The exceptional activity for methane combustion of modular palladium–ceria core–shell subunits on silicon-functionalized alumina that was recently reported has created renewed interest in the potential of core–shell structures as catalysts. Here we report on our use of advanced ex situ and in situ electron microscopy with atomic resolution to show that the modular palladium–ceria core–shell subunits undergo structural evolution over a wide temperature range. In situ observations performed in an atmospheric gas cell within this temperature range provide real-time evidence that the palladium and ceria nanoparticle constituents of the palladium–ceria core–shell participate in a dynamical process that leads to the formation of an unanticipated structure comprised of an intimate mixture of palladium, cerium, silicon and oxygen, with very high dispersion. This finding may open new perspectives about the origin of the activity of this catalyst.
Over the past several years, attention has increasingly been focused on efforts to engineer catalysts at the nanometre scale. These efforts have succeeded in generating a number of interesting and significant results, both in terms of the ability to synthesize new materials and to realize novel functionality. A recent example is the solution-based assembly of units composed of a palladium core and ceria shell (Pd@CeO₂)₁, which when homogeneously deposited onto a functionalized alumina support, yield a unique methane combustion catalyst².

Core–shell structures, such as noble metal (Ag, Au, Pd and Pt) particles in a carbon sphere³, Pt@CoO yolk/shell nanoparticles⁴, Pt@mSiO₂ (ref. 5), and Au nanoparticles in hollow ZrO₂ (ref. 6) and hollow SiO₂ (ref. 7) spheres, comprise a broad class of nanoengineered catalysts. In cases where a solid metal core is encapsulated in an oxide shell, the goal has usually been to isolate the metal particles from each other, in order to avoid sintering, while keeping active sites accessible. In the case of the Pd@CeO₂ catalyst¹, another goal was to ensure intimate contact between a central Pd nanoparticle and a surrounding shell, made of comparably sized CeO₂ nanocrystals, in order to promote more efficient total oxidation of methane. Electron microscopy characterization of the Pd@CeO₂ catalyst confirmed that a core–shell-like structure had initially been realized, thus apparently accounting for the unique catalytic performance observed.

In an attempt to better understand the connection between structure and activity, we perform a detailed electron microscopy study of supported Pd@CeO₂, including planar forms of the catalyst, using state-of-the-art ex situ and in situ transmission electron microscopy (TEM) with sub-angstrom resolution. Our results reveal an unexpected structural transformation that occurs upon air calcination at temperatures between 500 and 800 °C, which when homogeneously deposited onto a functionalized alumina support, yield a unique methane combustion catalyst².

Table 1 | HAADF images of the high-surface-area alumina-supported Pd@CeO₂ sample. (a–c) Calced at 500 °C and (d–f) calcined at 800 °C, both for 5 h. The arrow in (b) indicates an individual 2–3 nm particle. The arrows in (f) indicate very small, sub-nm features. Scale bars, 40 nm (a,d), 15 nm (b,e), 5 nm (c,f).
surface is due to the Si interlayer, according to EDS. EDS results, obtained from somewhat thicker regions of the layer, also confirmed the composition of palladium and ceria particles, inferred on the basis of lattice spacing, as shown in Fig. 2f. The valence state of Ce in this sample is 3+, according to electron energy loss spectroscopy (EELS); (Supplementary Fig. 3a,b).

Extended calcination and in situ observations. The presence of very small (1 nm across) features, found in both samples calcined at 800°C but in neither of the samples calcined at 500°C, prompted an examination of the effect of a short (30 min) 800°C ex situ air calcination treatment on the high-surface-area supported Pd@CeO₂ sample that had been calcined at 500°C. Surprisingly, this treatment caused the entire sample to become transformed into atom ‘clouds’ after about an hour. Since the alumina surface was Si functionalized, it seems likely that a silica layer is involved in the stabilization of these atomic-scale ‘clouds’. In fact, atom ‘clouds’ were not observed in analogous experiments performed on samples that did not contain Si (Supplementary Fig. 7). Although the zones around the particles shown in Fig. 4c gradually become blurred due to formation of the atom ‘clouds’, the shrinking particles are undoubtedly ceria, as shown by direct measurement of their lattice symmetry and spacing (Supplementary Fig. 6).

