Supporting Information for

Intriguing electronic and optical prospects of FCC bimetallic two-dimensional heterostructures: epsilon near-zero behaviour in UV-vis range

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METHODOLOGY:

Optical Property Calculation

A. TDDFT Formulation

TDDFT aims at mapping the time-dependent Schrödinger equation onto an effective one-electron problem, where time dependence is incorporated in the approximation of the exchange-correlation kernel (xck) from the explicit time dependence of the exchange-correlation potential and electron-density as:

$$f_{xc}(r,r',t-t') = \frac{\partial v_{xc}(r,t)}{\partial \rho(r',t')}$$

(1)

Calculation of optical absorption involves many-body purturbative approach of solution of Bethe Saltpeter Equation (BSE) using the one-body Green's function. In BSE, the dielectric function can be written in terms of the xck as [1] :

$$\epsilon_{GG'}^{-1}(q,\omega) = \delta_{GG'} + v_{GG'}(q)\chi'(q,\omega)$$,

(2)

where $v(q)$ is the bare Coulomb potential and χ is the full response function, which is related to the response function χ^0 of the non-interacting Kohn-Sham system as:

$$\chi'(q,\omega) = \frac{v_{GG'}(q)\chi_{GG'}^{0}(q,\omega)}{1 - \left[v_{GG'}(q) + f_{xc}(q,\omega)\right]\chi_{GG'}^{0}(q,\omega)}$$

(3)

The frequency independent approximation for the xck, known as the Bootstrap kernel, is computationally less exorbitant than a rigorous solution of the BSE:

$$f_{xc}^{TDDFT}(q,\omega) = \frac{\epsilon^{-1}(q,\omega=0)}{\chi_{GG'}^{0}(q,\omega=0)}$$

(4)

The coupled equations (2), (3) and (4) are solved by initially setting $f_{xc}^{TDDFT} = 0$ and then calculating $\chi'(q,\omega)$ and thus $\epsilon_{GG'}^{-1}(q,\omega)$. This value is then utilized in equation (6) to find out the new f_{xc}^{TDDFT}. This procedure is repeated until self-consistency is obtained at $\omega = 0$.

The long-range component of exchange-correlation kernel is frequency independent having the form $-\alpha^{static} / q^2$. More detailed and accurate formulation involves introducing frequency dependence. The long-range contribution kernel (LRC) assimilates the frequency dependence in the following form into the dynamical exchange:

$$f_{xc}^{dyn}(q,\omega) = -\frac{1}{q^2}(\alpha + \beta\omega^2)$$

(5)

This improvement of dynamical kernel has improved the calculations to obtained important information about the exciton and charged excitons[2].

B. Interband and intraband contribution to the dielectric response function

The real and imaginary parts of the interband dielectric response function in tensor form are computed as[3]:

$$\epsilon_{\alpha\beta}^{(1)}(\hat{q},\omega)$$
$$= 1 + \frac{4\pi e^2}{V}\lim_{q\to 0}\frac{1}{q^2}\sum_{nm\,k}2f_{nk}\langle u_{mk+e_{\alpha q}}|u_{nk}\rangle\langle u_{nk}|u_{mk+e_{\beta q}}\rangle \times \left(\frac{1}{\epsilon_{mk}-\epsilon_{nk-\omega}}+\frac{1}{\epsilon_{mk}-\epsilon}\right)$$

(6)

and

$$\epsilon_{\alpha\beta}^{(2)}(\hat{q},\omega)$$
$$= \frac{4\pi^2 e^2}{V}\lim_{q\to 0}\frac{1}{q^2}\sum_{nm\,k}2f_{nk}\langle u_{mk+e_{\alpha q}}|u_{nk}\rangle\langle u_{nk}|u_{mk+e_{\beta q}}\rangle \times \left(\delta(\epsilon_{mk}-\epsilon_{nk}-\omega)-\delta(\epsilon_{mk}\right.$$

(7)

For semiconductors and insulators, only interband transitions are important ($n \neq m$). For metals, due to the occurrence of partially occupied bands, transitions within a band, often referred to as intra-band transitions are also important. The real part of intra-band dielectric function, dependent only on frequency of the incident light and the energy dispersion, can be written as:

$$\epsilon_{\alpha\beta}^{1}{}_{intra} = -\frac{\bar{\omega}_{\alpha\beta}^2}{\omega^2}$$

