two-dimensinal individual GO sheets (15, 18). The physical entanglement and strong covalent cross-links between graphitic planes may strongly improve the mechanical properties of conventional PAN-based carbon fibers and carbon nanotube fibers (15-17). Additionally, high-performance carbon fibers and carbon nanotube fibers can achieve more compact and more dense structures (e.g., up to a theoretical density of 2.2 g/cm<sup>3</sup> for carbon fibers and thus minimized voids and defects) (15, 16, 33).

High-performance carbon fibers are typically categorized into high-strength PAN-based fibers and high-modulus mesophase pitch-based carbon fibers (15, 16, 22). Thermal conductivity is typically lower for PAN-based carbon fibers because cross-linking atoms behave as scattering centers to reduce phonon transport (15). A strong correlation among the tensile strength, Young's modulus, and thermal and electrical conductivities was identified for mesophase pitch-based carbon fibers (22). High-temperature carbonization allows the development and growth of the crystalline graphitic domains and thus enables simultaneously high modulus and high conductivities for mesophase pitch-based carbon fibers (15, 22, 24). The superior thermal conductivity but lower modulus of the optimized graphene fibers as compared with mesophase pitch-based carbon fibers is unexpected and could be attributed to the unique fiber structure by intercalating large- and small-sized graphene sheets and substantially larger crystalline domain sizes in both transverse and longitudinal directions.

For graphene-based materials, heat conduction is dominated by phonon transport from lattice vibrations of the covalent sp<sup>2</sup> bonding network, and the electron transport is largely determined by the delocalized  $\pi$ -bond over the whole graphene sheet (1, 3, 18, 30). The lattice vacancies and the residual functional groups on graphene sheets upon thermal reduction create substantial numbers of phonon- and electronscattering centers, significantly degrading the thermal and electrical properties (1, 3, 18, 30). High-temperature annealing heals defects in the lattice structure and removes oxygen functional groups and significantly increases the size of the sp<sup>2</sup> domains (fig. S6). The crystallite sizes (Fig. 4F) in parallel and perpendicular directions to the fiber axis have been calculated from the integrated intensity ratios of the Dband (1350  $\text{cm}^{-1}$ ) and the G-band (1581  $\text{cm}^{-1}$ ) based on polarized Raman spectra of the optimized graphene fibers annealed at different temperatures (Fig. 4E and fig. S8) (31, 32). At lower annealing temperatures (e.g., 1800°C), graphene fibers demonstrate smaller-sized sp<sup>2</sup> domains (40 to 50 nm) with residual defects. The domain sizes of the optimized graphene fibers in both longitudinal and transverse directions increase substantially with the annealing temperature (Fig. 4F) and approach 783 and 423 nm, respectively, upon annealing at 2850°C. This is further evidenced by the submicrometer-sized crystalline domains along the fiber axis for the high temperature-treated fibers as observed in the

bright-field transmission electron microscope images (fig. S6). These are orders of magnitude larger than the nanocrystalline graphitic domains (several tens of nanometers) inside the mesophase pitch-based and PAN-based carbon fibers (15, 22, 32). Despite the relatively lower density, the reduced phonon scattering from the boundary and interface due to the larger-sized crystalline domains enables more efficient phonon transport and, thus, enhanced thermal conductivity. The highly thermally conductive and mechanically strong graphene fibers with intercalated large- and small-sized graphene sheets have potential for thermal management materials in high-power electronics and reinforcing components for high-performance composite materials.

