Core@shell electrocatalysts for fuel cells have the advantages of a high utilization of Pt and the modification of its electronic structures toward enhancement of the activities. In this study, we suggest both a theoretical background for the design of highly active and stable core@shell/C and a novel facile synthetic strategy for their preparation. Using density functional theory calculations guided by the oxygen adsorption energy and vacancy formation energy, Pd₃Cu₁@Pt/C was selected as the most suitable candidate for the oxygen reduction reaction in terms of its activity and stability. These predictions were experimentally verified by the surfactant-free synthesis of Pd₃Cu₁/C cores and the selective Pt shell formation using a Hantzsch ester as a reducing agent. In a similar fashion, Pd@Pd₄Ir₆/C catalyst was also designed and synthesized for the hydrogen oxidation reaction. The developed catalysts exhibited high activity, high selectivity, and 4,000 h of long-term durability at the single-cell level.

Over the last few decades, advanced catalysts for low-temperature fuel cells have been extensively studied using theoretical design and experimental validation 1–5. Nonetheless, there are still critical hurdles to overcome for electrocatalysis in proton exchange membrane fuel cells (PEMFCs), including 1) overcoming the sluggish oxygen reduction reaction (ORR) kinetics with a minimum amount of Pt, 2) developing novel selective catalysts for the hydrogen oxidation reaction (HOR) for the shutdown/startup stability of the stack, and 3) enhancing the physical/chemical durability of the catalysts 6–10. Despite the synthetic challenges, several notable studies have found that non-noble metal-alloys had significant activity and durability.

The advantage of core@shell nanostructures is high Pt utilization by interposition of the non-noble core, which further alters the electronic structure of Pt and stabilizes it by enhancing the interfacial bonding between the core and shell11. To date, reports on core@shell ORR catalysts can be classified by their synthetic approaches, which include the seed mediated sequential method 12–13, the galvanic-replacement reaction 14,15, and structural rearrangement (de-alloying or segregation) 16–19. However, studies of well-defined multi-metallic core@shells smaller than 10 nm are rare, particularly for the supported form that exhibits significant activity and durability and can potentially be used in real cells.

In this study, we computationally screened the potential core@shell combination and devised a facile synthesis route for the proposed structures. We also characterized performance and durability at the single cell level. To determine the best core@shell combinations for ORR, we performed density functional theory (DFT) calculations using two descriptors. The first descriptor is the oxygen adsorption energy (OAE) on the Pt shell to measure the reactivity10. The other descriptor is the vacancy formation energy (VFE) of Pt in the Pt shell to measure stability proposed in this study.

**Results**

The computational screening of activity and durability was performed on the overlayer-substrate system, which mimics core@shells, to avoid the complexity introduced from multiple atoms in the particles. In order to screen as many core@shell systems as possible, the thickness of the Pt overlayer was fixed at 1 monolayer (ML) (see...
Supplementary Fig. S24, S25 for details). The OAEs and VFEs of the pure elemental cores (Pd, Ir, Ni) are presented as open squares in Fig. 1. The OAE on vertical scale is difference between bulk Pt and core@shell structured model catalysts. The optimum OAE value (the horizontal dashed line) was referred from the work by Nørskov et al. 24–27 and Greeley et al. 21, 28. The VFEs on the horizontal scale are the averages which represent mixed property for symctically two different sites of “Up” and “Down” (Fig. S25). The OAEs of some metal@Pt were predicted to have better reactivity or stability than pure Pt. However, the reactivity was still far from the optimum value (the horizontal dashed line), which prompted us to extend the combinations to alloy cores (black circles). Though Pt₃Ni₃@Pt was predicted to be the most reactive, it was excluded due to its poor stability (i.e., its VFE was the lowest in alloy cores), which would result in poor long-term operational performance. Pt₃Ni₃@Pt and Pd₃Fe₄@Pt were predicted to have weaker OAE and corresponded to the experimmental results. 24–27. The better activity of Pt₃Ni₃@Pt reported from experiment could be explained by fact that the OAE of Pt₃Ni₃@Pt is closer to the optimum value than that of Pt. However, for Pd₃Fe₄@Pt, calculation showed a slight disagreement with experiment; 21 the stronger OAE and better activity than that of the calculation. According to the experiment the activity of Pd₃Fe₄@Pt was several times higher than that of Pt. This discrepancy might be originated from the uncertainty in the optimum value or computational accuracy. However, based on the relatively good stability and reactivity of Pt@Pt, we focused our attention on Pd-based 3d transition metal alloy cores to minimize the cost/activity ratio. As shown in Fig. 1, Pd₃Cu₄@Pt has the most suitable OAE and VFE, implying significant activity and durability. In addition, we devised a facile and robust route to synthesize this core@shell. 22–23.

