysis of charge transfers from doped NCs to the HOPG substrate has  
49  
50 been carefully achieved in the 2-8 nm size range. We have shown evidence of a full ionization  
51  
52 regime for the smallest NCs in the case of n-type doped NCs and measured the NC active dopant  
53  
54 concentration (here,  $N_D = 8.10^{20} \text{ cm}^{-3}$  and  $N_A > 5.10^{20} \text{ cm}^{-3}$  for n- and p-type doping, respectively).  
55  
56  
57  
58  
59  
60

1  
2 A self-consistent tight-binding analysis of the InAs NC electronic structure has been proposed and  
3 compared with experiments. It shows that an electrostatic contribution is required in order to match  
4 with experimental data, which we attribute to dipolar effects at the NC-ligand interface. The  
5 estimated surface dipole density equals a few Debye/nm<sup>2</sup> (with a dipole oriented toward the outside  
6 of the NCs). This dipolar effect increases at small NC sizes, which follows the enhancement of  
7 ligand densities at small NC sizes reported for metallic or semiconducting NCs. Our results put  
8 forward the role played by the NC-ligand interface with respect to electronic applications.  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22

## 23 AUTHOR INFORMATION

### 24 25 **Corresponding Author**

26  
27 [thierry.melin@iemn.fr](mailto:thierry.melin@iemn.fr)  
28  
29  
30

### 31 **Author Contributions**

32  
33 The manuscript was written through contributions of all authors. All authors have given approval  
34 to the final version of the manuscript.  
35  
36  
37  
38  
39  
40  
41  
42

## 43 SUPPORTING INFORMATION

44  
45  
46 Figure S1: Excess ligand layer ordering upon sample annealing.  
47  
48

49 Figure S2: Nanocrystal KPFM signals before and after thermal annealing.  
50  
51

52 Figure S3: nc-AFM sample topography with and without KPFM signal regulation.  
53  
54

55 Figure S4: Comparative NC size distributions in optical-beam / stiff-probe AFM and TEM.  
56  
57  
58  
59  
60

1  
2 Figure S5: Relationship between the NC heights measured at small and large frequency shift  
3  
4 detuning  $\Delta f$ .  
5  
6

7  
8 Figure S6: Calculated electrostatic potential  $V_{\text{NC}}$  and KPFM signals  $V_{\text{KPFM}}$  for a NC carrying a  
9  
10 single charge.  
11  
12

13  
14 Figure S7: Undoped InAs NC analysis  
15  
16  
17  
18  
19

## 20 ACKNOWLEDGMENT

21  
22

23 This work has been performed by using the facilities of the French RENATECH network and of  
24 the ExCELSiOR Nanoscience Characterization Center at IEMN. We thank H. Diesinger for  
25 support with Kelvin probe microscopy experiments, and D. Guérin for fruitful discussions, and A.  
26 Dufrière for illustrations. We acknowledge financial support from the French National Research  
27 Agency under contracts ANR-11-BS10-000, ANR-15-CE09-0004-04 and ANR-13-BS09-0020.  
28  
29  
30  
31  
32  
33  
34  
35

## 36 ABBREVIATIONS

37  
38  
39

40 NC, nanocrystal; AFM, atomic force microscopy; DDA/DCAB, dedecylamine / didodecyl-  
41 dimethylammonium; HOPG, highly-oriented pyrolytic graphite; UHV, ultra-high vacuum ; AM,  
42 amplitude modulation; FM, frequency modulation; nc-AFM, non-contact AFM; KPFM, Kelvin  
43 Probe Force Microscopy; TEM, Transmission Electron Microscopy; STS, scanning tunneling  
44 spectroscopy.  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