(8)

where $\bar{\omega}_{\alpha\beta}$ is the material specific property, referred to as the plasma frequency tensor, represented as:

$$\bar{\omega}_{\alpha\beta}^2 = \frac{4\pi e^2}{V}\sum_{nk}2f_{nk}\frac{\partial^2\epsilon_{nk}}{\partial k_\alpha\partial k_\beta}$$

(9)

The imaginary part is obtained from the Kramers-Kronig transformation:

$$\epsilon_{\substack{\alpha\beta\\ intra}}^2 = -\pi\bar{\omega}_{\alpha\alpha}^2\frac{\partial\delta(\omega)}{\partial\omega}$$

(10)

After introducing the relaxation-time τ under semiclassical approximation, the real and imaginary part of the intraband dielectric function can be written as:

$$\epsilon^1(\omega) = 1 - \frac{\bar{\omega}^2\tau^2}{1 + \omega^2\tau^2}$$

(11)

$$\epsilon^2(\omega) = \frac{\bar{\omega}^2\tau}{\omega(1 + \omega^2\tau^2)}$$

(12)

Therefore, for metals, the intra-band dielectric function has a near-zero frequency negative and positive divergence respectively for real and imaginary parts, which constitutes the "Drude-like" terms.

Transmission coefficients calculation

Γ-point centred 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:

$$T^{\parallel}(E) = Tr\left[\Gamma_L^{\parallel}(E)g_{\parallel}(E)\Gamma_R^{\parallel}(E)g_{\parallel}^{\dagger}(E)\right]$$

(13)

where, $g_{\parallel}$ 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.
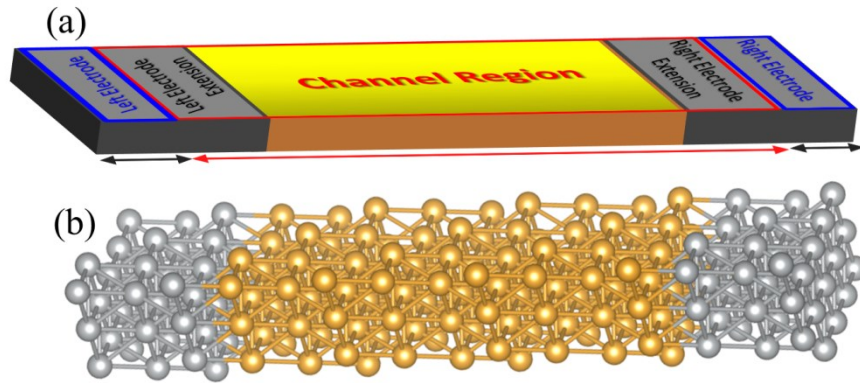
Scheme S1 *(a) A model device configuration having two electrodes, electrode extension and a central region, (b) model Au-channel Ag contact system.*

