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Reconstruction of Pd Particles Supported on Silica in the Presence of CO as Studied by Carbon-13 NMR

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The ^{13}C NMR spectrum of ^{13}CO adsorbed on Pd particles varies dramatically depending on dispersion. The spectrum of highly dispersed Pd particles supported on silica is a powder pattern ~800 ppm wide with a first moment of 410 ppm. A low dispersion sample has a motionally narrowed line centered at 750±10 ppm and only ~85 ppm full width at half height (FWHH). Over several years, high dispersion samples show an increase in the intensity near 750 ppm. These observations are interpreted as an increase of *mobile bridging* CO on high dispersion Pd surfaces of particles which resulted from smoothing of the metal particle surfaces in the presence of CO.

Introduction

The structure and surface chemistry of noble metal particles (Pt, Pd, Rh, Ru, etc.) supported on high surface area oxides have received a great deal of attention due to their wide application as catalysts in many technologically important reactions (CO oxidation, water gas shift reaction, hydrogenation, etc.).[1] One of the model systems most extensively studied is

CO adsorbed on such supported metal particles, and the results of these studies have formed the basis of the most widely accepted models of molecular chemisorption for many reasons. CO is for example an important reactant in the chemistry of the Fischer-Tropsch processes[2] and binds tightly to the majority of interesting catalytic metal surfaces[2-6] at ambient temperature. In addition, CO is implicated in the surface reconstruction or reforming of metal particles under certain conditions.[7-28] Thus, the study of the interaction of CO with supported metal particles has relevance to nearly

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every aspect of the chemistry of supported metal catalysts.

The reconstruction of highly dispersed ruthenium and rhodium catalysts in the presence of CO is one of the best known examples of an adsorbate affecting metal particle structure.[16-28] It appears that CO attacks the metal particle surfaces and weakens the metal-metal binding enough to allow atom-carbonyl species to migrate away from the particle. As a result the metal particles disintegrate and form isolated single atom species. Although palladium also belongs to group VIII and generally shows gas adsorption properties similar to those of Ru and Rh, the effects of adsorbed CO are observed to be quite different. Growth of metal-metal coordination rather than disintegration in highly dispersed silica supported Pd particles was observed for the first time by Anderson *et al.* using EXAFS (Extended X-ray Absorption Fine Structure), IR(Infrared) spectroscopy, X-ray diffraction, and CO uptake.[7] Stimulated by this work, we have undertaken a ^{13}C solid state nuclear magnetic resonance (NMR) spectroscopic study of CO induced reconstruction in highly dispersed silica supported palladium catalysts.

Our study relies on the observation that the ^{13}C NMR spectrum of [13]CO adsorbed on supported Pd undergoes a reversible motional narrowing transition, and the fact that the activation energy associated with this transition varies strongly with dispersion as we first reported[4] and later confirmed by other workers.[5] For a given sample, the ^{13}C spectrum will narrow dramatically and shift in resonance position above some characteristic temperature. Changes in the observed temperature for the motional narrowing transition for a particular sample then indicate the altered activation energy for diffusion which implies in turn morphological changes in the surfaces of the Pd particles. Changes in the appearance of the spectrum taken at a single fixed temperature for a sample can also then be used to monitor surface modification. For example, the post-treatment appearance of motionally narrowed component in the ^{13}C spectrum of a sample that previously showed no evidence for any motionally narrowed CO at room temperature, can be taken as evidence for the lowering of the activation energy of diffusion for at least a portion of the Pd particles present. In what follows we report on NMR experiments along these lines demonstrating the surfaces of silica supported Pd particles are reconstructed in the presence of CO. Such reconstruction may take place even at room temperature over extended periods of time and is manifested by the appearance of an increasing fraction of motionally narrowed CO in the ^{13}C NMR spectrum.

