Intriguing electronic and optical prospects of FCC bimetallic heterostructures: large area interface versus embedded and doped nanostructures

Tuhin Kumar Maji¹, Kumar Vaibhav², Ranjit Hawaldar³, K. V. Adarsh⁴, Samir Kumar Pal¹ and Debjani Karmakar⁵,*

¹Department of Chemical Biological and Macromolecular Sciences, S.N. Bose National Centre for Basics Sciences, Salt Lake, Sector 3, Kolkata 700106, India

²Computer Division, Bhabha Atomic Research Centre, Trombay 400085, India

³Centre for Materials for Electronics Technology, Off Pashan Road, Panchwati, Pune-411008, India

⁴Department of Physics, Indian Institute of Science Education and Research, Bhopal 462066, India

⁵Technical Physics Division, Bhabha Atomic Research Centre, Trombay 400085, India

*Corresponding author:
Debjani Karmakar: debjan@barc.gov.in
Abstract

Room temperature superconductivity and large-area epsilon-near-zero interfaces are long-standing goals of Condensed Matter Physics and Optics. Motivated by the recent advancements of experimental scenario of metallic nanostructures, we have theoretically investigated some bimetallic FCC combinations from first-principles, encompassing a wide range from large-area interface to embedded and doped nanostructures. Here, we propose the prospects of some selective bimetallic nanostructures like Au/Ag and Pt/Pd to exhibit some exotic phenomena. For such 2D doped and embedded nanostructures, non-trivial band-structure and Fermi-surface topology may be emblematic to the presence of instabilities like charge density waves or strong superconducting pairing together with near-zero behavior for both real and imaginary part of the dielectric constant in the optical range. We foresee that, if observed experimentally, such systems may lead to many fascinating physics and applications in many diverse fields ranging from condensed matter physics to optics or even more.

Keywords: Electronic Structure, Superconductivity, Fermi-surface nesting, quantum transport.
Current amelioration on bimetallic nanostructures (NS) [1-4] has instigated lot of activities in multi-revisited phoenix field, superconductivity, with concurrent genesis of controversies. The first and foremost impact of such studies is, to ignite the expectation to accomplish the long-prophesized goal of near-room temperature superconductivity. The theoretical scrutiny towards the experimental behavior have provided quite contrasting perspective towards the observed phenomenon, viz., electron-transfer induced strong perturbation in monovalent matrix possibly leading to granular superconductivity[5], percolative transition of the disjoint components of the NS, leading to a zero-resistive state [6], presence of van-hove singularities due to oxidative reactions[7] or prediction of superconducting $T_C$ calculated for 3D crystals and 2D slabs of Au-Ag alloys in mK range [8].

In this work, with an exhaustive electronic structure calculations and density functional theory (DFT)-coupled quantum transport study of some FCC bimetallic heterostructures, we have highlighted their interesting electronic prospects. Stability of such bimetallic clusters like Au-Ag or Pt-Pd had long since been predicted [9,10]. To emphasize more on the existing experimental scenario, we restrict the main-text investigations only on Au-Ag systems. In the supplementary studies[11], we have predicted another promising FCC combination, Pt-Pd. Other FCC and BCC combinations like Ir-Rh or Mo-W are also investigated without betterment of results. We concentrate on the [111] cleaved metallic surfaces, sharing hexagonal topology for the corresponding Brillouin zone (BZ) for all constructed systems, as is also seen by experimental findings.[2]