As the temperature of the sample in the gas cell was increased toward 650°C, other dynamical processes were also observed, as shown in Fig. 5a. In this example, the two particles in the dashed square are initially of equal size, with the lower one surrounded by a ‘cloud’. The contraction of the ‘cloud’, accompanied by the growth of the lower particle (again identified as ceria by its lattice symmetry and spacing) with time can be clearly seen in the sequential images between 15 and 21 min. Concurrently, the
particle appears to rotate and change shape in an attempt to minimize its surface energy, until it finally becomes a truncated octahedron bound by eight \{111\} planes (the lowest surface energy plane) and six \{100\} planes. This state is well accepted as the most stable shape for CeO$_2$ nanoparticles of this size$^9$–$^{11}$. Eventually, the two crystallites coalesce, driven by the tendency to lower overall surface energy. Many such examples of particle coalescence were observed, resulting in CeO$_2$ particles of 5–10 nm in diameter. However, very small (1–2 nm) features, similar to those observed in samples after \textit{ex situ} calcination at 800°C for 5 h, remained throughout the sample, as shown in Fig. 5b. The total heating time of the \textit{in situ} experiment was $\sim$250 min (Supplementary Fig. 8).

**Discussion**

In our attempt to better characterize Pd@CeO$_2$ supported on Si-functionalized alumina, the use of a novel \textit{in situ} electron microscopy technique has allowed us to observe the dynamics of structural transformations that occur under an oxidizing atmosphere. \textit{Ex situ} examination of samples calcined for 5 h at 500°C show that the Pd@CeO$_2$ structures are initially formed of a
energetically unfavourable at higher temperature. Atomic species structurally or chemically. However, the ‘clouds’ become with low mobility, where silica likely plays some role, either time: single atoms are released by smaller crystallites at 500 observations, where dynamic processes were followed in real {111} lattice planes in the larger particle-labelled ‘21’, 3.1 Å, confirms it is used to delineate the periphery of the atom ‘cloud’. The spacing between in its close vicinity, followed by particle coalescence. The dashed line is disappearance of an atom ‘cloud’ accompanied by the growth of a particle coexist with the large ceria and palladium particles. These scale species may have appeared first, and that the larger particles coarsely dispersed on the support. ex situ likely derived from ceria, but possibly also including palladium. group8,12–14. Similar arguments have been made concerning the surface-to-bulk ratio and valence state change from 4 + to 3 + when the thickness of the wall of ceria nanotubes change from 10 to 5 nm (ref. 14). In any case, initiation of such a reaction between ceria and silica could be facilitated by the lower cohesive energy of the ceria particles, arising both from their high surface area and excess surface oxygen vacancies. It has been shown in other studies that one such compound, Ce 9.33(SiO4)6O2, tends to gradually decompose back into a mixture of nanoscale ceria and silica as temperature is increased to ~800 °C in air15,16. Such decomposition and phase separation is consistent with our observation of the eventual growth of large particles and the appearance of Si-rich deposits around them in the model planar sample calcined at 800 °C.

