



Size-dependent luminescence of small palladium particles

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Abstract

We report cathodoluminescence spectra of small Pd clusters of various size deposited on a thin, well-ordered oxide film. The size distribution of the deposited metal aggregates can be chosen and deliberately varied. The luminescence spectra vary characteristically as a function of the variation of particle size. The resonance energy at the highest luminescence energy with decreasing average particle size vary as expected for electronic states in a quantum confined metal particle. For an average aggregate size of 10 Å the luminescence is maximum. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

The study of optical properties of small metal particles has a long tradition. In an early and arguably most influential publication in this field, Mie published his theory of light scattering by small spheres and already speculated that optical spectroscopy can reveal the transition from atomic to bulk properties [1]. Research has been conducted with a variety of systems and methods. Colloidal solutions of metals have played a prominent role in elucidating the properties of small metal aggregates [2]. These solutions frequently contain additives that attach on to the cluster's surface to avoid agglomeration [3]. Observed size effects were often of extrinsic character (e.g. shape, adsorbed molecules) and could be explained by Mie's theory or extensions of it. Intrinsic size effects resulting in shifts of adsorption and emission bands with cluster size have been found in semiconductor nanoparticles [4–6]. They

were attributed to changes in the electronic structure for particle sizes of a few tens to a few hundred Ångström. For metal particles one has to approach considerably smaller particle sizes due to the change in the mean-free path of electrons in the particle. An experiment with a remarkable mechanism for luminescence of metal particles was recently reported by König et al. [7]. Light emission was observed during the agglomeration of copper and silver atoms in a noble gas matrix. The heat of formation of the chemical bonds between the metal atoms leads to the ejection of electronically excited atoms and dimers, which in turn emit photons. This observation is different from ours presented in the following as we found light emission from the clusters themselves after direct excitation by impinging electrons. Light emission from matter upon interaction with electrons is a well-studied phenomenon in solid state physics. Inverse photoemission (Bremsstrahlungsschicht) [8] or scanning-tunnelling-microscopy (STM)–light-emission-spectroscopy [9] are methods based upon the injection and capturing of electrons

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by matter in an unoccupied state and the consequent radiative transition to an unoccupied state at lower energy. Radiationless transitions, however, compete with the radiative decay. In fact, the radiative decay is a rather improbable process in the case of electrons interacting with metals, because radiationless transitions induced by electron–electron and electron–phonon scattering become highly probable. Cathodoluminescence, on the other hand, has been successfully applied to the study of buried metal–semiconductor interfaces [10,11]. In this case electrons with kinetic energies in the range of 300–3000 eV are accelerated towards a target and the luminescence is recorded with a spectrometer. It is generally assumed that the metal layer does not luminesce and only enhances the metal–substrate interface signal. However, it is obvious that these phenomena must strongly depend on metal coverage and, in particular, on the morphology of the deposited metal film, i.e. size of the deposited aggregates. There has so far been no experimental confirmation of this dependence with respect to the latter aspect.

We present here experimental evidence for strongly size-dependent cathodoluminescence intensity of Pd aggregates supported on a thin alumina film. Thin films are particularly useful in this connection because the strong cathodoluminescence observed for bulk sapphire is considerably suppressed. The metal aggregates have been prepared by nucle-

ation and growth of deposited metal vapor. We have determined the average aggregate size and distance as a function of these parameters by three independent methods in situ, i.e. by spot profile low-energy electron diffraction analysis [12], STM [13] and transmission electron microscopy [14]. The thin-film model system allows for a full characterization of the system with surface science tools including STM. Fig. 1 shows a STM micrograph of Pd aggregates which are typical for samples used for the cathodoluminescence measurements. In the following we shall describe the cathodoluminescence spectra of these morphologically well-characterized systems.

2. Experimental

The experiment was performed in an ultra-high vacuum chamber (base pressure of 2×10^{-10} mbar) equipped with LEED/Auger, a sputter gun, an electron beam Pd evaporator and a quartz micro balance.