### REFERENCES AND NOTES

- 1. A. A. Balandin, Nat. Mater. 10, 569-581 (2011).
- W. Jang, Z. Chen, W. Bao, C. N. Lau, C. Dames, Nano Lett. 10, 3909-3913 (2010).
- J. H. Seol et al., Science 328, 213-216 (2010). 3
- 4. C. Lee, X. Wei, J. W. Kysar, J. Hone, Science 321, 385-388
- (2008). X. Du, I. Skachko, A. Barker, E. Y. Andrei, Nat. Nanotechnol. 3, 491-495 (2008).
- Z. Xu, C. Gao, Nat. Commun. 2, 571 (2011). 6.
- Z. Xu. C. Gao, Acc. Chem. Res. 47, 1267-1276 (2014).
- 8. Z. Xu, H. Sun, X. Zhao, C. Gao, Adv. Mater. 25, 188-193 (2013).
- 9 H.-P. Cong, X.-C. Ren, P. Wang, S.-H. Yu, Sci. Rep. 2, 613
- (2012).
- 10. M. K. Shin et al., Nat. Commun. 3, 650 (2012).
- 11. X. Hu, Z. Xu, Z. Liu, C. Gao, Sci. Rep. 3, 2374 (2013).
- 12. C. Xiang et al., ACS Nano 7, 1628-1637 (2013).
- 13. Z. Xu, Z. Liu, H. Sun, C. Gao, Adv. Mater. 25, 3249-3253 (2013).
- 14. P. M. Adams, H. A. Katzman, G. S. Rellick, G. W. Stupian, Carbon 36, 233-245 (1998).

- 15. X. Oin, Y. Lu, H. Xiao, Y. Wen, T. Yu. Carbon 50, 4459-4469 (2012).
- 16. K. Naito, Y. Tanaka, J.-M. Yang, Y. Kagawa, Carbon 46, 189-195 (2008).
- 17. N. Behabtu et al., Science 339, 182-186 (2013).
- 18. G. Xin et al., Adv. Mater. 26, 4521-4526 (2014).
- 19. C. Xiang et al., Adv. Mater. 25, 4592-4597 (2013). 20. L. Chen et al., Nanoscale 5, 5809-5815 (2013),
- 21. Materials and methods are available as supplementary
- materials on Science Online.
- 22. F. G. Emmerich, Carbon 79, 274-293 (2014).
- 23. J.- Wang, M. Gu, W.- Ma, X. Zhang, Y. Song, New Carbon Mater. 23, 259-263 (2008).
- 24. N. C. Gallego et al., Carbon 38, 1003-1010 (2000).
- 25. A. F. Thünemann, W. Ruland, Macromolecules 33, 1848-1852
- (2000). 26. A. Gupta, I. R. Harrison, J. Lahijani, J. Appl. Cryst. 27, 627-636 (1994).
- 27. C. Zhu et al., Carbon 50, 235-243 (2012).
- 28. S. Zhang et al., Nat. Mater. 9, 594-601 (2010).
- 29. L. Song et al., Carbon 52, 608-612 (2013).
- 30. S. Pei, H.-M. Cheng, Carbon 50, 3210-3228 (2012).
- 31. L. G. Cançado et al., Appl. Phys. Lett. 88, 163106 (2006).
- 32. M. Endo et al., Phys. Rev. B 58, 8991-8996 (1998).
- 33. J. N. Wang, X. G. Luo, T. Wu, Y. Chen, Nat. Commun. 5, 3848 (2014).

#### ACKNOWLEDGMENTS

This work is financially supported by the U.S. National Science Foundation under awards DMR 1151028 and CMMI 1463083.

#### SUPPLEMENTARY MATERIALS

www.sciencemag.org/content/349/6252/1083/suppl/DC1 Materials and Methods Supplementary Text Figs. S1 to S8 Table S1 References (34-40)

8 January 2015; accepted 30 July 2015 10.1126/science.aaa6502

# CATALYSIS

# **Sustainable Fe-ppm Pd nanoparticle** catalysis of Suzuki-Miyaura cross-couplings in water

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Most of today's use of transition metal-catalyzed cross-coupling chemistry relies on expensive quantities of palladium (Pd). Here we report that nanoparticles formed from inexpensive FeCl<sub>3</sub> that naturally contains parts-per-million (ppm) levels of Pd can catalyze Suzuki-Miyaura reactions, including cases that involve highly challenging reaction partners. Nanomicelles are employed to both solubilize and deliver the reaction partners to the Fe-ppm Pd catalyst, resulting in carbon-carbon bond formation. The newly formed catalyst can be isolated and stored at ambient temperatures. Aqueous reaction mixtures containing both the surfactant and the catalyst can be recycled.

recious metal catalysis has been and continues to be a predominant means of C-C, C-H, and C-heteroatom bond construction in organic synthesis. In particular, palladium-catalyzed Suzuki-Miyaura, Heck,

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and Negishi couplings are indispensable, as recognized by the 2010 Nobel Prize (1, 2). However, economically accessible supplies of Pd and other precious metals are dwindling, thus raising concerns about the sustainability of this chemistry (3).