Table S1: Bader Charge table of different systems

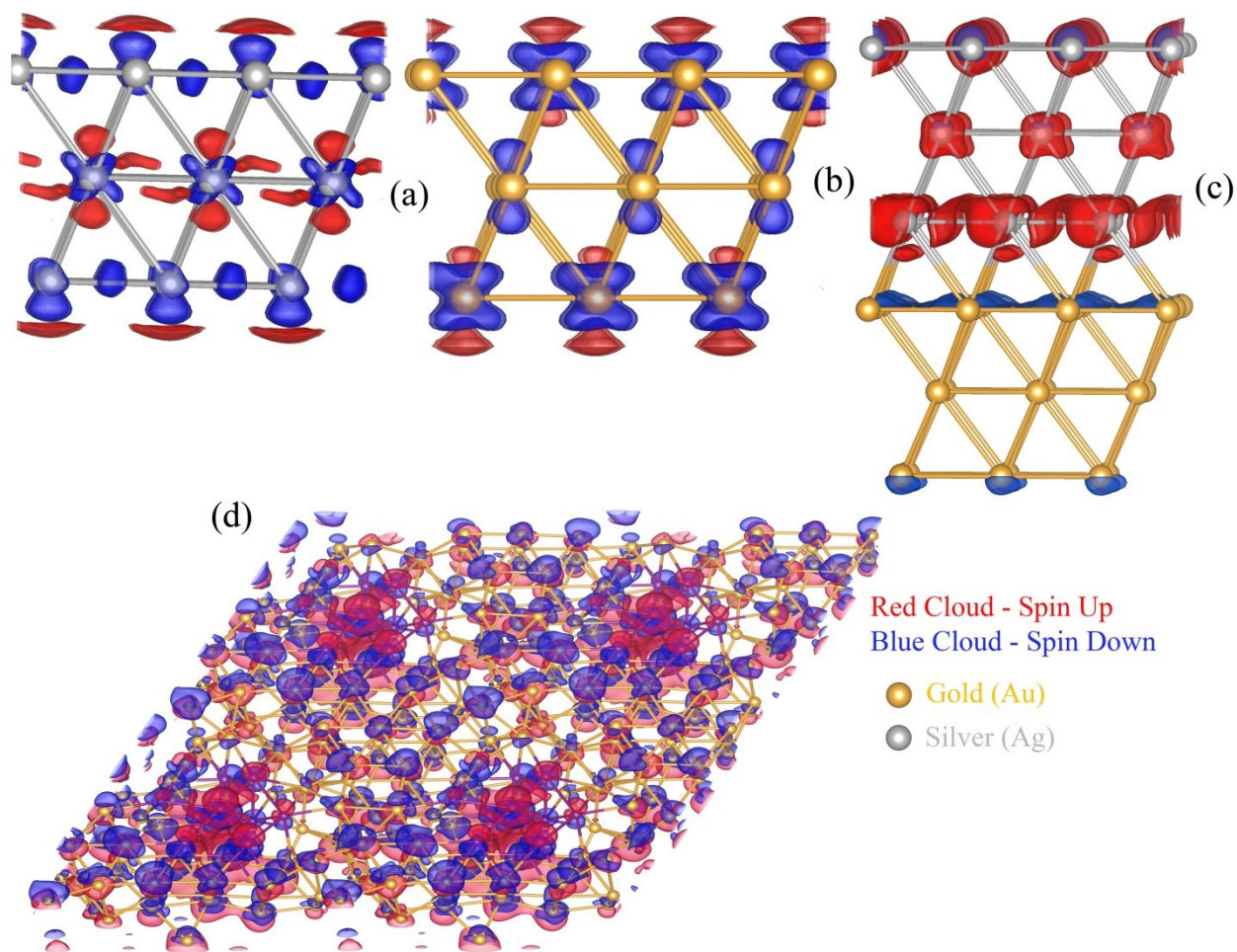| System	Total Charge (ideal)	Total Charge Bader	Ag Part		Au Part	
			Ideal Charge	Bader Charge	Ideal Charge	Bader Charge
Au/Ag-111	378	383.46	141	168.78	237	214.68
Embedded	20439	20001.45	2585	2534.65	17854	17466.8
Ag-doped Au	3536	3607.74	376	371.54	3160	3236.20