We have constructed the [111] cleaved trilayer of Au and Ag and analyzed the electronic band structure for five systems including the parent layers, viz, 1) Ag-111 matrix, 2) Au-111 matrix, 3) large-area interface formed from (1) and (2) having lattice mismatch of 0.12% (Au/Ag-111), 4) Ag-cluster of ~1nm embedded in Au-matrix and 5) Ag-doped Au matrix. System (4), the closest simulation of the experiment[2], where few-atom cluster (~ 1 nm in average diameter) of Ag is embedded in an Au-111 trilayer surface matrix, is a 3D NS system. Since reducing the dimensionality will be beneficial to avoid the complexities due to z-directional dispersion of the calculated Fermi-surfaces, we have studied the 2D system of Au-matrix (system 5), doped centrally with a few Ag atoms. Fig 1 delineates the orbital-projected spin-orbit coupling (SOC) incorporated electronic fatbands for all the five structurally relaxed systems along high-symmetry directions within the hexagonal BZ, as depicted in Fig 2(d). The first column of Fig 1 represents the converged charge densities. Relevant details of the calculations are described in reference [11]. In contrast to the bulk bands, [111] surfaces of both Ag and Au have conceded presence of flat-bands near Fermi-energy ($E_F$) between X-Y, manifesting mostly $p$-$d$ (Fig 1(d)) and $s$-$d$ (Fig 1(e)) hybridized characters respectively. Highly localized electrons in these flat-bands may be responsible for promoting non-Fermi liquid (NFL) nature, as also observed in $p$-typed doped cuprates[23,24]. The filled $4d$ levels of Ag [111] are lying ~ 0.7 eV deeper than the Au-5$d$ levels. In Au/Ag-111 (Fig 1(f) and (g)), electrons from near- $E_F$ Au $s$-$d$ hybridized levels are transferred to the $p$-$d$ hybridized levels of Ag, leading to an upshift for the Au-5$d$ levels between the energy range 0 to -2 eV, earlier empty for system 1 or 2. The nature of charge transfer between Au and Ag will be evident from the Bader charge table [11], mainly pin-pointing towards $p$-type doping for Au. Near – $E_F$ bands are mostly $p$-$d$ hybridized for both Ag and Au and the system, being devoid of localized flat-bands due to inter-layer electron transfer,
may regain the Fermi-liquid (FL) nature of Au or Ag. Loss of NFL nature is an indication of lacking correlated electron behavior, as seen experimentally for large-area interfaces[25]. The flatness of bands is retrieved back for the embedded NS, as is evident by comparing the energy scales of first two and last two band columns of Fig 1. With the flat-bands near $E_F$ from X to Y, possessing all three orbital characters, the system loses the inherent symmetry of the band-structure, as existing in system 1-3. Fig S4 [11] displays the PDOS of systems 3 and 4, indicating that for both of them, the partially-filled Au-5$d$ levels have the most contribution at $E_F$. The symmetric band-dispersion can be recovered along with the NFL nature for system (5) (Fig 1(j) and 1(k)), where the 4$d$ and 5$d$ derived carriers are highly localized from $\Gamma$-X and $\Gamma$-Y. Interestingly, the band-topology within X-Y, having s-p hybridized levels, exhibits almost linear dispersion with approximate electron-hole symmetry near $E_F$. The band-structure clearly indicates the possibility of minute fluctuation or perturbation to be capable of opening up a gap.

Figure 1: (color online) Converged charge densities of a) Au/Ag-111, b) Embedded, c) Ag-doped Au systems. The orbital projected fatbands for d) Ag-111 e) Au-111, orbital projection of f) Ag in Au/Ag-111 system, g) Au in Au/Ag-111 system, h) Ag in Embedded system and i) Au in Embedded system, j) Ag in Ag-doped Au system and k) Au in Ag-doped Au system with the respective orbital characters denoted in figure.

The interdependence of Fermi-surface nesting (FSN) and presence of charge/spin-density waves (CDW/SDW) in metals have originated from Peierl’s formulation of instability for 1D periodic
half-filled system[26]. Presence of instabilities like CDW/SDW conceives new periodicity within an electronic system either compatible (commensurate) or incompatible (incommensurate) with the lattice periodicity[27]. In presence of any perturbation from ground state[28], the occupied ($k$) and unoccupied ($k'$) electronic levels interact to generate a superposed density wave of periodicity defined by $q.R$, where $q = k-k'$ and $R$ represents direct lattice position. While doubly occupied density wave orbitals represents CDW, an SDW constitute orbitals, singly-occupied with different spin states. In presence of a FSN, the levels corresponding to electron (occupied) and hole (unoccupied) pockets connected by $q$ are almost degenerate for all $k$ near a FS sheet. For metallic systems with reduced dimensionality, a nested FS poses an indication to the presence of CDW/SDW, whereby the nested portions of FS are removed by opening a gap. A recent reclassification[29-31] of CDW implies that for type I CDW, purely electronic FSN can be the origin of CDW and lattice distortion can be generated as an after-effect. For type II, CDWs are driven by electron-phonon coupling (EPC). To obtain the FSN-driven CDW, reduced dimensionality is an essential criterion to generate a perfectly diverging response function. For such systems, whenever symmetry is broken macroscopically by doping or other means, the FS undergoes a reconstruction forming electron and hole pockets, embodying closed orbits for quasiparticles[32].