To circumvent this situation, alternative metals such as nickel (4, 5) and copper (6, 7) have been studied, especially as applied to the heavily used, Pd-catalyzed Suzuki-Miyaura reactions (8, 9). Despite varying degrees of success, Pd remains, by far, the most effective metal for such reactions. In trace levels, perhaps as impurities in salts of less expensive metals, Pd could ultimately prove to be both natural and sustainable for use in catalysis. Here we disclose such a discovery: a technique that takes a readily available commercial salt derived from Earth-abundant iron which naturally contains parts-per-million (ppm) levels of Pd—and processes it, in a single step, into highly active nanoparticles capable of mediating Suzuki-Miyaura cross-couplings in recyclable water as the reaction medium.

At the heart of this advance lies the confluence of several reaction variables: the origin and source of the iron salt, the presence of ppm levels of Pd, the manner through which these are converted to nanoparticles, and the use of aqueous micellar conditions for catalysis. The catalyst preparation calls for the use of inexpensive (97% purity) FeCl<sub>3</sub> containing ppm levels of Pd, admixed with a ligand and dissolved specifically in tetrahydrofuran (THF). Treatment of this solution at room temperature with two equivalents of a Grignard reagent, also in THF, quickly affords nanoparticles that, after solvent removal in vacuo, can be used directly in Suzuki-Miyaura reactions. The in situ generation of 5 mole percent (mol %) of these Fe-ppm Pd nanoparticles was found empirically to be sufficient. Next, an aqueous solution containing 2 weight percent (wt %) of our commercially available designer surfactant TPGS-750-M (10) and a base ( $K_3PO_4$ · $H_2O$ , 1.5 to 2.0 equivalents) is added to the nanoparticles. Reaction partners 1 and 2 as model substrates are then introduced, leading to biaryl product 3 (Fig. 1). The choice of ligand is crucial (Fig. 1), with SPhos (2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl) and XPhos (2-dicyclohexylphosphino-2',4',6'triisopropylbiphenyl) affording the best results. Vigorous stirring at temperatures between ambient and 45°C, depending upon the extent of crystallinity of the reaction partners, is sufficient to drive couplings to completion, typically in the 12- to 24-hour time frame (at a global concentration of 0.5 M).

We examined the scope of this technology and found that many representative cases afford good-to-excellent isolated yields (Fig. 2). A broad variety of aromatic and heteroaromatic arrays, with either partner being the aryl halide or boron derivative, can be tolerated. Functional groups including CF<sub>3</sub>, amines, acetals, amides, aldehydes, esters, ketones, phosphate esters, nitro groups, polyaromatics, sulfonamides, and carbamates are represented among these examples. Several types of heteroaromatic arrays are also amenable, including nitrogen-containing moieties that might present complications as competing ligands for Pd. Both bromides and iodides are excellent educts, and the boron species involved can be any of those commonly employed: boronic acids, Bpin (boronic acid pinacol ester) (11) or N-methyliminodiacetic acid (MIDA) boronates (12, 13), and BF<sub>3</sub>K salts (14, 15).