Experimental

Sample Preparation. A 5.4 weight % Pd/SiO$_2$ catalyst was prepared by dropwise addition of a [Pd(NH$_3$)$_4$ (OH)$_2$] solution to a vigorously stirred silica gel (Degussa Aerosil 200, 200 m^2/g). The [Pd(NH$_3$)$_4$(OH)$_2$] solution was prepared by treat- ment of a [Pd(NH$_3$)$_4$Cl$_2$] solution with an OH saturated anion exchange-resin (Amberlite IRN-78). Metal content was determined by atomic absorption of a solution obtained from acid extraction of Pd. Oxidation of the catalyst at 573 K in flowing O$_2$ was followed by reduction for 3 hours at the same temperature in a flow of H$_2$. After evacuation, [13]CO was introduced at room temperature and then the catalyst was transferred through a

sidearm on the Pyrex reactor to a 5 mm NMR tube that was flame sealed after evacuation. Details of the sample preparation have been published elsewhere.[6] Chemisorption of CO for sample I was carried out using 5 short contacts (~1 minute each) at 10 Torr (1 Torr=133.3 N/m^2) of [13]CO and followed by evacuation to 10^{-8} Torr. Sample II was prepared with a single contact at 10 Torr of [13]CO for 5 minutes followed by evacuation to 10^{-5} Torr. Initially these samples were prepared with different contact times to CO in order to study effect of contact time on the CO coverage and distribution on Pd surfaces. Both samples had the same [13]CO coverage of close to 0.5 (saturation) and distribution. Both samples were prepared from the same catalyst described above.

Palladium particle sizes were determined by H$_2$ chemisorption at 373 K. The H/Pd ratio was found to be 0.47, corresponding to a dispersion of 56% or an average particle diameter of 19 Å.[29] High resolution electron microscopy using a JEOL 100 CX revealed a narrow size distribution with a majority of the particles being 15 Å (57%), some at 20 Å (37%), and a few at 10 Å (7%) and 25 Å (4%). This distribution is consistent with the average size obtained by hydrogen chemisorption.

NMR Spectroscopy. Details concerning the NMR instruments used are contained in a previous publication.[6] Experiments were carried out at field strength of 7.05 T and at room temperature unless stated otherwise. In all determinations, spin echo sequences[30] and phase cycling of the pulses[31] were used to suppress pulse breakthrough and other artifacts. This is especially important as the low intensity and large width of the NMR line shape exacerbates baseline problems. The separation τ between the $\pi/2$ pulse and the π pulse in the Hahn echo was typically 30-50 μs. Room temperature static spectra typically require over 4000 accumulations. Spin lattice relaxation time T$_1$ values were measured by the inversion recovery pulse sequence. A single 180 pulse (for low dispersion samples) or a composite 180 pulse[32] (for the high dispersion samples) was used for the inversion. All echo signals were acquired in quadrature with the carrier placed close to the resonance center of gravity. Line shapes were checked for independence of resonance offset. Since the phasing of powder spectra can be quite subjective if there are no well defined features present, zero order phasing was determined using the powder pattern from 10% Ba[13]CO$_3$. Chemical shifts reported here are relative to external tetramethysilane (TMS) with down field shifts taken as positive and have a precision of about 1 ppm.

Results

The static Hahn echo ^{13}C NMR spectra of [13]CO adsorbed on Pd catalysts at room temperature were previously reported to depend strongly on dispersion.[4,5,33] A low dispersion sample (19%) is known to have a motionally narrowed line with the first moment of 750±10 ppm and a full width at half height (FWHH) of only ~85 ppm (Figure 1A). On the other hand, [13]CO adsorbed on highly dispersed Pd particles (56%) is known to have a wide ^{13}C NMR powder pattern covering an ~800 ppm range with a first moment of 410± 30 ppm (Figure 1B).

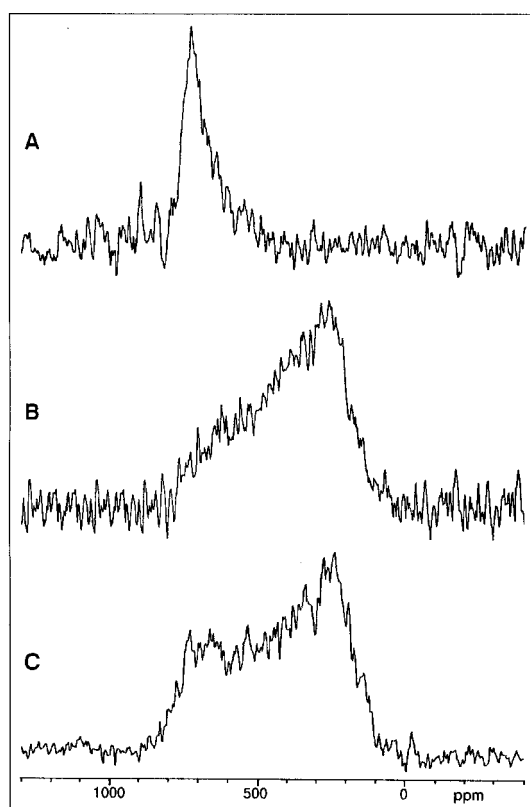Over several years, the spectra for high dispersion samples