In addition to CDW/SDW, there are contradicting studies about the FSN to be sole responsible for generating spin/orbital fluctuation-induced unconventional superconducting pairing in Fe-pnictides[33-35].

![Figure 2](image_url) (color online) Merged Fermi Surface sheets corresponding to all bands crossing $E_F$ for a) Au/Ag-111 b) Embedded, c) Ag-doped Au systems within the hexagonal BZ. The rhombus represents the unit cell in the reciprocal lattice, d) Hexagonal BZ with high-symmetry directions.

Reliance of perfection of nesting on the superconducting pairing strength [36] has motivated the analysis of FS topology for systems (3), (4) and (5). The resultant FS, for all these three cases, is complicated and composed of several individual sheets containing the electron and hole pockets,
as shown in reference [11]. Fig 2 depicts the 2D projection of the merged FS sheets within the BZ for all three cases, whereas the top superposed rhombus represents a single FS sheet within the \(k\)-space unit cell. The tip of the rhombus within the BZ designates the \(\Gamma\)-point. In Fig 2(a), for Au/Ag-111, the \(\Gamma\)-centred hole pocket nests partially to the small electron pockets at the corner of the BZ with \(q\) (yellow arrow). There is another incomplete nesting designated by \(q'\) towards some of the mid-sides of the BZ (red arrow). Partial nesting and electron-hole asymmetry leads to the inequality of size/shape of electron and hole pockets and also connote its lacking potential for CDW or superconducting pairing. For the embedded system (Fig 2(b)), FSN is more complicated due to the \(z\)-directional dispersion of the sheets. Near \(\Gamma\), two merged hole pockets nests with electron pockets at the mid-side (\(q'\)) with few FSN to the corner electron pockets (\(q\)). In Fig 2(c), due to the near-2D nature of the doped system, the \(\Gamma\)-centred hole pocket nests with all the electron pockets situated at the corners (\(q\)) and at the mid-sides (\(q'\)). The reconstruction of FS and nesting-like features suggests that system 4 and 5 may be promising solitcants for CDW/unconventional superconductivity. In [11], we have found similar nesting behavior of the Pt/Pd doped and large area systems. However, in all these systems, the FSN is incommensurate in nature. Since size of the carrier pockets will be highly dictated by the near-\(E_F\) band and FS topology, which in turn is subtly coupled with the interfacial structure of the system, reproducing systems with similar electronic response will be difficult.

**Figure 3:** (color online) Real (\(\varepsilon_1\)) and imaginary (\(\varepsilon_2\)) parts of dielectric constant (\(\varepsilon\)) and refractive index plot for different systems.

Calculation of complex dielectric function (\(\varepsilon\)) and henceforth derived optical attributes provides an overview of the alluring electronic behavior of the system. For bosonic model of superconductivity [33,37], having the coupling parameter \(\lambda\) corresponding to any boson field, the superconducting \(T_c \sim 1.14 \theta_D \exp[-1/N(0)V]\), where the monotonic increase of \(T_c\) for materials with high Debye frequency (\(\theta_D\)) is balanced by the saturation of the screened coulomb repulsion (\(\mu\)). To obtain high \(T_c\) and to satisfy \(\lambda > \mu\) from the relation, \(\mu - \lambda = N(0) \int dq \left( \frac{4\pi e^2}{q^2 \varepsilon(q,0)} \right) = N(0)V\), with \(N(0)\) being DOS at \(E_F\) and \(V\) is the average coulomb repulsion, \(\varepsilon(q,0)\) should be
negative [37]. In other words, when the real part of dielectric function is negative, the attractive
coulomb interaction (V) between the electron pairs can lead to an exponential increase of T_c, if
other instabilities are arrested[38,39]. This simple scenario, although gets disturbed with the
simplest possible instability, provides ideas about the potential optical parameters. The
calculated real (ε_1) and imaginary (ε_2) parts of ε are presented in Fig 3, along with their
respective refractive indices, which clearly indicate the fascinating optical potential of the
systems 4 and 5. For both of these systems, the x and y components of ε_1 acquire a negative
value between 0-1 eV. Beyond 1eV, both ε_1, ε_2 and thereby calculated refractive index undergo
a transition to a minuscule value after a zero-energy near-divergence, revealing their propitious
usage in the field of non-linear optics, where a gigantic search for epsilon near-zero (ENZ)
materials is underway [40,41]. These systems may have a large non-linear refractive index and
thus may be used for optical switching. The near-perpendicular exit of transmitted light also
prompts their use as optical interconnectors. Due to their 2D nature, the z-component remains
always negligible. For the Pt/Pd system, as presented in [11], negative and ENZ values are
plausible for both large-area interfaces and doped systems.