Figure S1: *Converged spin density plot for a) Ag111, b) Au111, c) Au/Au-111 and d) Embedded system.*
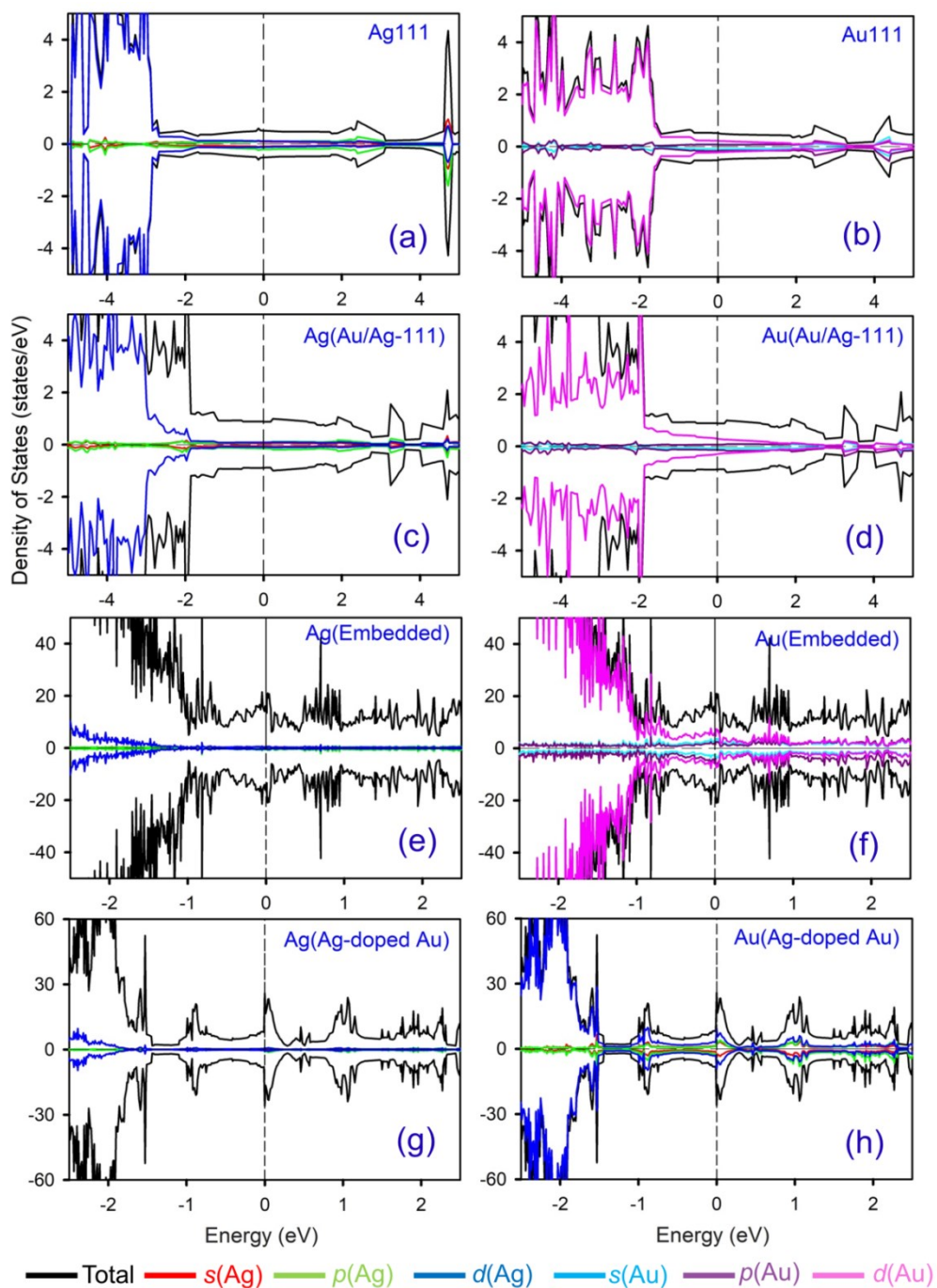
Figure S2: *Orbital Projected Density of States for a) Ag111, b) Au111, c) contribution of Ag in Au/Ag-111, d) contribution of Au in Au/Ag-111, e) contribution of Ag in embedded, f) contribution of Au in embedded, g) contribution