Figure 1. ^{13}C static spin echo spectra of (A) a low dispersion CO/Pd/silica sample, (B) fresh high dispersion sample I, (C) aged high dispersion sample I. All spectra were acquired at room temperature.
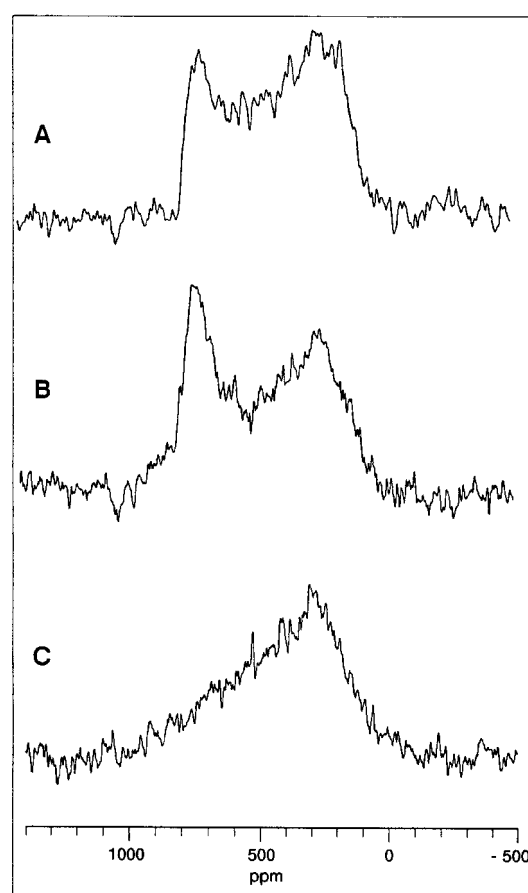

Figure 2. ^{13}C static spin echo spectra at room temperature of (A) aged high dispersion sample II, (B) aged high dispersion sample II after heating at 95±2°C for about 10 hours and (C) aged high dispersion sample II at - 158±2°C with 1 s recycle time.

were observed to show an increase of intensity near 750 ppm (Figure 1C). The spectrum of sample II freshly prepared (not shown) was the same as that of sample I shown in Figure 1B. The spectrum in Figure 2A of sample II after several years aging also displays the same overall line shape change. This change can be accelerated by heating the sample. Sample II was artificially aged by heating at 95±2 °C for about 10 hours. When it was cooled back to room temperature, the spectrum in Figure 2B was obtained. The narrow feature appearing at 750 ppm in the room temperature spectrum observed for sample II after annealing broadens when the spectrum is taken at a lower temperature (-158±2 °C) as shown in Figure 2C. This indicates that this feature is motionally narrowed at room temperature.

The appearance of the 750 ppm feature with aging or heat treatment in these samples is not to be confused with the reversible motional narrowing characterized by Slichter and co-workers.[5] The 750 ppm feature in these samples displays a similar reversible motional narrowing transition. The new observation made here is that the motional narrowing transition temperature for a portion of the chemisorbed CO changes irreversibly with prolonged aging or heat treatment.

The 750 ppm peak that appears over time or with sample annealing also has similar room temperature relaxation times T$_1$ (30±5 ms) and T$_2$ (270±30 μs) to those (64±10 ms and 265±135 μs, respectively)[5b] reported for ^{13}CO adsorbed on a low dispersion silica supported Pd catalyst. The T$_1$ for the motionally narrowed peak also seems to be affected by

sample preparation and composition. Thus, while T$_1$ of 64± 10 ms and 74±10 ms were reported for low dispersion Pd on silica (12% dispersion) and Pd on alumina (19% dispersion) supported samples,[5b,6,33] respectively, recently measured T$_1$'s of low dispersion samples in our laboratory were 56±6 ms for another silica supported sample, and 36±6 ms and 24± 5 ms for alumina supported samples. The T$_1$ and T$_2$ relaxation behavior of the 750 ppm feature does not appear to change upon aging.