Figure 4: (color online) a) Comparative I-V characteristics for I) Au channel with Ag contact and II) Ag
channel with Au contact, b) 1-D projected LDOS for device I and II and c) 3D coloured plot for
LDOS of device I and d) device II.
The resistivity measurements of reference[1,2], have persuaded the reconnaissance of the room-temperature DFT-coupled quantum transport behavior of the simplest possible device geometry, where the trilayer surface of Au(Ag) will constitute a channel with lateral contacts of Ag(Au) [11]. We designate them as I) Au channel with Ag contact and II) Ag channel with Au contact. In Fig 4(a), the I-V transport characteristics are plotted, implying that the absolute current value will be higher for the device II with a maximum bias of upto 2V across the contacts. More details of transport behavior could be seen from Fig 4(b), where we plot the 2D projection of the local DOS (LDOS) in the b-c plane passing through the center of the device-BZ (Γ point) with respect to the current-transport (c) axis. Comparison of the details of LDOS suggests that device I, displaying more DOS at channel, have lesser interfacial backscattering at the contacts than device II and thus results lesser DOS at contacts. Contribution from the incident and reflected states from the contact-channel interfaces will also be evident from the 3D LDOS plots (Fig 4(c), (d)). The nature of electrical transports will be more elusive from the interpolated transmission contour plots through the central a-b plane (perpendicular to the current transport), passing through the Γ-point for different biases along with the total integrated transmission spectra with respect to energy. For Au-channel (device I), with increasing bias, highly transmitting zone around Γ-point starts depleting, while the edges transmits more (Fig 5(b), (c) and (d)). The integrated transmittance plot with respect to energy (Fig 5(a)) also demonstrates the reduction of total transmission through the central zone with increase in the applied bias. For device II with Ag channel, on the other hand, the transmission color-maps contain more intricacies (Fig 5(f), (g) and (h)). In addition to the depleting central zone, highly transmitting pockets are created over the Γ-centered cross-sectional area of the device.

Figure 5: (color online) Transmittance plot for a) device I (see text) and corresponding interpolated Γ-centered contour plots corresponding to bias voltages b) 0V, c)1V and d) 2V, transmittance plot of e) device II and corresponding interpolated contour plot with respect to bias voltages f) 0V, g)1V and h) 2V.

With increasing bias, the regions with different transmissions are reorganized, keeping the trend of having higher transmission at edges. For highest bias, even the edges contain some low-transmission region. The integrated transmittance plot in Fig 5(e) shows the clear reduction of transmission through the central plane with bias. Therefore, the transport details for the simplest
possible device made out of Au/Ag are far more complicated than anticipated. Experimental NS system \[1-3\] will contain more complexities because of the presence of defects, grain boundaries and different sample morphologies. The interfacial and defect scattering effects will complicate the scenario by many orders.

In conclusion, we have analyzed the electronic and optical attributes of NS and large-area interfaces of the Au-Ag system. The presence of FSN, flat-band induced NFL nature, negative as well as near-zero values of the real part of dielectric constant entails that the NS of such simple bimetallic systems can pose a challenge to both the experimental and theoretical physicists to accomplish a thorough understanding of physics of the observed NS.