## REFERENCES

- (1) *see e.g.* Norris, D.J.; Efros, A.L.; Erwin, S.C. Doped Nanocrystals, *Science* **2008**, *319*, 1776.
- (2) *for a recent review, see* Pradhan, N.; Adhikari, S. D., Nag, A., Sarma, D. D. Luminescence, Plasmonic, and Magnetic Properties of Doped Semiconductor Nanocrystals, *Angew. Chem. Int. Ed.* **2017**, *56*, 7038–7054.
- (3) Gur, I., Fromer, N. A.; Geier, M. L.; Alivisatos, A. P. Air-Stable All-Inorganic Nanocrystal Solar Cells Processed from Solution, *Science* **2005**, *310*, 462.
- (4) Wang, T.; Radovanovic, P.V. Free Electron Concentration in Colloidal Indium Tin Oxide Nanocrystals Determined by Their Size and Structure, *J. Phys. Chem. C* **2011**, *115*, 406–413.
- (5) Buonsanti, R. ; Llordes, A.; Aloni, S.; Helms, B. A.; Milliron, D. J. Tunable Infrared Absorption and Visible Transparency of Colloidal Aluminum-Doped Zinc Oxide Nanocrystals, *Nano Lett.* **2011**, *11*, 4706–4710.
- (6) Rowe, D. J.; Jeong, J. S.; Hoyan, K. A.; Kortshagen, U. R. Phosphorus-Doped Silicon Nanocrystals Exhibiting Mid-Infrared Localized Surface Plasmon Resonance, *Nano Lett.* **2013**, *13*, 1317–133.
- (7) Zhang, H. ; Zhang, R. ; Schramke, K. S. ; Bedford, N. M. ; Hunter, K. ; Kortshagen, U. R. ; Nordlander, P. Doped Silicon Nanocrystal Plasmonics *ACS Photonics* **2017**, *4*, 963–970.
- (8) Pi, X.; Delerue, C. Tight-Binding Calculations of the Optical Response of Optimally P- Doped Si Nanocrystals: A Model for Localized Surface Plasmon Resonance. *Phys. Rev. Lett.* **2013**, *111*, 1–5.
- (9) *see e.g.* Erwin, S. C.; Zu, L.; Haftel, M. I.; Efros, A. L.; Kennedy, T. A.; Norris, D. J. Doping Semiconductor Nanocrystals, *Nature* **2005**, *436*, 91-94.
- (10) Bhargava, R. N.; Gallagher, D.; Hong, X.; Nurmikko, A. Optical properties of manganese-doped nanocrystals of ZnS. *Phys. Rev. Lett.* **1994**, *72*, 416.

1  
2  
3 (11) Mocatta, D.; Cohen, G.; Schattner, J.; Millo O.; Rabani, E.; Banin, U. Heavily Doped  
4 Semiconductor Nanocrystal Quantum Dots. *Science* **2011**, *332*, 77-81.

5  
6  
7 (12) Geyer, S.M.; Allen, P.M.; Chang, L.-Y.; Wong, C.R.; Osedach, T.P.; Zhao, N.; Bulovic, V.;  
8 Bawendi, M.G. Control of the carrier type in InAs Nanocrystal Films by Predeposition  
9 Incorporation of Cd. *ACS Nano* **2010**, *4*, 7373-7378.

10  
11  
12 (13) Dalpian, G. M.; Chelikowsky, J. R. Self-Purification in Semiconductor Nanocrystals. *Phys.*  
13 *Rev. Lett.* **2006**, *96*, 226802-1–226802-4.

14  
15  
16 (14) Sahu, A.; Kang, M. S.; Kompch, A.; Notthoff, C.; Wills, A. W.; Deng, D.; Winterer, M.;  
17 Frisbie, C. D.; Norris, D. J. Electronic Impurity Doping in CdSe Nanocrystals. *Nano Lett.* **2012**,  
18 *12*, 2587–2594.

19  
20  
21 (15) Amit, Y.; Eshet, H.; Faust, A.; Patllola A.; Rabani, E.; Banin, U.; Frenkel, A. Unravelling the  
22 Impurity Location and Binding in Heavily Doped Semiconductor Nanocrystals: The Case of Cu  
23 in InAs Nanocrystals. *J. Phys. Chem. C* **2013**, *117*, 13688-13696.

24  
25  
26 (16) Amit, Y.; Li, Y.; Frenkel, A. I.; Banin, U. From Impurity Doping to Metallic Growth in  
27 Diffusion Doping: Properties and Structure of Silver-Doped InAs Nanocrystals. *ACS Nano* **2015**,  
28 *9*, 10790–10800.

29  
30  
31 (17) Martinez-Martin, D.; Longinhos, R.; Izquierdo, J.G. ; Marele, A.; Alexandre, S.S.; Jaafar,  
32 M. ; Gómez-Rodríguez, J.M.; Bañares, L.; Soler, J.M. ; Gomez-Herrero, J. Atmospheric  
33 contaminants on graphitic surfaces. *Carbon* **2013**, *61*, 33-39.

34  
35  
36 (18) Giessibl, F.J. A direct method to calculate tip-sample forces from frequency shifts in  
37 frequency-modulation atomic force microscopy. *Applied Physics Letters* **2001**, *78*, 123.

38  
39  
40 (19) *see e.g.* Berger, J.; Spadafora, E.J.; Mutombo, P.; Jelínek, P.; Svec, M. Force-Driven Single-  
41 Atom Manipulation on a Low-Reactive Si Surface for Tip Sharpening. *Small* **2015**, *11*, 3686–  
42 3693.

43  
44  
45 (20) *For a review see* Kelvin Probe Force Microscopy. Editors Sascha Sadewasser and Thilo  
46 Glatzel *Springer* **2011**.