Discussion

Previous work[5b,6,33] has shown that the 750 ppm peak observed at room temperature in low dispersion samples arises from mobile CO in a largely bridging configuration. This motion allows the CO to sample an entire particle's surface rapidly on the NMR time scale leading to a motionally narrowed line. By decreasing the temperature the motion may be slowed sufficiently to permit acquisition of the much broader static line shape with the first moment of 540 ppm.[33] In high dispersion samples much of the CO is found to bind in a linear fashion on electron deficient edge, kink or corner sites which are more prevalent on smaller metal particles.[4] The binding is much tighter at these sites and the linear CO is observed to be immobilized on the NMR time scale. The presence of this more tightly

bound CO on the rough surfaces of high dispersion Pd catalysts also obstructs the motion of the bridging CO effectively pinning these CO molecules as discussed elsewhere.[4]

Slichter and co-workers have found that the motional narrowing of the CO in the ^{13}C spectrum is associated with a surface phase transition in the ordering of the CO on the Pd surface.[5] In the low temperature phase the CO binding is of both the linear and bridging type. When the transition to the mobile high temperature phase has taken place, they describe the binding as predominantly bridging. Their work confirms our previous results[4] which showed that CO on highly dispersed Pd displays much less mobility than CO adsorbed on low dispersion Pd particles, and that the differences arise due to the increased importance of the more tightly bound linear CO as dispersion increases.

The similarity of the relatively large Knight shifted[30] resonance position and the fast NMR relaxation times for the 750 ppm peak in the aged samples reported in this paper and those observed previously in low dispersion samples indicates that the conduction electron densities at CO for the 750 ppm peaks in both samples are similar. This similar conduction electron density suggests that the CO for the 750 ppm must be on the surface of Pd particles which have at least several layers of Pd atoms. The line shape and temperature dependence of the line shape for the 750 ppm peak in the aged samples are also quite similar to those of observed in low dispersion samples. It implies that diffusion properties of CO for the 750 ppm peaks in both samples are almost identical. These observations permit us to assign this peak to *bridging mobile phase CO* in the aged samples. On the basis of these observations we conclude that the surfaces of the Pd Particles are smoothed by a reconstruction process.

We arrive at this conclusion as follows. As the surface is reconstructed, the defect sites such as kink or adatom sites are removed. With the removal of these defect sites, the bridging CO of which the mobility was obstructed by tight CO binding defect sites may diffuse more freely over the Pd particle surfaces. During the initial stages of reconstruction the defect sites were still remained enough to hinder the big increase of the diffusion rate. This diffusion rate at the initial stages of reconstruction will have little effect on the line shape observed at a single temperature. However, once this rate passes the critical threshold for motional line narrowing, the NMR line width will decrease rapidly.[5b,34] The growth of the 750 ppm peak then roughly monitors the increase in the number of mobile bridging CO molecules on particles where the surface diffusion has surpassed this critical rate. Increases in this peak that occur with time or heat treatment indicate further reconstruction so long as the spectra compared are measured at a single temperature. The NMR data presented in themselves indicate only that the fraction of the Pd surface where CO diffuses freely enough to give a motionally narrowed line increases with time. The reconstruction process observed here then seems to be a smoothing of the surface of the Pd particles which results in conversion of *bridging CO with little mobility* to *mobile bridging* CO rather than linear CO to mobile bridging CO. Edge sites where CO binds linearly must have increased in number as defect sites such as kink or adatom sites where

CO binds linearly also are removed from no change of the ratio of linear and bridging CO in IR spectra[7] over time. In addition, this surface smoothing must not result in a large reduction in the number of CO binding sites.[9] This conclusion follows from the fact that our samples were initially saturated with CO and sealed before aging or annealing. If particle surface smoothing occurred at the expense of the number of CO binding sites, some CO would have to be expelled into the gas phase. Gas phase CO gives a very narrow line in the ^{13}C NMR spectrum and is easily detected in samples of this sort. Since no such resonance line for gas phase CO was detected in any of the samples studied, we conclude that the reduction of the number of CO binding sites due to surface smoothing must not be significant enough to be detected in our NMR observations.