Acknowledgements:
T.K.M. wishes to acknowledge the support of DST India for the INSPIRE Research Fellowship and SNBNCBS for funding. We also thank DAE (India) for financial Grant No. 2013/37P/73/BRNS. D.K. would like to acknowledge the BARC ANUPAM supercomputing facility for computational resources, BRNS CRP on Graphene Analogues for support. We also acknowledge discussions with Shouvik Dutta from IISER Pune, Kausik Majumdar from IISC, Bangalore and Kantimay Dasgupta from IIT, Bombay.

Associated Content

Supporting Information
The Supporting Information is available free of charge on the APS Publications website. The supplementary information contains the methodology of the computational calculations and theoretical overview of optical and transport property. It also contains converged spin density, orbital projected density of states, optical properties and individual sheets of Fermi surfaces of different Ag-Au systems. The orbital projected fatband, DOS and Fermi surface of Pt-Pd system is also listed in the supplementary article.
References

[1] S. Islam, R. Mahadevu, S. K. Saha, P. S. Mahapatra, B. Bhattacharyya, D. K. Thapa, T. P. Sai, S. Patil, A. Pandey and A. Ghosh, arXiv preprint arXiv:1906.02291 (2019).
[2] D. K. Thapa, S. Islam, S. K. Saha, P. S. Mahapatra, B. Bhattacharyya, T. P. Sai, R. Mahadevu, S. Patil, A. Ghosh and A. Pandey, arXiv preprint arXiv:1807.08572 (2019).
[3] D. K. Thapa, S. K. Saha, B. Bhattacharyya, G. P. Rajasekar, R. Mahadevu and A. Pandey, arXiv preprint arXiv:1906.05342 (2019).
[4] M. Hooda, P. Kumar, V. Balakrishnan and C. Yadav, arXiv preprint arXiv:1906.00708 (2019).
[5] G. Baskaran, arXiv preprint arXiv:1808.02005 (2018).
[6] D. Pekker and J. Levy, arXiv preprint arXiv:1808.05871 (2018).
[7] S. R. Barman and A. Chakrabarti, arXiv preprint arXiv:1810.01454 (2018).
[8] S. Singh, S. Char and D. L. Prasad, arXiv preprint arXiv:1812.09308 (2018).
[9] H. M. Lee, M. Ge, B. Sahu, P. Tarakeshwar and K. S. Kim, J. Phys. Chem. B 107, 9994 (2003).
[10] V. Ozoliņš, C. Wolverton and A. Zunger, Phys. Rev. B 57, 6427 (1998).
[11] See Supplemental Material at http://link.aps.org/ for the details of computation methods, optical property, DOS and fatband of different Au-Ag and Pt-Pd systems which includes References [12-22].
[12] G. Kresse and J. Furthmüller, .Comput. Mater. Sci6, 15 (1996).
[13] G. Kresse and D. Joubert, Phys. Rev. B 59, 1758 (1999).
[14] J. P. Perdew and Y. Wang, Phys. Rev. B 45, 13244 (1992).