The preparation of a thin, well-ordered γ - Al_2O_3 film on the NiAl(110) substrate followed a standard procedure [15,16]. Pd particles were deposited by nucleation and growth of evaporated Pd. Average cluster size and island density were controlled by the amount of deposited metal and by the sample temperature. Deposition at room temperature lead to larger particles that preferentially decorated domain boundaries, while formation at 90 K results in a higher density of smaller particles that are more homogeneously distributed on the film although even at this temperature Pd tends to nucleate at defects [13]. Amounts of metal varied in the range of an effective thickness of 0.1–10 Å, resulting in particle diameters of 5–70 Å as determined earlier. Luminescence was recorded at the same sample temperature at which Pd was deposited if not mentioned otherwise.

Light emission was stimulated by electron impact from a tungsten field emitter tip. The tip was placed approximately 1 mm in front of the sample surface. A potential in the range of a few hundred up to about 1000 V was applied between the sample and the tip causing field emission of electrons from the tip with an electron energy corresponding to the applied volt-

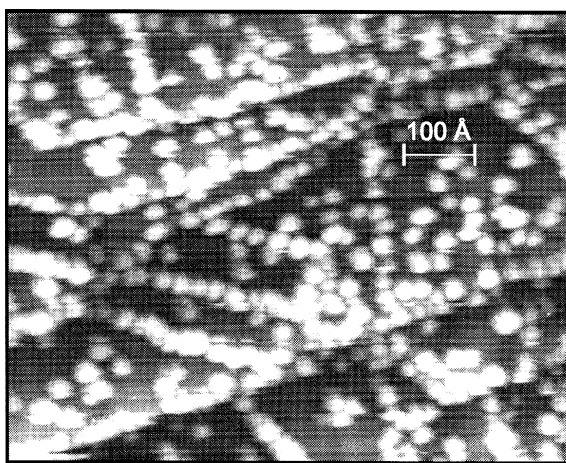


Fig. 1. STM micrographs of Pd aggregates [13].

age. In order to allow for comparison of luminescence spectra, the electron current was held constant at $5 \mu\text{A}$ by adjusting the applied voltage. We did not observe changes in the spectra for identical samples when applying different potentials for tips of different quality. We used field emitter tips as electron guns because thermionic electron sources (e.g. conventional LEED guns) emit light in the spectral region of our very weak signals and would hence obscure them. Field emitter tips provide an easy-to-use and simple-to-operate solution. The two major drawbacks are the high energy of the emitted electrons and, in particular, the limited lifetime.

Fig. 2 shows a schematic drawing of the experimental set-up. The ceramic holder for the tungsten field emitter was at a fixed position in the UHV chamber. The sample could be moved along a circular path to place it at the appropriate positions for the different experiments.

Luminescence spectra were recorded with a UV–VIS spectrometer in connection with a liquid nitrogen cooled CCD detector (Triax 180, Instruments) in the range of 1.2–6.2 eV photon energy. The sample was placed about 30 cm in front of the entrance slit of the monochromator. Integration time for quality spectra was 25 min. The spectra were corrected for spectral sensitivity of the CCD detector.

For CO adsorption experiments the sample was cooled to 100 K and a continuous background pres-

sure of 5×10^{-8} mbar of carbon monoxide was maintained. Such rather drastic conditions were necessary to have sufficiently high CO coverages since large amounts of CO were desorbed by electron impact. It should be mentioned that the clean alumina film does not adsorb CO under the given conditions [15,16].

3. Results

In the following section we present in Fig. 3 UV–VIS spectra for the clean NiAl(110) crystal, the oxide film-covered NiAl single crystal and for small Pd particles of various sizes deposited on the alumina film.

The photon emission of the clean NiAl(110) crystal shown in Fig. 3a is very weak. Two broad bands can be distinguished centered at photon energies of about 2.3 and 3.0 eV.