of Ag in Ag-doped Au and h) contribution of Au in Ag-doped Au*
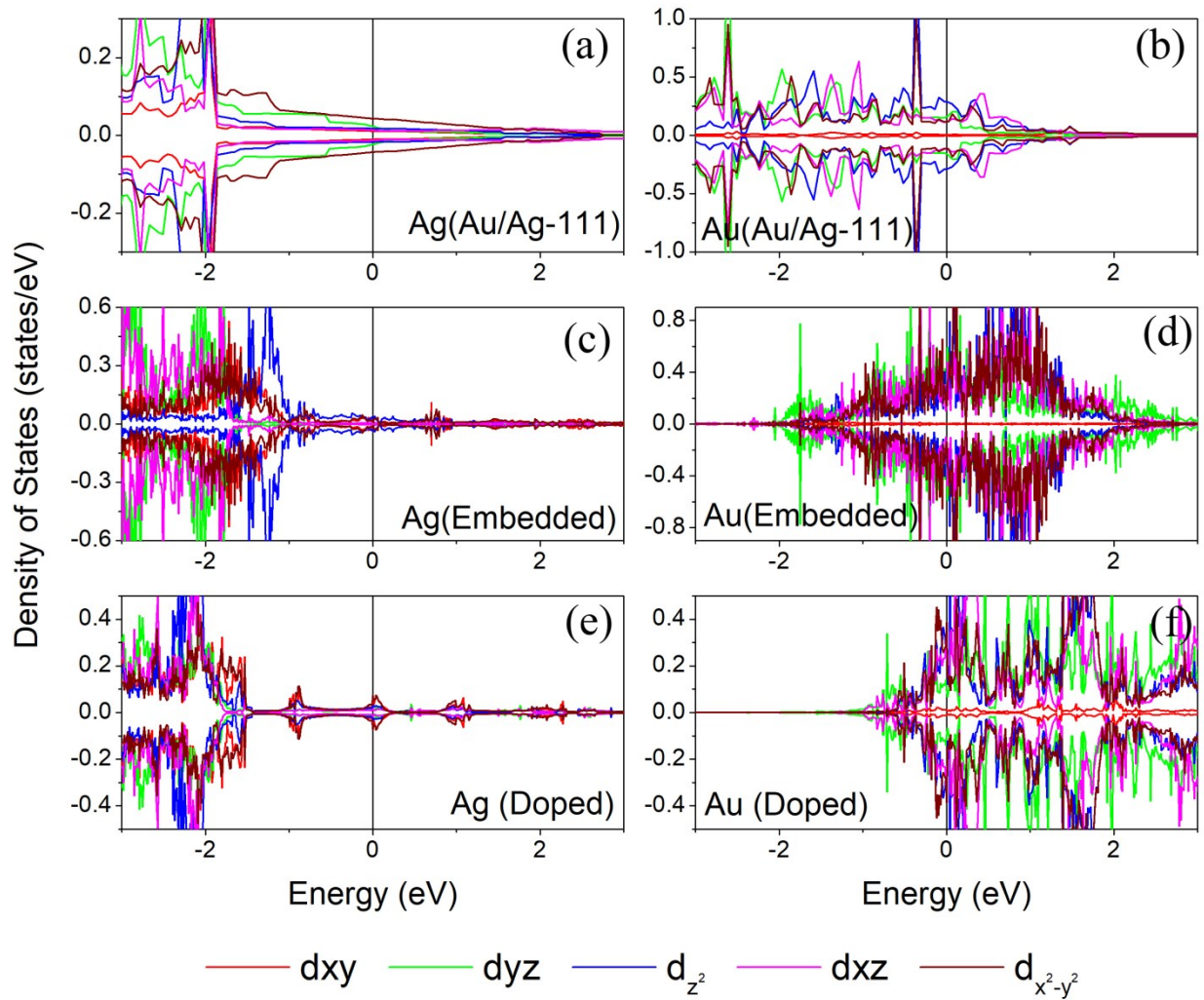
Figure S3: *d-orbital Projected Density of States for a) contribution of Ag in Au/Ag-111, b) contribution of Au in Au/Ag-111, c) contribution of Ag and d) contribution of Au in embedded system, e) contribution of Ag and f) contribution of Au in doped system.*