This surface reconstruction could also be accompanied by agglomeration of the Pd particles. Since the ^{13}C NMR spectra of the CO are primarily sensitive to surface effects, our data do not rule this possibility out. However, if particle growth takes place, in general it is expected to result in a larger number of reduction in dispersion than surface smoothing. Therefore, particle growth must not play a major role.

The ^{13}C NMR results reported in this manuscript should be compared with the EXAFS and IR results described by Anderson *et al.*[7] These workers found that the Pd-Pd EXAFS peak intensity nearly doubles after exposure to CO for only a few hours. Contact with CO for 30 hours or up to a month results in additional increases in the Pd-Pd peak of 13% and 18%, respectively. Comparable time dependent changes were not observed in their IR spectra. We judge their samples to be of somewhat higher dispersion than ours on the basis of the 1 : 1 bridging to linear CO intensity ratio[35] in their IR data. From their evidence Anderson *et al.* concluded that CO adsorption increased the ordering of the Pd in the supported metal particles and/or the particle growth took place.

In comparing these results to the NMR results contained herein it is important to note the differences in the experimental time scales. For our experiments the samples were exposed to CO and usually first investigated 1-2 days later. The time frame of the reconstruction observed here by NMR then is comparable only to that used in the longer time EXAFS measurements reported in reference 7. However, no significant changes in the NMR spectra were observed for such periods of time unless the samples were annealed at elevated temperatures. Exposure to CO at room temperature produced large changes in the ^{13}C NMR spectra only after several years.

The differences in the observations made by NMR and EXAFS can be attributed to several factors. One possibility is that this is simply a result of our catalysts having a lower dispersion and higher metal loading. Another possibility is that a portion of CO molecules not detected initially in NMR is observed after aging or heat treatment. However, this increase of CO detectable in NMR should have shown corresponding changes of IR spectra which was not observed. It can also be attributed to the fact that NMR and EXAFS probe the Pd ordering in very different ways. In EXAFS the average ordering of Pd in entire particles, which is a volumetric average rather than a surface average, is detected.

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Carbon-13 NMR of the adsorbed CO on the other hand is most sensitive to changes in the surface of the Pd particles, but not much sensitive to reordering of the inner atoms in Pd particles. Furthermore the appearance of a motionally narrowed peak occurs only after the surface reconstruction is sufficient to result in a diffusion rate that exceeds a critical value. The surface NMR probe as used here may easily be argued to become sensitive to the reconstruction only some time after it is apparent in the EXAFS. Thus, the kinetics of the slower reconstruction process as probed by NMR and EXAFS can be very different. Nevertheless, since the reconstruction as monitored by either the NMR or EXAFS techniques arises from the adsorption of CO, the structural changes in the Pd particles being observed must be related.

Another point to bear in mind in comparing our results to those of Anderson et al. is that the initial reconstruction observed by EXAFS occurs quite rapidly (minutes). Since CO was not adsorbed on the NMR samples in situ in the NMR spectrometer, one can argue that this step in the reconstruction took place already in our sample preparation. What is observed in the NMR experiments then is likely to be analogous to the changes observed in the long time EXAFS measurements. The surface reconstruction observed by NMR then occurs after the initial fast reconstruction, interpreted as particle growth by Anderson et al.

The NMR results reported here clearly indicate that surface reconstruction of Pd in the presence of CO takes place, and the EXAFS results show a definite increase in the average Pd coordination. While our NMR results and the previous IR results[7] favor reconstruction without particle growth, the previous EXAFS study[7] as well as oxide support effect study[7] favored particle growth. However, Anderson et al. noted that both were consistent with their EXAFS results. Differences in the dispersion of the catalysts studied and the manner in which the different techniques probe the samples make it difficult to draw further conclusion. Further experimentation is needed to determine what role particle growth plays in this reconstruction. A combined NMR, IR, and EXAFS study on catalysts from same batch would be helpful. EXAFS measurements taken on a sample quickly cooled to 77 K or below after the initial CO adsorption at room temperature would also be informative as to whether initial CO induced reconstruction observed in the EXAFS data in rapid enough to be missed in NMR measurements.