The composition of the iron salt plays a role in the activity of the resulting nanoparticles, as

does the manner in which the salt is reduced. Attempts to use  $Fe(acac)_3$  (acac, acetylacetonate) and iron pyrophosphate  $[Fe_4(P_2O_7)_3]$ , as well as several other salts (table S2), led to a far less reactive catalyst (also formed in situ) than that derived from FeCl<sub>3</sub>. Analysis of FeCl<sub>3</sub> from a commercially available source by inductively coupled plasma (ICP) atomic absorption spectrometry showed that ~300 to 350 ppm Pd was present. Sources that contained less precious metal (16, 17) led to incomplete reactions under otherwise identical conditions. Doping alternative sources of  $\text{FeCl}_3$  ( $\geq 97\%$  purity) with 350 ppm Pd(OAc)<sub>2</sub> (OAc, acetate) yielded nanoparticles of identical activity, as assessed by using the model reaction that produced 3 (table S14) (17-20). However, attempts to use these ppm levels of Pd in the absence of preformed iron-based nanoparticles led to virtually no reaction, suggesting that the release of Pd into the aqueous medium is not responsible for the catalysis observed. Although the use of Grignard reagents MeMgX (X = Cl or Br) and *i*-PrMgCl yielded material of comparable activity, both PhMgCl and *n*-hexyl-MgBr, among other reductants (e.g., NaBH<sub>4</sub>, polymethylhydrosiloxane), led to nanoparticles of inferior quality (table S4).

Successful couplings require the presence of both Fe and Pd within these nanocomposites, as determined by several control reactions (Fig. 3). Reactions that were attempted using 400 ppm Pd(OAc)<sub>2</sub>, with SPhos as a ligand in various ratios, did not lead to product formation. The use of 5 mol % pure FeCl<sub>3</sub> with 400 ppm Pd(OAc)<sub>2</sub> and 500 ppm SPhos, without prior treatment with MeMgCl, afforded none of the biaryl product. However, upon reduction of 5 mol % pure FeCl<sub>3</sub> with 10 mol % MeMgCl in the presence of 320 ppm  $Pd(OAc)_2$  and 5 mol % SPhos, a highly active nanocatalyst was generated that mediated the desired coupling to deliver pure product in a 95% isolated yield.

Doping pure FeCl<sub>3</sub> with 500 ppm of other metals, such as NiCl<sub>2</sub>, Ni(acac)<sub>2</sub>, CoCl<sub>3</sub>, MnCl<sub>2</sub>, Cu(OAc)<sub>2</sub>, or CuBr<sub>2</sub>, led to catalysts that produced variable levels of product formation. In all cases, the yields were  $\leq$ 38%, as compared with 95% obtained in the presence of added Pd(OAc)<sub>2</sub> (table S5).

Solid iron nanoparticles formed from FeCl<sub>3</sub> and MeMgCl were collected and analyzed by transmission electron microscopy (TEM) and x-ray photoelectron spectroscopy (XPS) (figs. S8 to S11). As illustrated in fig. S11, XPS analysis revealed that most of this nanomaterial is raft-shaped; composed of large amounts of carbon (57.4%), oxygen (23.6%), magnesium (6.5%), and chlorine (9.8%); and characterized by an essentially 1:1 ratio between iron (1.4%) and phosphorus (in SPhos; 1.3%). The high levels of carbon and oxygen are associated with residual solvent (THF) integrated within these clusters; the C-O signal appears as a shoulder in the C1s spectrum (286.5 eV) (figs. S9 to S11). Only 1.4% iron, in the form of iron oxides (Fe 2p3, 710.86 eV), was present in the nanoparticles produced via reduction of FeCl<sub>3</sub> with MeMgCl in THF.

Cryogenic TEM (cryo-TEM) analysis revealed the aggregation of rafts of metal nanoparticles, either inside or around the nanomicellar surface (Fig. 4, A to C). Scanning electron microscopy (SEM), together with energy-dispersive x-ray (EDX) analyses, showed the presence of hybrid nanoparticles containing both iron and ligand (Fig. 4, D and E, and figs. S12 to S14). Further analyses by atomic force microscopy (AFM)