The two bands of the NiAl substrate are also found for the $\gamma\text{-Al}_2\text{O}_3$ oxide covered NiAl crystal (Fig. 3b). The intensity of the low-energy band is comparable to the clean NiAl crystal, while the one of higher energy appears largely attenuated. A new, sharper band is observed at 1.8 eV that also has only weak intensity.

For larger amounts of deposited Pd (effective thickness 1–100 Å; average particle size ≈ 35 Å to complete coverage) we do not observe new bands in the UV–VIS spectra (Fig. 3c), only a spectrum for 1 Å is shown. However, both the absolute and relative intensities of the peaks at 1.8, 2.3 and 3.0 eV change with average particle size.

For very small particles of ca. 5–15 Å diameter (effective thickness 0.1 Å (not shown here) to 0.5 Å) broad bands are observed at photon energies of 3.7 and 4.6 eV with the higher-energy band more pronounced for smaller particles. The spectra in Fig. 3d,e illustrate this by comparing the luminescence spectra for samples with 0.5 Å effective Pd thickness deposited at 300 and 100 K, respectively. In the case where the metal was deposited at 300 K, i.e. the average diameter is larger, the band at 3.7 eV is much less pronounced while the one at 4.6 eV is almost vanished. For the sample of smaller clusters (100 K deposition temperature) the band at 3.7 eV is

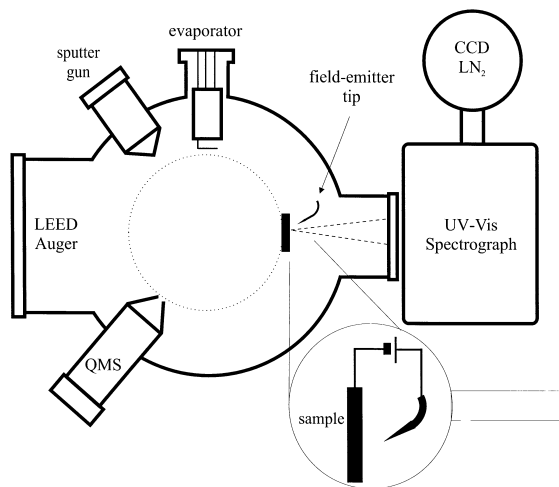


Fig. 2. Schematic drawing of the experiment. For details see text.