Our novel two-step synthetic method is illustrated in Fig. 2. For the production of the C-supported form, the shell generation is typically achieved by reduction of the precursor on the prepared cores/C using a mild reducing reagent with the proper surfactants (i.e., amine reagents containing long alkyl chains and phosphine ligands) have traditionally been employed to synthesize the monodispersed metal nanoparticles, their residues may deteriorate the activities of the nanoparticles. Thus, understanding the surface chemistry of colloidal nanoparticles is crucial for developing an efficient stabilizing system. We postulated that benzyl ether could be utilized as a solvent and weak coordinating surfactant for the synthesis of Pd-based cores. Its short alkyl chain and weak coordinating property compared to nitrogen or phosphorous eliminates the need for its removal by unwanted heat treatment. Based on these characteristics, the synthesis of Pd/C and Pd₃Cu₁/C has been accomplished using benzyl ether and a mild borane tert-butylamine complex as a reducing reagent. A TEM image showed that Pd/C and Pd₃Cu₁/C are mono-dispersed with particle sizes of 3.5 nm (Fig. 3a and 3b). The lattice distances of Pd (2.41 Å) and Pd₃Cu₁ (2.12 Å), which were also analyzed by HRTEM, corresponded well with the XRD data (Supplementary Fig. S8–S12).

Adzic showed examples of Pd@Pt or PdAu@Pt electrocatalysts using galvanic displacement with sacrificing CuP. 29 Though the displacement enabled the preferential deposition of Pt on the cores, the retention of Cu as an alloy core material may be difficult with their method. We have tried to find mild redox systems that are capable of reducing the precursor on the metal surface but not strong enough to reduce the precursor on the carbon. A naturally occurring hydrogenation rebox process involving a combination of enzymes and hydride reduction cofactors is a good example. The Hantzsch ester, which was developed to perform the highly enantioselective transfer hydrogenation in organometallic chemistry, 30 is a suitable reducing agent for the preferential deposition of the shell on the cores. To the best of our knowledge, this is the first study that uses the Hantzsch ester as a reducing agent for the synthesis of inorganic nanoparticles.

The TEM micrographs (Fig. 3c and 3d) show well-dispersed spherical Pd₃Cu₁@Pt/C and Pd₃Cu₁@Ir/C particles that are larger than the cores (5 nm for Pd₃Cu₁@Pt and 8 nm for Pd₃Cu₁@Ir). It should be noted that isolated Pt or Pd₃Ir₆ nanoparticles were not found on the carbon, implying the exclusive deposition of the shell material on the cores. Although Cu loss due to displacement with the Pt precursor occurred in the absence of the Hantzsch ester, no such loss occurred in its presence. The unique function of the Hantzsch ester was further verified by the failure to form a selective shell in the presence of ascorbic acid or sodium borohydride, which are common reducing agents for core@shell synthesis (Supplementary Fig. S5, S6). Figure 3e,f depict the line-profile analysis using aberration-corrected STEM/energy dispersive spectrometry (EDS), revealing the distribution of the components in Pd₃Cu₁@Pt/C and Pd₃Cu₁@Ir/C. The lower Ir and Pt intensities and higher Pd and Cu intensities at the center clearly verify the formation of core@shell structures. The shell thicknesses and composition/amounts of the core were easily controlled (note that the shell thickness of Pd₃Cu₁@Pt was approximately 1 nm; 2–3 monolayers of Pt).