B(OH)<sub>2</sub> conditions 24 h, 45 °C MeO 2 3 1 yield 3 (%)\* ligand yield 3 (%)\* ligand entry entry 1 8 IPr 70 none 2 PPh<sub>3</sub> 28 9 SPhos 98 3 70 t-BuSPhos 92 dppf 10 75 4 dtbpf 11 **XPhos** 94 5 **Bidime** 81 12 t-BuXPhos 89 6 Tangphos 69 13 **BrettPhos** 44 7 **IMes** 50 14 t-BuBrettPhos 40

**Fig. 1. Ligand optimization for Fe-ppm Pd catalysis of Suzuki-Miyaura cross-couplings.** Conditions were as follows: 4-bromoanisole (0.5 mmol), naphthalene-1-boronic acid (0.75 mmol), 5 mol % Fe-ppm Pd nanoparticles, K<sub>3</sub>PO<sub>4</sub>•H<sub>2</sub>O (0.75 mmol), 2 wt % TPGS-750-M (1 ml). Asterisks indicate yields based on gas chromatography-mass spectrometry (GC-MS).



**Fig. 2. Couplings between aryl halides (Ar-X) and aryl (Ar') or alkenyl boron derivatives.** Unless otherwise noted, conditions for these couplings were as follows: Ar-X (0.5 mmol), Ar'-BRn (0.6 mmol), FeCl<sub>3</sub> (5 mol %), SPhos (5 mol %), MeMgCl (10 mol %), K<sub>3</sub>PO<sub>4</sub>•H<sub>2</sub>O (0.75 mmol), TPGS-750-M (2 wt %, 1 ml), 45°C. Room temperature, rt. Asterisks indicate the use of Ar-B(OH)<sub>2</sub> or Ar-B(MIDA) (1.2 mmol) and K<sub>3</sub>PO<sub>4</sub>•H<sub>2</sub>O (1.5 mmol). Reported yields are for isolated, chromatographically purified materials. 320 ppm Pd is required (the general procedure is described in detail in the supplementary materials).



Fig. 3. Control reactions documenting the importance of **both Fe and Pd in catalyst formation.** Details are provided in the supplementary materials.

(Fig. 4F) revealed an atypical arrangement of iron atoms intermixed mainly with Mg. These particles have a long shelf life ( $\geq 1$  month at

room temperature) and are virtually identical in catalytic activity to those prepared and used in situ.



Fig. 4. Catalyst characterization. (A to C) Cryo-TEM images of Fe-Pd nanorods in aqueous TPGS-750-M. (D and E) SEM images of the solid nanomaterial. (F) AFM image of the solid nanomaterial.

Thermogravimetric analysis (TGA) of nanomaterial revealed about a 40% total drop in weight between 60° and 145°C, corresponding to the loss of THF bound within the catalyst. Material heated beyond 145°C was stable up to 380°C. However, when the catalyst was preheated at 80°C under a vacuum for 12 hours (fig. S6), a loss of catalytic activity was observed, indicating the importance of THF in maintaining the nanocage structure.

Upon completion of a Suzuki-Miyaura coupling, in-flask extraction with a single organic solvent (e.g., ethyl acetate or methyl tert-butyl ether) at ambient temperatures produces crude material that can be further purified by standard means (fig. S2). The remaining aqueous mixture containing both nanomicelles and nanoparticles of iron can then be recycled, with a modest augmentation of Pd [i.e., 160 ppm Pd(OAc)<sub>2</sub>] at every other recycling to compensate for losses during extraction. Although the external addition of this Pd salt extends the catalyst activity, the manner in which it is reduced to active Pd(0) and how it is incorporated into the Fe nanoparticles remain unclear. Either the same or different educts can be used in these couplings, indicating the robustness of the process. Alternatively, with solid products, dilution with water could be followed by simple filtration to produce the targeted material

# A 1-pot sequential reactions



# **B** Fe-ppm Pd technology applied to a Sonogashira coupling



Fig. 5. Further applications of Fe-ppm Pd-catalyzed couplings. (A) Sequential reactions, including a Suzuki-Miyaura coupling using Fe-ppm Pd nanoparticles as the catalyst (TMSI, TMS iodide; DIPEA, diisopropylethylamine; cBRIDP, di-t-butyl(2,2-diphenyl-1-methyl-1-cyclopropyl)phosphine; KO-t-Bu, potassium t-butoxide; TIPSOH, triisopropylsilyl alcohol). (B) A representative example suggestive of the extension of this approach to Sonogashira couplings (OTBS, t-butyldimethylsilyloxy).