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 S5. Partially filled *d*-bands of both Pt and Pd generate flat-bands near Fermi-level.
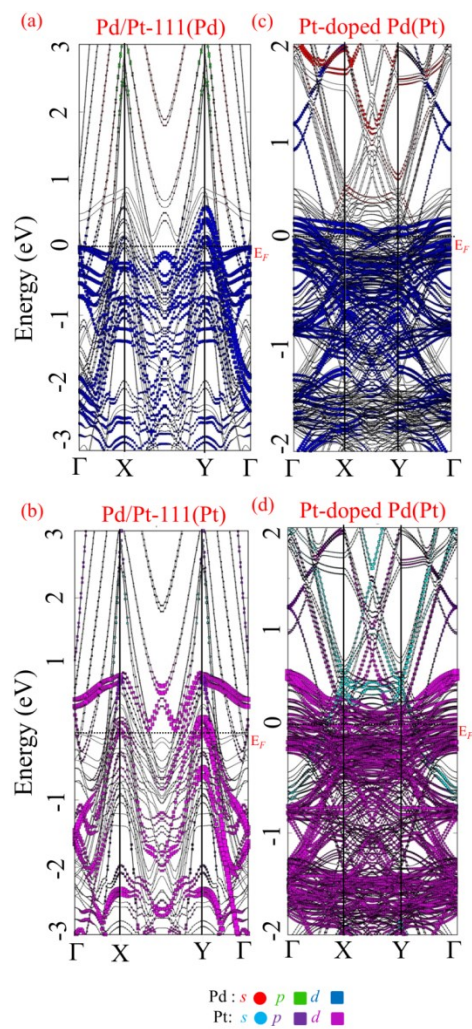
Figure S4: *The orbital projected fatbands for orbital components of a) Pd in Pt/Pd-111 system, b) Pt in Pt/Pd-111 system, c) Pd in Pd-doped Pt system and d) Pt in Pd-doped Pt system.*
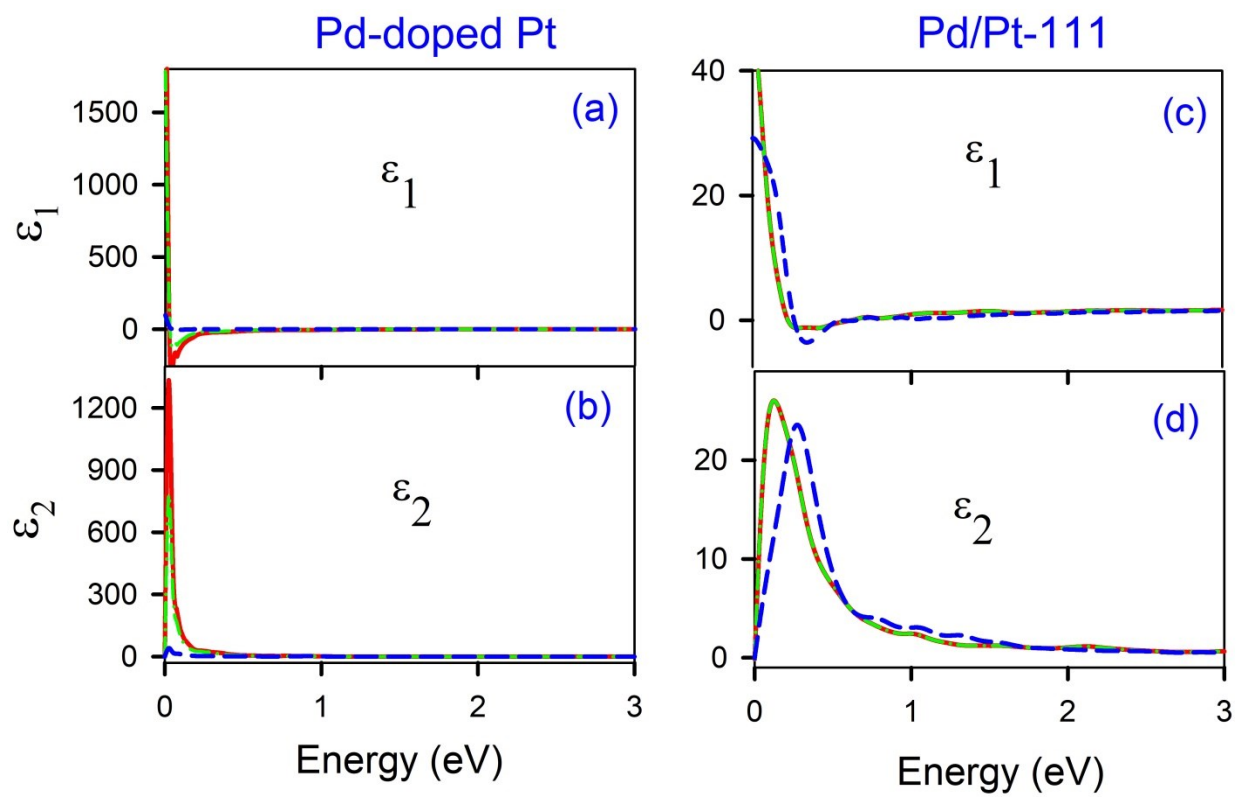
Figure S5: *Real and Imaginary part of dielectric constant of Pd-doped and Pd/Pt-111 system.*

References

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[3]   J. Harl, The Linear Response Function in Density Functional Theory (Dissertation), University of Vienna, 2008.