We performed an in-depth analysis by powder X-ray diffraction (PXRD) and extended X-ray absorption fine structure (EXAFS) studies to characterize the structure of the core@shell. Supplementary Figure S12 shows the PXRD scans, in which the Pd (111) of Pd₃Cu₁/C shifted to higher angles than that of pure Pd/C, indicating lattice contraction due to alloy formation. The contribution of Pt became clear after coating the Pt shell on the Pd₃Cu₁/C, which again shifted the peak to lower angles. This re-shifting indicates that the preparation of the Pt atoms on the Pd₃Cu₁ surface was satisfactory (note that Pt (111) exhibits an angle that is 0.356 degrees lower than that of Pd (111)). The local structural information of Pd₃Cu₁@Pt, such as the geometric effect of the Pd₃Cu₁ substrate on the contraction of the Pt shell due to variations in the shell thickness and Pt–Pt coordination number (CN), was obtained by Fourier-transformed (FT) k₃-weighted EXAFS analysis at the Pt LIII edge (Fig. S16). The peak centered at 2.5 Å represents the contribution of the first

![Figure 1](https://www.nature.com/scientificreports/) The computational screening of Pt-coated suitable core materials for the high activity and durability. The calculation was performed on the overlayer-substrate system with the fixed thickness of the Pt overlayer (1 monolayer). The optimum value of the reactivity indicated in the horizontal dashed line.
Figure 2 | Illustration of our novel two-step synthetic schemes for core@shell catalysts. Benzyl ether was utilized as a solvent as well as a weak coordinating surfactant for the synthesis of Pd-based cores without using surfactants. The Hantzsch ester is capable of reducing the shell precursors Pd$_3$Cu$_1$ greatly enhanced the ORR activity, the Pd$_4$Ir$_6$ shell coating from 30 to 45% is equivalent to an increase in the core size by around 1.5 eq Pt shell, which corresponds to a shell that is 1.8 times thicker, and the smaller Pt shell content (0.7 eq) was 1.7 times higher than that of the 30% core. The increase in the loading amounts results indicate the dependency of Pd$_3$Cu$_1$@Pt activity on the thickness of the Pt shell. A similar effect was achieved by tuning the core size and shell thickness with our simple and novel synthetic method.

The single cell performances for both Pd$_3$Cu$_1$@Pt/C and JM Pt/C as cathode catalysts (0.3 mgmetal/cm$^2$) are shown in Fig. 4c under the following operation conditions: 10 cm$^2$ active area, 70°C, and atmospheric pressure. The MEA with Pd$_3$Cu$_1$@Pt/C catalysts exhibited the best performance in the range of >0.5 V, particularly in the high voltage area (0.9–0.6 V), where the currents were 1.6 and 2.0 times higher than those of Pt/C MEA at 0.7 V and 0.8 V, respectively. The mass activities (inset) were also compared in terms of Pt mass and Pt + Pd mass and showed a higher mass activity for Pd$_3$Cu$_1$@Pt/C even when based on the Pt + Pd mass. The stability test of the Pd$_3$Cu$_1$@Pt/C single cell was performed at 400 mA/cm$^2$ (Fig. 4d) and resulted in an approximately 8% (0.73 V to 0.67 V) decay rate, even after 4,000 h of operation. The inset of Fig. 4d provides the results of the accelerated stability tests with potential cycling between open circuit voltage to 0.35 V and a scan rate of 10 mA/cm$^2$ at 70°C. After 3,000 min of potential cycling, the Pt/C cell performance decreased to 65% and 45% of its initial performance at 0.6 V and 0.7 V, respectively. However, the degradation of the Pd$_3$Cu$_1$@Pt/C single cell was half of the Pt/C cell degradation, indicating the superior stability of Pd$_3$Cu$_1$@Pt/C.

The OAEs with various Pt thickness for Pd$_3$Cu$_1$@Pt/C were presented in Fig. S27 (b). The OAE for Pt 2 ML showed the closest value to the optimum and corresponded well to experimental results for 2 ML of Pt covered the Pd$_3$Cu core. However, from the viewpoint of durability, Pt 1 ML showed the largest VFE as shown in Fig. S27 (a). This enhanced durability for Pt 1 ML were investigated using a Bader analysis of Pd$_3$Cu$_1$@Pt/C with Pt 1 ML compared to pure Pt layers (table S2). For pure Pt, there was a slight charge transfer from the subsurface to the surface by Friedel oscillations. The total charge at the surface Pt was estimated to be 10.045. The Bader charges of Pd and Cu in the bulk Pd$_3$Cu$_1$ phase are 10.10 and 10.70, respectively, implying a transfer of 0.1 electron from Cu to Pd. There was a
significant charge transfer from Pd$_3$Cu to Pt (Table S2: 0.112 electron from Pd, and 0.06 electron from Cu). Because Pd had already gained electrons from Cu, it had a sufficient amount of potential to transfer electrons to Pt. In addition, Cu was expected to exhibit a small amount of charge transfer. By increasing the Pt thickness to more than 2 ML, the charge at the surface Pt atom approached the value of pure Pt (10.045), which predicted the same VFEs for Pt layers thicker than 2 ML.