directly. The diluted filtrate could be augmented with TPGS-750-M to the original level (2 wt %) and reused, thereby creating little to no wastewater stream. The environmental factor (E factor) (21), a metric of "greenness" that has previously been applied to micellar catalysis (22), is very low (E factor = 3).

We used ICP to analyze the palladium content (<10 ppm) of a product formed via the technology presented here, and we compared the result with that quantified following a traditional Suzuki-Miyaura coupling in organic solvent (fig. S4). Residual palladium in the product derived from a standard coupling in dioxane was far higher than that observed using our nanoparticle approach.

Prospects for incorporating this water-based nanomicelle-nanometal technology into a onepot sequence of reactions are shown in Fig. 5A. Heteroaryl iodide 4, containing carbamate and trimethylsilyl (TMS) protecting groups, was generated in situ and then subjected to cross-coupling with alkenyl tetrafluoroborate salt 5, using the Fe-ppm Pd nanoparticle protocol. The coupling product 6 was then exposed to aqueous base to remove the TMS groups and effect elimination to 7, followed by butoxycarbonyl (Boc) deprotection to 8. Final aryl amination with bromobenzene to 9 provided entry to the bioactive class of 2,4,5substituted pyrazol-3-one compounds in a onepot sequence with an overall isolated yield of 68% (23).

In addition, testing the potential for this mixedmetal catalyst system to effect other important Pd-catalyzed reactions, such as Sonogashira couplings, was carried out (in the absence of added copper), following the example illustrated in Fig. 5B. The prognosis for a similar outcome is good.

#### **REFERENCES AND NOTES**

- 1. C. C. C. Johansson Seechurn, M. O. Kitching, T. J. Colacot,
- 1147–1164 (2012).
  J. Kooroshy, C. Meindersma, R. Podkolinski, M. Rademaker, T. Sweijs, A. Diederen, M. Beerthuizen, S. de Goede, *Scarcity* of *Minerals: A Strategic Security Issue* (No. 02/01/10, The Hague Center for Strategic Studies, The Hague, Netherlands, 2009).
- 4. F.-S. Han, Chem. Soc. Rev. 42, 5270-5298 (2013).
- J. C. Tellis, D. N. Primer, G. A. Molander, *Science* **345**, 433–436 (2014).
- S. K. Gurung, S. Thapa, A. Kafle, D. A. Dickie, R. Giri, Org. Lett. 16, 1264–1267 (2014).
- Y. Zhou, W. You, K. B. Smith, M. K. Brown, Angew. Chem. Int. Ed. 126, 3543–3547 (2014).
- M. R. Netherton, G. C. Fu, Adv. Synth. Catal. 346, 1525–1532 (2004).
- G. D. Allred, L. S. Liebeskind, J. Am. Chem. Soc. 118, 2748–2749 (1996).
- B. H. Lipshutz et al., J. Org. Chem. 76, 4379–4391 (2011).
  A. J. J. Lennox, G. C. Lloyd-Jones, Chem. Soc. Rev. 43,
- 412-443 (2014).
- 12. N. A. Isley, F. Gallou, B. H. Lipshutz, J. Am. Chem. Soc. 135, 17707–17710 (2013).
- S. J. Lee, T. M. Anderson, M. D. Burke, *Angew. Chem. Int. Ed.* 49, 8860–8863 (2010).
- 14. G. A. Molander, Y. Yokoyama, *J. Org. Chem.* **71**, 2493–2498 (2006).
- 15. S. Darses, J.-P. Genet, *Chem. Rev.* **108**, 288–325 (2008).
- 16. T. H. Bointon et al., Nano Lett. 14, 1751–1755 (2014).
- S. L. Buchwald, C. Bolm, Angew. Chem. Int. Ed. 48, 5586–5587 (2009).