While it is clear that the very small entities exist in both powder and model planar catalyst samples, calcined at 800 °C, we propose that a high concentration of the atom-scale species, seen most clearly in the model planar sample, is also present in the powder sample. In contrast, the 2–3 nm ceria and palladium particles do not survive the 800 °C calcination treatment. The structure of supported Pd@CeO2 thus evolves as shown in Fig. 6, according to all of our new observations. At the low-temperature extreme, this structure bears some resemblance to the core–shell structure, since 2–3 nm particles of ceria and palladium may be intimately mixed together, but at the high-temperature extreme, which corresponds closely to the calcination treatment used for the previously reported methane combustion experiments (850 °C)2, the structure consists of essentially two distinct forms, a mixture of coarse particles of ceria and palladium, that should be characterized by conventional catalytic behaviour, and a new structure in which ceria, palladium and silica are all present in a very highly dispersed form. It would thus appear that the unique catalytic properties arise from the new structure. A question that remains unanswered is the precise composition and structure of the material comprised of the atom-scale species. It has been reported that Pd-doped ceria–zirconia, or ionic Pd incorporated into the surface of ceria, can inhibit the PdO–Pd transformation17–19, which plagues the conventional methane combustion catalyst2. It is possible that the material in...
our newly found structure contains ionic Pd bonded to ceria in such a fashion. Post-reaction TEM examination, or in situ TEM studies performed under methane combustion conditions, could provide useful tests of this hypothesis.

Methods
Sample preparation. The preparation of Pd@CeO₂ and its deposition onto SiO₂-functionalized surfaces of Sasol TH100/150 alumina and yttria-stabilized zirconia single crystals was performed as described previously²⁸. All samples were initially calcined in laboratory air for 5 h at either 500 or 800 °C. The short (30 min) 800 °C ex situ air calcination treatment, subsequently performed on the high-surface-area sample that had initially been calcined at 500 °C, was done using compressed air.

TEM specimen preparation. High-surface-area samples were suspended in methanol with sonication and drop cast onto lacy carbon-on-copper grids (Pella). Cross-sectional and plan-view specimens of model planar samples were prepared by standard sample preparation methods. The model planar sample was first glued to a silicon sacrificial layer to protect the surface before diamond saw sectioning into small pieces, followed by mechanical polishing with diamond lapping film and low-angle (3°) Ar ion milling at 3 kV to electron transparency. Plan-view specimens were mechanically polished and ion milled from the substrate side only, thus no surface damage can be created.

Electron microscopy. Specimens were examined in a spherical aberration (Cₐ)-corrected JEOl JEM-2100F operated at 200 keV, equipped with EDS detectors and Gatan image filters for EELS acquisition. In situ observation was carried out on the same microscope using the Protochips Atmosphere system, which consists of a micro-electro-mechanical-systems (MEMS)-based closed cell, a heating holder, and a gas delivery manifold. The sample was situated between two SiN windows, each of 30–50 nm in thickness, with a 5 µm gap in between. The purity of oxygen used in the in situ experiment was 99.9995%. All reported temperatures are based on the Protochips calibration.