- 1  
2  
3 (21) Borowik, Ł.; Kusiaku, K.; Deresmes, D.; Théron, D.; Diesinger, H.; Mélin, T. Mapping  
4 charge transfers between quantum levels using noncontact atomic force microscopy. *Physical*  
5 *Review B* **2010**, *82*, 073302.  
6  
7  
8 (22) Borowik, Ł.; Kusiaku, K.; Théron, D.; Mélin, T. Calculating Kelvin force microscopy signals  
9 from static force fields. *Applied Physics Letters* **2010**, *96*, 103119.  
10  
11  
12 (23) Fuchs, F.; Caffy, F.; Demadrille, R.; Mélin, T.; Grévin, B. High-Resolution Kelvin Probe  
13 Force Microscopy Imaging of Interface Dipoles and Photogenerated Charges in Organic  
14 Donor–Acceptor Photovoltaic Blends. *ACS Nano* **2016**, *10*, 739-746.  
15  
16  
17 (24) Borowik, Ł.; Nguyen-Tran, T.; Roca i Cabarrocas, P.; Mélin, T. Doped semiconductor  
18 nanocrystal junctions. *Journal of Applied Physics* **2013**, *114*, 204305.  
19  
20  
21 (25) Jancu, J.M.; Scholz, R.; Beltram, F.; Bassani, F. Empirical spds\* tight-binding calculation for  
22 cubic semiconductors: General method and material parameters, *Phys. Rev. B* **1998**, *57*, 6493.  
23  
24  
25 (26) Delerue, C.; Lannoo, M., *Nanostructures: Theory and Modelling* (Springer, Berlin, **2004**)  
26  
27  
28 (27) Delerue, C. Minimum Line Width of Surface Plasmon Resonance in Doped ZnO  
29 Nanocrystals, *Nano Lett.* **2017**, *17*, 7599.  
30  
31  
32 (28) Hansen, W. N.; Hansen, G.J. Standard reference surfaces for work function measurements in  
33 air, *Surf. Sci.* **2001**, *481*, 172-184.  
34  
35  
36 (29) Niquet, Y.M.; Delerue, C. ; Lannoo, M. ; Allan, G Single-particle tunneling in semiconductor  
37 quantum dots *Physical Review B* **2001**, *64*, 113305.  
38  
39  
40 (30) Ebenstein, Y; Nahum, E; Banin, U. Tapping Mode Atomic Force Microscopy for  
41 Nanoparticle Sizing: Tip–Sample Interaction Effects. *Nano Letters* **2002**, *9*, 945–950.  
42  
43  
44 (31) Fuchs, F.; Grévin, B.; Bocquet, F.; Nony, L.; Loppacher, C. Correct height measurements by  
45 Kelvin probe force microscopy: Poly(3-dodecylthiophene) on highly oriented pyrolytic graphite.  
46 *Physical Review B* **2013**, *88*, 205423.  
47  
48  
49 (32) Geva, N.; Shepherd, J. J.; Nienhaus, L.; Bawendi, M. G.; Van Voorhis, T. Morphology of  
50 Passivating Organic Ligands around a Nanocrystal, *J. Phys. Chem. C* **2018**, *122*, 45, 26267-26274.  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60



1  
2  
3 (33) Copie, G.; Biaye, M.; Diesinger, H.; Mélin, T.; Krzeminski, C.; Cleri, F. Deformation  
4 Localization in Molecular Layers Constrained between Self-Assembled Au Nanoparticles.  
5 *Langmuir* **2017**, *33*, 2677–2687.  
6  
7

8  
9 (34) Jacobs, H. O.; Leuchtman, P.; Homan, O. J.; Stemmer, A. Resolution and contrast in Kelvin  
10 probe force microscopy, *Journal of Applied Physics* **1998**, *84*, 1168.  
11  
12

13 (35) Hostetler, M.J.; Wingate, J.E.; Zhong, C.J.; Harris, J.E.; Vachet, R.W.; Clark, M.R.; Londono,  
14 J.D.; Green, S.J.; Stokes, J.J.; Wignall, G.D., Glish, G.L.; Porter, M.D.; Evans, N.D.; Murray, R.W.  
15 Alkanethiolate Gold Cluster Molecules with Core Diameters from 1.5 to 5.2 nm: Core and  
16 Monolayer Properties as a Function of Core Size, *Langmuir* **1998**, *14*, 17-30.  
17  
18  
19  
20

21 (36) De Roo, J; Yazdani, N. Drijvers, E. Lauria, A.; Maes, J; Owen, J.S.; Van Driessche, I.;  
22 Niederberger, M.; Wood, V.; Martins, J.C.; Infante, I.; Hens, Z. Probing Solvent–Ligand  
23 Interactions in Colloidal Nanocrystals by the NMR Line Broadening, *Chem. Mater.* **2018**, *30*,  
24 5485–5492.  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

## TOC GRAPHIC