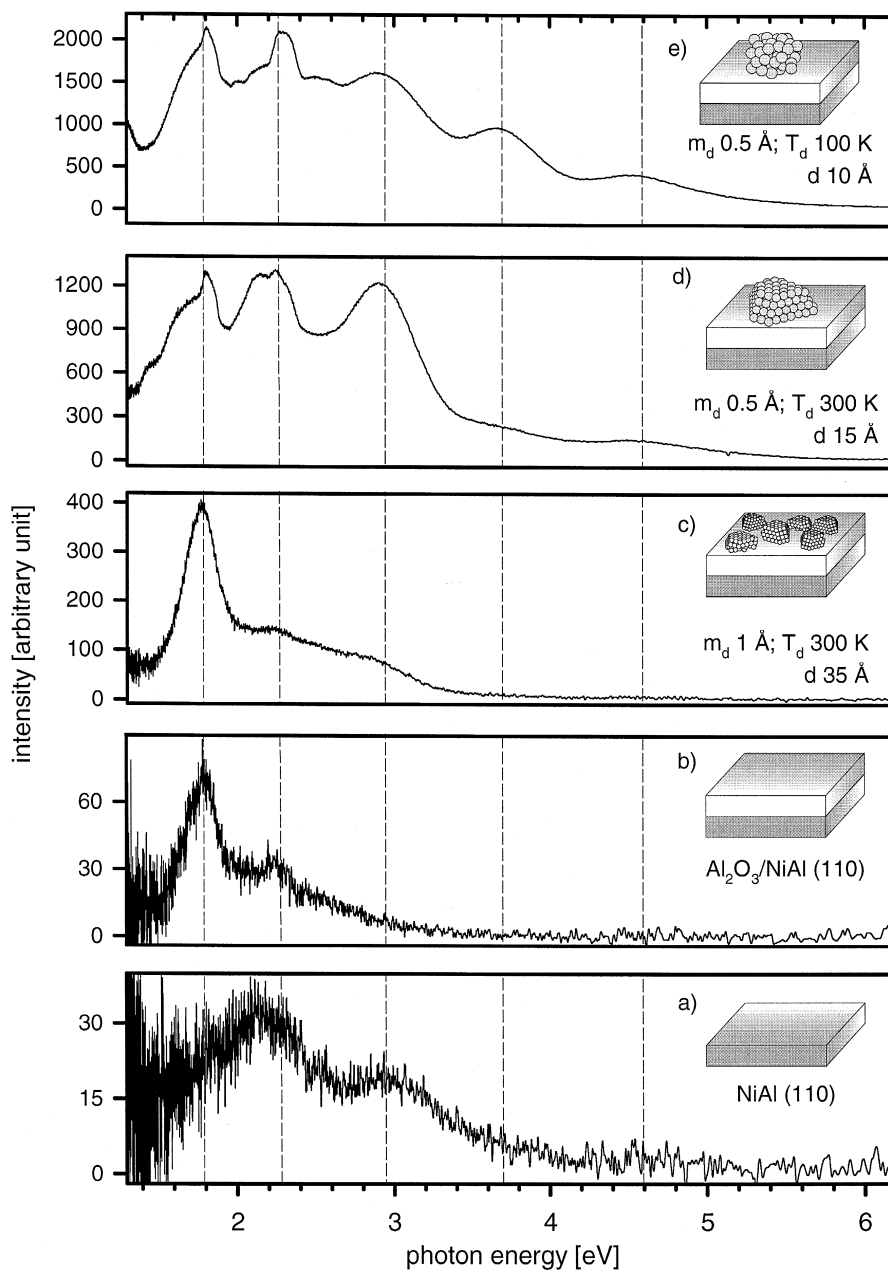


Fig. 3. Luminescence spectra of various Pd coverages. m_d denotes the amount of deposited Pd while T_d is the sample temperature during deposition. The average particle diameter d was determined by SPA-LEED measurements [13]. Notice the different intensity scales for the spectra.

pronounced while the one at 4.6 eV is also observed (Fig. 3e). In the spectrum recorded for aggregates of an average diameter of 5 Å (not shown) the band at 4.6 eV is dominant. There are small feature in the

spectra of Fig. 3d,e between the main bands at low energy. We are not sure whether they are artefacts.

The largest gain in intensity of the three low-energy bands of the substrate is observed for a Pd

particle size of 10 Å. The intensity is almost two orders of magnitude larger than for clean γ - $\text{Al}_2\text{O}_3/\text{NiAl}(110)$.

CO adsorption onto the Pd aggregates has a pronounced effect on the spectra (Fig. 4). Upon backfilling the chamber with CO (5×10^{-8} mbar) and cooling the sample to 100 K, the luminescence intensity of the band at 3.0 eV is reduced. A new broad peak is observed at 4.5 eV photon energy. This is found for all particle sizes; however, it is strongest for smaller particles. This band should not be confused with the band at 4.6 eV observed for very small particles. Careful measurements proved that these are two different bands that are accidentally degenerate. The necessity of rather drastic conditions for the CO adsorption experiment corroborates this.

4. Discussion

The most important finding is the emission of UV-photons for very small Pd particles, whose frequency depends on the particle size. Before we discuss this aspect, some general remarks and comments on other features of the UV–VIS emission spectra are appropriate.