References
1. Cargnello, M., Wieder, N. L., Montini, T., Gorte, R. J. & Fornasiero, P. Synthesis of dispersible Pd@CeO₂ core – shell nanostructures by self-assembly. J. Am. Chem. Soc. 132, 1402–1409 (2009).
2. Cargnello, M. et al. Exceptional activity for methane combustion over modular Pd@CeO₂ subunits on functionalized Al₂O₃. Science 337, 713–717 (2012).
3. Sun, X. & Li, Y. Colloidal Carbon spheres and their core/shell structures with noble-metal nanoparticles. Angew. Chem. Int. Ed. Engl. 43, 597–601 (2004).
4. Yin, Y. et al. Formation of hollow nanocrystals through the nanoscale Kirkendall effect. Science 304, 711–714 (2004).
5. Joo, S. H. et al. Thermally stable Pt/ mesoporous silica core-shell nanocatalysts for high-temperature reactions. Nat. Mater. 8, 126–131 (2009).
6. Arnl, P. M., Comotti, M. & Schüth, F. High-temperature-stable catalysts by hollow sphere encapsulation. Angew. Chem. Int. Ed. Engl. 118, 8404–8407 (2006).
7. Lee, J., Park, J. C. & Song, H. A nanoreactor framework of a Au@ SiO₂ yolk/shell structure for catalytic reduction of p-nitrophenol. Adv. Mater. 20, 1523–1528 (2008).
8. Adijanto, L. et al. Exceptional thermal stability of Pd@ CeO₂ core-shell catalyst nanostructures grafted onto an oxide surface. Nano Lett. 13, 2252–2257 (2013).
9. Zhang, F., Jin, Q. & Chan, S. W. Ceria nanoparticles: size, size distribution, and shape. J. Appl. Phys. 95, 4319 (2004).
10. Wang, Z. L. & Feng, X. Polyhedral shapes of CeO₂ nanoparticles. J. Phys. Chem. B 107, 13563–13566 (2003).
11. Zhang, F., Jin, Q. & Chan, S. W. Ceria nanoparticles: size, size distribution, and shape. J. Appl. Phys. 95, 4319–4326 (2004).
12. Reddy, B. M. et al. Structural characterization of nanosized CeO₂-SiO₂, CeO₂-TiO₂, and CeO₂-ZrO₂ catalysts by XRD, Raman, and HREM techniques. J. Phys. Chem. B 109, 3355–3363 (2005).
13. Tschöpe, A. Interface defect chemistry and effective conductivity in polycrystalline cerium oxide. J. Electroceram. 14, 5–23 (2005).
14. Han, W.-Q., Wu, L. & Zhu, Y. Formation and oxidation state of CeO₂-x nanotubes. J. Am. Chem. Soc. 127, 12814–12815 (2005).
15. Kępiski, L., Wolczer, M. & Marchewka, M. Structure evolution of nanocrystalline CeO₂ supported on silica: effect of temperature and atmosphere. J. Solid State Chem. 168, 110–118 (2002).
16. Rocchini, E. et al. Relationships between structural/morphological modifications and oxygen storage–redox behavior of silica-doped ceria. J. Catal. 194, 461–478 (2000).
17. Primavera, A., Trovarelli, A., de Leitenburg, C., Dolcetti, G. & Llorca, J. Reactivity and characterization of Pd-containing ceria-zirconia catalysts for methane combustion. Stud. Surf. Sci. Catal. 119, 87–92 (1998).
18. Priolkar, K. et al. Formation of Ce₁-x PdₓO₂-x Solid solution in combustion-synthesized Pd/CeO₂ Catalyst: XRD, XPS, and EXAFS Investigation. Chem. Mater. 14, 2120–2128 (2002).
19. Colussi, S. et al. Nanofaceted Pd-O sites in Pd-Ce surface superstructures: enhanced activity in catalytic combustion of methane. Angew. Chem. Int. Ed. Engl. 48, 8481–8484 (2009).

Acknowledgements
The microcopy work was performed at Electron Microbeam Analysis Laboratory (EMAL) at the University of Michigan. This work was supported by Ford Motor Company under a University Research Proposal grant and the National Science Foundation under grants CBET-1159240 and DMR-0723032.

Author contributions
S.Z. performed the electron microscopy study and analysed the data. C.C. and M.C. synthesized material and prepared samples. G.W.G. and X.P. supervised the work. S.Z. performed the electron microscopy study and analysed the data. C.C. and M.C. synthesized material and prepared samples. G.W.G. and X.P. supervised the work. S.Z. performed the electron microscopy study and analysed the data. C.C. and M.C. synthesized material and prepared samples. G.W.G. and X.P. supervised the work. S.Z. performed the electron microscopy study and analysed the data. C.C. and M.C. synthesized material and prepared samples. G.W.G. and X.P. supervised the work.

Additional information
Supplementary Information accompanies this paper at http://www.nature.com/naturecommunications

Competing financial interests: The authors declare no competing financial interests.

Reprints and permission information is available online at http://npg.nature.com/reprintsandpermissions/

How to cite this article: Zhang, S. et al. Dynamic structural evolution of supported palladium–ceria core–shell catalysts revealed by in situ electron microscopy. Nat. Commun. 6:7778 doi: 10.1038/ncomms8778 (2015).

This work is licensed under a Creative Commons Attribution 4.0 International License. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in the credit line; if the material is not included under the Creative Commons license, users will need to obtain permission from the license holder to reproduce the material. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/