In addition, the electron donation from the Pd$_3$Cu$_1$ sub-layer to Pt was verified by the X-ray absorption near-edge structure (XANES) on the Pt $L_{III}$ edges of Pd$_3$Cu$_1$@Pt/C by varying the Pt thickness (Fig. 5a). The Pt $d$-band vacancy from the Pt $L_{III}$ white lines verified the electron transfer between the core and shell. It is important to note that the intensity of the white line, the magnitude of which is a direct measure of $d$-band vacancies, decreases as the Pt shell thickness decreases. Based on the studies by other researchers and our previous study, these XANES data clearly indicate electron donation from the Pd$_3$Cu$_1$ to Pt through strong metal-metal interactions.

For a more precise understanding of the electronic origin, we plotted the OAEs as a function of the local density of state (LDOS) at the Fermi level, as shown in Supplementary Fig. S28. As with the previous results, a linear relationship was observed, which indicated that the LDOS at the Fermi level was a good descriptor for predicting ORR activity. For predicting the stability, we plotted the difference in the charge density of Pd$_3$Cu$_1$@Pt from its pure states of Pd$_3$Cu$_1$ and Pt (Fig. 5b). Charge accumulation (yellow) along the Pt and Pd$_3$Cu$_1$ interface was obtained, while charge dissipation was found in the...
Pd₃Cu₁ substrate, implying charge transfer from the substrate to the Pt overlayer (Fig. 5c). The distribution of the transferred charge from Pd₃Cu₁ differs from other Pt₃M systems. Compared to the triangular-shaped charge transfer for other Pt₃M systems (Supplementary Fig. S29), the transferred charge in the Pd₃Cu₁ system forms a hexagonal ring consisting of three Pd and three Pt atoms (Fig. 5b), indicating that the active material for the charge transfer and interfacial bonding of Pd₃Cu₁@Pt was Pd.

**Discussion**

We have designed and developed highly active and stable Pd₃Cu₁@Pt/C (ORR) and Pd@PdIr₆ (HOR) electrocatalysts. The new core@shell combinations were designed using DFT calculations guided by the OAE and VFE. First, the surfactant-free synthesis of core/C and the subsequent exclusive shell formations on the core using the Hantzsch ester as a reducing agent were demonstrated for the first time. Superior characteristics, such as high activity, HOR selectivity, and 4,000 h of long-term durability, were achieved with the novel core@shell/C catalysts. The DFT calculations and XANES analysis strongly support the origin of the enhanced characteristics. The descriptors used in this study can be extended to screen other core@shell combinations.

**Methods**

**Chemical and materials.** Dihydrogen hexachloroplatinate (IV) hexahydrate, (H₂PtCl₆·6H₂O, 99.9%) was purchased from Alfa Aesar. Palladium (II) acetylacetonate (Pd(C₅H₈O₂)₂, 99%), Copper (II) acetylacetonate (Cu(C₅H₈O₂)₂, $^{99.99}$%), Iridium (III) chloride hydrate (IrCl₃·H₂O, $^{99.9%}$), Borane tert-butylamine complex (C₄H₁₄BN, 97%), benzyl ether (C₁₄H₁₄O, 98%), 200 proof anhydrous ethanol (C₂H₆O, $^{99.5%}$), and perchloric acid (HClO₄, 70%) were purchased from Aldrich. Diethyl 1,4-dihydro-2,6-dimethyl-3,5-pyridinedicarboxylate (C₁₃H₁₉NO₄, Hantzsch ester) was purchased from TCI. Unless otherwise stated, all commercial reagents and solvents were used without additional purification.