The thickness of the oxide film is 5 Å [15,16]. Electrons and photons in the energy range of the experiment are not significantly attenuated by such a thin layer [17]. This holds for the Pd particles as well. It explains why the emission of the NiAl substrate is observed in all experiments. The large majority of the impinging electrons reaches the covered NiAl substrate where they create secondary

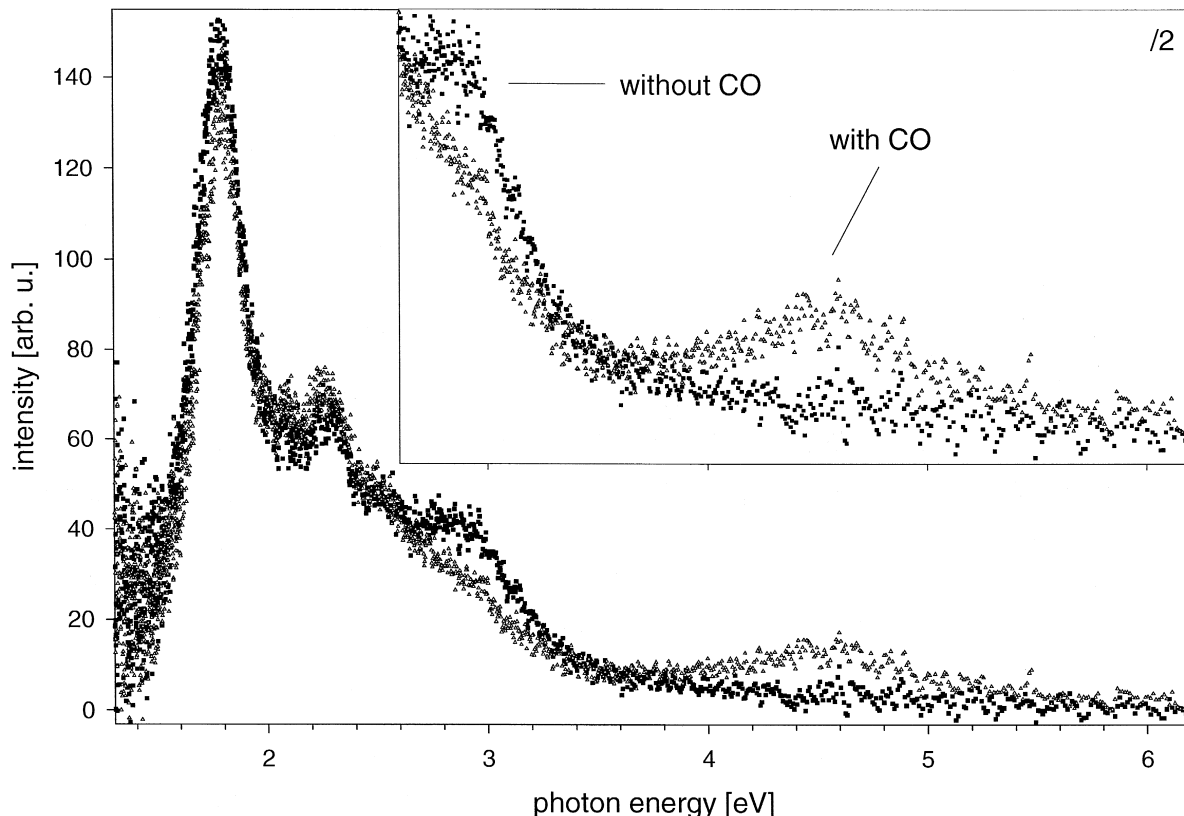


Fig. 4. Luminescence spectra showing the effect of CO adsorption. A new band is found at 4.5 eV, while the one at 3.0 eV decreases (\square) compared to the spectrum without CO (\blacktriangle). CO background pressure 5×10^{-8} mbar; 0.8 Å Pd, preparation at 300 K, average particle size ca. 30 Å.

electrons of lower energy. Some of the secondary electrons are able to reach the alumina film and even the Pd particles and can cause excitation, which subsequently leads to photon emission. Of course, secondary electrons are also created in the oxide film and the clusters. The excitation by secondary electrons of low energy is certainly the most important mechanism since their number is much higher than the number of primary electrons.