Conclusion

Carbon-13 NMR of CO adsorbed on highly dispersed Pd on silica shows that the surfaces of the Pd particles are reconstructed or smoothed in the presence of CO. This is indicated by the irreversible increase in the mobility of the chemisorbed CO at a particular temperature with aging or heat treatment. This reconstruction in the presence of CO has also been previously studied by EXAFS and IR measurements by Anderson et al.: Pd particle growth and/or reordering of Pd atoms in a particle were concluded. It is argued that particle growth which would greatly reduces the number of CO binding sites must take place, if it happens, during the NMR sample preparation and not afterwards. Differences in the catalysts studied and the manner in

which ^{13}C NMR and EXAFS probe the Pd particle structure make it difficult to compare the results. Nevertheless, the combined body of experimental data provides a very convincing case for the CO absorption induced reconstruction of high dispersion Pd particles.

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Structural and Optical Properties of the (C$_n$H$_{2n+1}$NH$_3$)$_2$SnCl$_4$ (n=2, 4, 6, 8, and 10) System

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K$_2$NiF$_4$-type layered compounds of the (C$_n$H$_{2n+1}$NH$_3$)$_2$SnCl$_4$ (n=2, 4, 6, 8, and 10) system have been synthesized from a stoichiometric mixture of SnCl$_2$ and alkyl ammonium salt using a low temperature solution technique under the inert atmosphere condition. Their crystal structures are assigned to the orthorhombic system by X-ray powder diffraction analysis. The a and b cell parameters show small changes. However, the c parameter is varied significantly according to the increment of alkyl chains of the organic layer which is located between inorganic layers in the compounds. The conformational phase transitions of the compounds are studied by the DSC in the temperature range of 300 to 500 K. FT-IR and Raman spectra are analyzed in the ranges of 1300 to 4000 cm^{-1} and of 50 to 360 cm^{-1} with Ar-laser (λ=514.5 nm) excitation, respectively. Photoluminescence phenomena are observed for some compounds. The bond-length of Sn-Cl is determined by the EXAFS spectroscopic analysis.

Introduction

Recently, much attention has been focused on organic-inorganic layered perovskites due to the tuneability of their special structural features and interesting physical properties. In the K$_2$NiF$_4$ type families of the formula (C$_n$H$_{2n+1}$NH$_3$)$_2$-MX$_4$ (where M is a divalent metal, and X is halogen), the MX$_4^2$ layers are sandwiched between organic barrier layers consisting of alkylammonium chains. As shown in Figure 1, the inorganic layers are built up from corner sharing halogen octahedra with an M^{2+} ion in the centers. The cavities between the octahedra are occupied by the RNH$_3^+$ polar head.[1]

Since the dielectric constant of barrier layer is much smaller than that of perovskite layers, the above compounds are known as natural quantum-well structures and fabricated to obtain devices with the required performance such as an electroluminescent device. Another benefit of the quantum-well structure is the ability to provide stages to study some basic phenomena such as the transport mechanism or the control of spontaneous emission by designing appropriate

structures.[2]

In low dimensional semiconductor quantum-well structures, the Coulomb interaction between an electron and a hole is enhanced by the quantum confinement effect.[3] The exciton binding energy in the two-dimensional structure is known to be four times larger than that in the bulk structures.[4] The quantum-well materials are applicable for use in non-linear optical, photoluminescent and electroluminescent devices due to excitonic effects.

The mechanism of the structural phase transition has been divided into two main classes.[5] One is an order-disorder transition of the rigid alkylammonium chains. The other is conformational transitions leading to a partial "melting" of the hydrocarbon atom with large enough n$\geq$4. Some of them show one main and other minor transitions. The main transition with the largest enthalpy variation is often referred to as the "melting" of the alkylchain and the minor transition has been assigned to the onset of reorientational motions of the NH$_3^+$ head group.[6]

A heterostructure electroluminescent device using (C$_6$H$_5$C$_2$H$_4$NH$_3$)$_2$PbI$_4$ as an emitter material has been demonstrated. The device produces highly intense green electroluminescence of the luminosity more than 10,000 cd/

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