[15] S. Grimme, J. Antony, S. Ehrlich and H. Krieg, J. Chem. Phys. 132, 154104 (2010).
[16] H. J. Monkhorst and J. D. Pack, Phys. Rev. B 13, 5188 (1976).
[17] A. Kokalj, J. Mol. Graph. Model. 17, 176 (1999).
[18] D. R. Smith, S. Schultz, P. Markoš and C. Soukoulis, Phys. Rev. B 65, 195104 (2002).
[19] J. M. Soler, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejón and D. Sánchez-Portal, J. Phys. Condens. Matter. 14, 2745 (2002).
[20] A. M. Hafez, N. M. Salem and N. K. Allam, Phys. Chem. Chem. Phys. 16, 18418 (2014).
[21] www.quantumwise.com.
[22] M. Fox, (Oxford University Press, Oxford, 2001).
[23] D. S. Dessau, Z. X. Shen, D. M. King, D. S. Marshall, L. W. Lombardo, P. H. Dickinson, A. G. Loeser, J. DiCarlo, C. H. Park, A. Kapitulnik and W. E. Spicer, Phys. Rev. Lett. 71, 2781 (1993).
[24] H. Maeda, Y. Tanaka, M. Fukutomi and T. Asano, Jpn. J. Appl. Phys. 27, L209 (1988).
[25] A. Biswas, S. Parmar, A. Jana, R. J. Chaudhary and S. Ogale, arXiv preprint arXiv:1808.10699 (2018).
[26] J.-P. Pouget, C R Phys. 17, 332 (2016).
[27] V. Brouet, W. Yang, X. Zhou, Z. Hussain, N. Ru, K. Shin, I. Fisher and Z. Shen, Phys. Rev. Lett. 93, 126405 (2004).
[28] M.-H. Whangbo, E. Canadell, P. Foury and J.-P. Pouget, Science 252, 96 (1991).
[29] X. Zhu, Y. Cao, J. Zhang, E. Plummer and J. Guo, Proc. Natl. Acad. Sci. 112, 2367 (2015).
[30] S. Dugdale, Phys. Scr. 91, 053009 (2016).
[31] M. D. Johannes and I. I. Mazin, Phys. Rev. B 77, 165135 (2008).
[32] S. Chakravarty and H.-Y. Kee, Proc. Natl. Acad. Sci. 105, 8835 (2008).
[33] M. L. Cohen and P. W. Anderson, AIP Conf. Proc. 4, 17 (1972).
[34] R. Arita and H. Ikeda, J. Phys. Soc. Jpn. 78, 113707 (2009).
[35] M. Sunagawa, T. Ishiga, K. Tsubota, T. Jabuchi, J. Sonoyama, K. Iba, K. Kudo, M. Nohara, K. Ono and H. Kumigashira, Sci. Rep. 4, 4381 (2014).
[36] K. Terashima, Y. Sekiba, J. Bowen, K. Nakayama, T. Kawahara, T. Sato, P. Richard, Y.-M. Xu, L. Li and G. Cao, Proc. Natl. Acad. Sci. 106, 7330 (2009).
[37] M. Gulian, G. Melkonyan and A. Gulian, Phys. Procedia 67, 963 (2015).
[38] C. Chu, F. Chen, J. Shulman, S. Tsui, Y. Xue, W. Wen and P. Sheng, in Strongly Correlated Electron Materials: Physics and Nanoengineering (International Society for Optics and Photonics, 2005), p. 59320X.
[39] O. Dolgov, D. Kirzhnits and E. Maksimov, Rev. Mod. Phys53, 81 (1981).
[40] M. Z. Alam, I. De Leon and R. W. Boyd, Science 352, 795 (2016).
[41] I. Liberal and N. Engheta, Nat. Photonics 11, 264 (2017).
Supplementary Article for