Definite assignments of the observed emission bands to specific electronic transitions are not yet possible due to the lack of theoretical predictions. Qualitatively, the photon emission of the clean NiAl(110) substrate at 2.3 and 3.0 eV is considered as Bremsstrahlung. It is worth mentioning that in absorption spectra of NiAl a band is found at 2.6 eV, which was assigned to a transition from the Fermi level to an unoccupied state above the Fermi level [18]. As stated above, we find an additional band for the oxide-covered substrate at 1.8 eV. The emission of the F and paramagnetic F^+ centers in sapphire, however, is found at 3.0 [19] and 3.8 eV [20], respectively, well separated from the band at 1.8 eV that we observe for the thin alumina film. On the other hand, we know that paramagnetic centers exist

in the oxide film which may cause the observed emission band. Very weak absorption bands between 1.9 and 2.8 eV were found in sapphire [21]. Another possible explanation for the observed band is a radiative transition to or from an interface state.

The bands at 1.8, 2.3 and 3.0 eV photon energy gain almost two orders of magnitude in intensity when Pd particles of an average size of 10 Å are deposited. An amplification effect is also observed to a smaller extent for smaller and larger aggregates. It can be qualitatively rationalized by a simple antenna model that is also used for explaining intensity increases in surface enhanced Raman spectroscopy (SERS) [22]. Secondary electrons reach the oxide surface where they fluctuate during a short but finite period of time. They form dipoles together with their image charges in the NiAl substrate and the Pd clusters before they tunnel into the NiAl substrate. These dipoles work as antennas by causing a field enhancement that amplifies photon emission. The effect can lead to increases in intensity of up to four orders of magnitude in SERS [23]. No detectable emission was observed from a sample with a complete Pd layer since the proposed mechanism cannot work under these circumstances. We did notice emis-

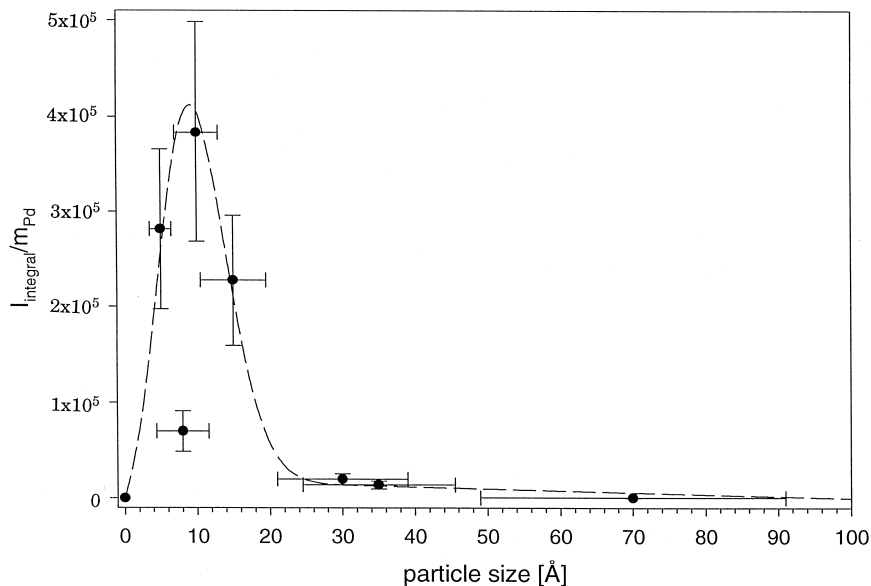


Fig. 5. Integral photon emission normalized to the amount of deposited metal plotted versus average aggregate size.

sion similar to the one of the $\text{Al}_2\text{O}_3/\text{NiAl}[110]$ sample at much higher field emission currents. The relationship between the panchromatic photon emission and the particle size is illustrated in Fig. 5. The integral intensity was normalized to the amount of deposited metal in order to account for different island densities.