**Synthesis of carbon-supported Pd electrocatalysts (30 wt % of Pd/C).** To a three-neck round bottle flask (250 mL), carbon black (Vulcan XC-72R, 0.10 g) was dispersed in the 40 mL of benzyl ether, and stirred for 10 min at room temperature. Pd(acac)₂ (121.9 mg, 0.40 mmol) dissolved in benzyl ether (40 mL) were added to the reaction mixture at 70 °C, followed by the addition of the solution, borane tert-butylamine complex (97%, 600 mg) in 20 mL of benzyl ether. The resulting mixture was sealed with a Teflon and stirred at 100 °C for 4 h under Ar atmosphere. The reaction was cooled to room temperature, filtered through washing with pure ethanol (J.T. Baker, 99.0%). The filtered pastes were dried in the vacuum oven at 40 °C for 4 h.

Pd₃Cu₁/C core nanoparticles were prepared in the same manner as described above, except that 119.4 mg of Pd(acac)₂ and 34.2 mg of Cu(acac)₂ were used as the precursors of the metal for forming core materials.

**Shell deposition on carbon-supported core nanoparticles using Hantzsch ester.** Pt and Pd@Ir₆ shell layer on the surface of the core nanoparticles follows the same procedure as that for both Pd₃Cu₁/C and Pd/C. For the formation of Pt or PdIr shell electrocatalysts, 50 mg of Pd₃Cu₁/C or Pd/C was dispersed in 150 mL of anhydrous ethanol (99.9%) and sonicated for 30 s. Dihydrogen hexachloroplatinate (IV) hexahydrate, (H₂PtCl₆·6H₂O, 124.3 mg, 1.5 eq) and Hantzsch ester (5 eq of a Pt precursor, 1.2 mmol) dissolved in 40 and 20 mL of anhydrous ethanol respectively were added to the reaction solution at room temperature. The reaction mixture was then heated to 80 °C. Once the temperature of the reaction mixture reached 80 °C, the reaction was cooled down to room temperature and stirring was continued. The reaction mixture was then filtered through a Teflon membrane filter (pore size, 0.22 μm). The filtered pastes were dried in the vacuum oven at 60 °C for 4 h.
Characterization. Prepared Pd/C, Pd₃Cu₁/C, Pd₃Cu₁@Pt/C, and Pd@Pd₄Ir₆/C electrocatalysts were examined by X-ray diffraction (XRD, Rigaku D/Max 2500) with Cu Kα radiation, and X-ray photoelectron spectra (XPS, PHI 5800 ESCA) were obtained from a monochromator (Al Kα source) calibrated with respect to the C (1s) peak at 284.6 eV. EXAFS and XANES were conducted at the Pohang Light Source (PLS) with a ring current of 120–170 mA at 2.5 GeV using the 5A1 beamline. Particle size, size distribution, dispersion were confirmed by transmission electron microscopy (TEM, Philips CM30) and high resolution transmission electron microscopy (HR-TEM, FEI, 200 keV). The core@shell structure and chemical distribution of Pd₃Cu₁@Pt/C and Pd@Pd₄Ir₆/C nanoparticles were examined using an aberration-corrected 200 keV scanning transmission electron microscope (STEM) (Titan, FEI).

Figure 5 | Analysis and simulation of electronic structure in carbon-supported core@shell catalysts. (a), Pt L₃-edge XANES spectra and variation in unfilled d-states for samples having different shell thickness. Inset: enlargement of Pt L₃-edge XANES white line. (b), The distribution of the transferred charge from Pd₃Cu₁ in comparison with other Pt₃M (M = Ni, Co, Fe). (c), Charge accumulation (yellow) along the Pt and Pd₃Cu₁ interface and charge dissipation (cyan) in the Pd₃Cu₁ substrate.
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Author contributions
S.I.H., S.-C.L. and S.-K.K. conceived the project and designed the experiments. S.J.H., S.J.Y., Y.-H.C. performed the experiments. S.J.H., S.J.Y. performed the EXAFS and XANES measurement and analysis. J.S. and S.-C.L. contributed to the calculation work. J.H.J., E.C., Y.-E.S., S.W.N., T.-H.L. analyzed the data. S.I.H., S.-C.L. and S.-K.K. co-wrote the paper. All authors discussed the results and commented on the manuscript.

Additional information
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