Intriguing electronic and optical prospects of FCC bimetallic heterostructures: large area interface versus embedded and doped nanostructures

Tuhin Kumar Maji\textsuperscript{1}, Kumar Vaibhav\textsuperscript{2}, Ranjit Hawaldar\textsuperscript{3}, K. V. Adarsh\textsuperscript{4}, Samir Kumar Pal\textsuperscript{1} and Debjani Karmakar\textsuperscript{5}\textsuperscript{*}

\textsuperscript{1}Department of Chemical Biological and Macromolecular Sciences, S.N. Bose National Centre for Basics Sciences, Salt Lake, Sector 3, Kolkata 700106, India
\textsuperscript{2}Computer Division, Bhabha Atomic Research Centre, Trombay 400085, India
\textsuperscript{3}Centre for Materials for Electronics Technology, Off Pashan Road, Panchwati, Pune-411008, India
\textsuperscript{4}Department of Physics, Indian Institute of Science Education and Research, Bhopal 462066, India
\textsuperscript{5}Technical Physics Division, Bhabha Atomic Research Centre, Trombay 400085, India

\textsuperscript{*}Corresponding author: Debjani Karmakar: debjan@barc.gov.in

METHODOLOGY:

The geometry optimization and electronic structure calculations of the combined systems are performed using the projector augmented wave (PAW) pseudopotential method as implemented in the Vienna ab initio simulation package (VASP).\cite{1,2} The valence levels for Au and Pt consist of 5d, 6s orbitals and those for Ag and Pd constitute 5s and 4d orbitals. We have used the generalized gradient approximation (GGA) exchange-correlation interactions incorporating spin-orbit coupling with Perdew-Burke-Ernzerhof (PBE) functionals\cite{3} with vdW
corrections after including a semi-empirical dispersion potential to the DFT energy functional as according to the Grimme DFT-D2 method[4]. The cut-off energy for the plane wave expansion is set to 500 eV and an equivalent Monkhorst-Pack $k$-points grid[5] $5\times 5\times 3$ is used for Brillouin zone sampling for all calculations. During optimization calculation, the ionic positions are fully relaxed until the Hellmann-Feynman force on each ion is less than 0.01 eV/Å. Conjugate gradient algorithm has been used for relaxation of ionic position. For the Fermi surface calculations for different systems, we have used a finer grid $7\times 7\times 5$. [6]

The static optical properties and the DFT quantum transport calculations are executed by using the Atomistic Toolkit 15.1 package[7], with the GGA-PBE exchange correlation.[8,9] We have employed the double-zeta plus polarization (SZP) basis set for the device calculation and for expansion of electronic density. During simulation, vdW corrections are taken into account by following DFT-D3 method. For calculation of dielectric functions, a finer $k$-point mesh of 11×11×11 was used with a broadening of 0.1 eV. For geometry optimization, the real-space density mesh cutoff is taken 200 Hartree with the maximum force of 0.01 eV/Å. For quantum transport properties in the two-probe model, DFT coupled nonequilibrium Green’s function (NEGF) method is employed. We have constructed two types of devices, viz., Silver (Ag) channel with Gold (Au) contact and Au channel with Ag contact, as shown in scheme 1. The temperature is set to 300K. On the surfaces connecting the electrodes and the central region, Dirichlet boundary condition has been employed to ensure the charge neutrality in the source and the drain region. The channel length was optimized to ensure zero contributions from the inter-electrode transmissions. The Monkhorst-Pack $k$-point mesh is sampled with $5\times 5\times 50$. The transport properties are studied and the corresponding transmission coefficients are calculated by averaging over a $k_x \times k_y$ mesh of 10×10 in a direction perpendicular to the current transmission.
Scheme 1 (a) A model device configuration having two electrodes, electrode extension and a central region, (b) model Au-channel Ag contact system.

Optical Property Calculation

Kubo-Greenwood formula is used to calculate the susceptibility tensor as,

\[ \chi_{ij}(\omega) = \frac{-e^2 \hbar^4}{m^2 \epsilon_0 \omega^2} \sum_{nm} \frac{f(E_m)-f(E_n)}{E_{nm}-\hbar \omega-i\Gamma} M_{nm}^i M_{mn}^j \]

(1)

where \( M_{nm}^i \) is the \( i \)-th component of the dipole matrix element between states \( n \) and \( m \). \( V, \Gamma \) and \( f \) are the corresponding volume, broadening and Fermi function respectively. The relative dielectric constant is related to the susceptibility by following the relation,

\[ \epsilon_r(\omega) = (1 + \chi(\omega)) \]

(2)

Optical properties of different systems have been derived from the complex dielectric function by using the following relations[10,11] –

Extinction Coefficient

\[ k(\omega) = \left[ \sqrt{\epsilon_1^2(\omega) + \epsilon_2^2(\omega)} - \epsilon_1(\omega) \right]^{1/2} / \sqrt{2} \]

(3)

Absorbance

\[ \alpha(\omega) = 2\omega k(\omega) / c \]

(4)

AC Conductivity

\[ \sigma = \omega \epsilon_0 \epsilon_1 \tan \delta \]

where \( \tan \delta = \frac{\epsilon_2}{\epsilon_1} \)

(5-a)

\[ \sigma = \omega \epsilon_0 \epsilon_2 \]

(5-b)

Refractive Index

\[ n(\omega) = \left[ \sqrt{\epsilon_1^2(\omega) + \epsilon_2^2(\omega)} + \epsilon_1(\omega) \right]^{1/2} / \sqrt{2} \]

(6)