Metal clusters of size 100 \AA or larger have basically the same electronic and dielectric functions as the bulk material as has been shown for the mint metals but also for other metals [24]. Changes in light absorption and emission spectra for such particles are due to extrinsic effects that reflect the shape and the environment of the particle [24,25]. The optical properties can be understood on the basis of Mie's theory as collective oscillations of the electrons (plasmons and plasmon–polaritons). For palladium, the energy of the surface plasmon is 7.3 eV [26], which can be expected to shift to higher energy for decreasing particle size [24]. Hence, it is not surprising that we do not see luminescence of Pd aggregates of diameter 35 \AA or larger since we performed our experiments in the energy range of 1.2–6.2 eV.

Aggregates of smaller average size similar to those showing characteristic luminescence in our experiment can be better described by a quantum chemical approach than by solid-state theory. Two important and unique properties of such particles should be pointed out: due to the limited size of the particle the phonon spectrum at low frequencies is not fully developed, which leads to reduced electron–phonon coupling, which in turn causes longer lifetimes for excited electronic states. The electron mean-free path for the bulk metal is of the same order of magnitude or even smaller than the particle diameter. The electronic states are therefore largely determined by the dimension and the shape of the particle (quantum size or confinement effect). Closely related to this phenomenon is the non-metal-to-metal transition which takes place at slightly larger clusters [27]. For our specific system this transition occurs at a Pd particle size in the range of 10–50 \AA [28]. Unfortunately, it is computationally expensive to calculate the electronic structure of particles with a few to several dozens of atoms of electron-rich metals. One simple textbook model that produces qualitative results to be compared with experiment is

the three-dimensional particle in a box. We performed calculations for cubicles with edge length of the size of aggregates for which we observed characteristic luminescence, and larger. The potential walls were not infinitely high but the well of the box was chosen to be 10 eV deep, the band width of the s + p and d band in Pd [29]. Each state was filled with two electrons according to Hund's rule while each Pd atom contributed one s-electron. This can be justified by the fact that the unoccupied states in Pd have mainly s + p character, while the d-orbital derived states are mostly below the Fermi edge [29] and we are interested in the density of states (DOS) above the Fermi level. The density of states was convoluted by Gaussian functions to account for thermal broadening. The energy separation between the Fermi level and regions with a high density of states is of the order of a few electron volts for small particles. If luminescence results from deactivation out of these regions of excited states we expect photon energies of the order observed in our experiment. If one assumes that the regions of excited states are separated from the Fermi level by an energy zone with a low density of states then an excited electron has to release its energy in one single step to return to the Fermi level after excitation. The radiative pathway is largely enhanced due to the decreased phonon–electron coupling mentioned above and therefore photon emission can be expected. Quantum mechanical calculations of the electronic structure of Pd_{44} clusters by Roesch et al. could be useful in the future to interpret such results [30].

Upon CO exposure the CO molecules interact with the Pd particles while the non-metal-covered substrate does not adsorb CO. The interaction influences the electronic structure of the Pd aggregates, which is reflected in the luminescence spectra in Fig. 4. A relative change in intensity of the band at 2.9 eV can be explained by a decrease of the density of states in the clusters. The adsorbate feature near 4.5 eV mirror images the unoccupied $\text{Pd} 2d\text{-CO} 2\pi^*$ state. Light emission of an electron from this state to the Fermi level represents a channel for radiative decay. This state has been observed in inverse photoemission and has been subject of an intense discussion in the past. Both theoretical [31] and experimental [32] investigations on bulk palladium place this state at approx. 4 eV above the Fermi level, which is

only in rough agreement with the value of 4.5 eV that we found. The observation of this state therefore confirms our above interpretation.

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