Transmission coefficients calculation

\( \Gamma \)-point-centered interpolated transmission coefficients at zero bias perpendicular to the transport axis within the irreducible Brillouin zone (IBZ) are obtained for both the device geometries by using:
$T^\parallel(E) = Tr[\Gamma^\parallel_L(E)\mathcal{G}^\parallel(E)\Gamma^\parallel_R(E)\mathcal{G}^\parallel(E)]$  \hspace{1cm} (7)

where, $\mathcal{G}^\parallel$ is the retarded Green’s function, $\Gamma_{L/R}$ is the level broadening with respect to the corresponding self-energies of the electrodes. This function, while integrated over the $k$-point mesh in the IBZ, results the transmission coefficient.

| System          | Total Charge (ideal) | Total Charge Bader | Ag Part       | Au Part       |
|-----------------|----------------------|--------------------|---------------|---------------|
|                 |                      |                    | Ideal Charge  | Bader Charge  |
|                 |                      |                    | Ideal Charge  | Bader Charge  |
| Au/Ag-111       | 378                  | 383.46             | 141           | 168.78        |
| Embedded        | 20439                | 20001.45           | 2585          | 2534.65       |
| Ag-doped Au     | 3536                 | 3607.74            | 376           | 371.54        |
Figure S1: Converged spin density plot for a) Ag111, b) Au111, c) Au/Au-111 and d) Embedded system.
Figure S2: Orbital Projected Density of States for a) Ag111, b) Au111, c) contribution of Ag in Au/Ag-111, d) contribution of Au in Au/Ag-111, e) contribution of Ag in embedded, f) contribution of Au in embedded, g) contribution of Ag in Ag-doped Au and h) contribution of Au in Ag-doped Au.
Figure S3: Absorbance, ac conductivity and extinction coefficient of Ag111, Au111, Au/Ag111, Ag doped Au and Embedded system.
Figure S4: $d$-orbital Projected Density of States for a) contribution of Ag in Au/Ag-111, b) contribution of Au in Au/Ag-111, c) contribution of Ag and d) contribution of Au in embedded system.
Figure S5: Fermi surface plot of different band of Au/Ag-111 systems.

Figure S6: Fermi surface plot of different band of Embedded systems.
Pd-Pt system
For this combination, we have created large-area interfaces created from Pt[111] and Pd[111]. The doped nanostructure was formed by doping Pt[111] matrix centrally with some Pd atoms. Both of these systems are having interesting optical properties. The epsilon-near-zero property, energy-zero divergence and the negative value of real part of epsilon is present as can be seen from Fig S9. Partially filled d-bands of both Pt and Pd generate flat-bands near Fermi-level.
Figure S8: The orbital projected fatbands for orbital components of a) Pd in Pt/Pd-111 system, b) Pt in Pt/Pd-111 system, c) Pd in Pd-doped Pt system and d) Pt in Pd-doped Pt system.
Figure S9: Real and Imaginary part of dielectric constant of Pd-doped and Pd/Pt-111 system.

Figure S10: Fermi surface plot of different band of Pd/Pt-111 systems.
Figure S11: Fermi surface plot of different band of Pd-doped Pt systems.

References
[1] G. Kresse and J. Furthmüller, Comput. Mater. Sci. 6, 15 (1996).
[2] G. Kresse and D. Joubert, Phys. Rev. B 59, 1758 (1999).
[3] J. P. Perdew and Y. Wang, Phys. Rev. B 45, 13244 (1992).
[4] S. Grimme, J. Antony, S. Ehrlich and H. Krieg, J. Chem. Phys. 132, 154104 (2010).
[5] H. J. Monkhorst and J. D. Pack, Phys. Rev. B 13, 5188 (1976).
[6] A. Kokalj, J. Mol. Graph. Model. 17, 176 (1999).
[7] www.quantumwise.com/.
[8] D. R. Smith, S. Schultz, P. Markoš and C. Soukoulis, Phys. Rev. B 65, 195104 (2002).
[9] J. M. Soler, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejón and D. Sánchez-Portal, Journal of Physics: Condensed Matter 14, 2745 (2002).
[10] M. Fox, Oxford University Press, 2001.
[11] A. M. Hafez, N. M. Salem and N. K. Allam, Phys. Chem. Chem. Phys. 16, 18418 (2014).