- C. L. Chun, D. R. Baer, D. W. Matson, J. E. Amonette, R. L. Penn, Environ. Sci. Technol. 44, 5079–5085 (2010).
- Y.-P. Sun, X. Q. Li, J. Cao, W.-X. Zhang, H. P. Wang, Adv. Colloid Interface Sci. 120, 47–56 (2006).
- 20. I. Thomé, A. Nijs, C. Bolm, *Chem. Soc. Rev.* **41**, 979–987 (2012).
- 21. R. A. Sheldon, Green Chem. 9, 1273 (2007).
- R. A. Sheldon, *Green Chem.* 9, 1273 (2007).
  B. H. Lipshutz, N. A. Isley, J. C. Fennewald, E. D. Slack, *Angew.*
- Chem. Int. Ed. 52, 10952–10958 (2013).
- 23. P. N. Dube et al., Chem. Biol. Drug Des. 84, 409-419 (2014).

## ACKNOWLEDGMENTS

We thank Novartis for financial support; J. Feng for technical assistance; M. Cornish for acquisition of the AFM images; S. Kraemer for obtaining the cryo-TEM, SEM, and EDX data; and J. Matthey for providing Pd salts. Parts of this work were carried out in the Characterization Facility. University of Minnesota, which receives partial support from NSF through the Materials Research Science and Engineering Center (MRSEC) program. This work also made use of the University of California–Santa Barbara (UCSB) Materials Research Laboratory Central Facilities, supported by NSF's MRSEC program under award no. DMR-1121053. ICP-MS analyses were provided by J. Reilly (Novartis, Cambridge, MA). We also acknowledge support from NIH in the form of a Shared Instrument Grant to UCSB(IS100D012077-01A1). A preliminary patent covering this chemistry has been filed by the University of California–Santa Barbara. The experimental data reported in this paper are available in the supplementary materials.

### SUPPLEMENTARY MATERIALS

www.sciencemag.org/content/349/6252/1087/suppl/DC1 Materials and Methods Figs. S1 to S18 Tables S1 to S15 References (24–34)

13 June 2015; accepted 30 July 2015 10.1126/science.aac6936

# NATURAL HAZARDS

# Slip pulse and resonance of the Kathmandu basin during the 2015 Gorkha earthquake, Nepal

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Detailed geodetic imaging of earthquake ruptures enhances our understanding of earthquake physics and associated ground shaking. The 25 April 2015 moment magnitude 7.8 earthquake in Gorkha, Nepal was the first large continental megathrust rupture to have occurred beneath a high-rate (5-hertz) Global Positioning System (GPS) network. We used GPS and interferometric synthetic aperture radar data to model the earthquake rupture as a slip pulse ~20 kilometers in width, ~6 seconds in duration, and with a peak sliding velocity of 1.1 meters per second, which propagated toward the Kathmandu basin at ~3.3 kilometers per second over ~140 kilometers. The smooth slip onset, indicating a large (~5-meter) slip-weakening distance, caused moderate ground shaking at high frequencies (>1 hertz; peak ground acceleration, ~16% of Earth's gravity) and minimized damage to vernacular dwellings. Whole-basin resonance at a period of 4 to 5 seconds caused the collapse of tall structures, including cultural artifacts.

he shape of the slip-rate time function (STF) during a seismic rupture provides critical insight into the constitutive fault properties. The abruptness of the slip on-

set determines the high-frequency content of the STF, and hence the intensity of the near-field ground motion (1), whereas the tail, which discriminates pulse-like and crack-like ruptures (2), has a low-frequency signature. Therefore, resolving the STF with band-limited strong-motion records is difficult. Combining high-rate Global Positioning System (GPS) waveforms (3, 4), which capture both dynamic and permanent deformation, overcomes this limitation.

The 25 April 2015 moment magnitude  $(M_w)$  7.8 earthquake in Gorkha, Nepal resulted from the unzipping of the lower edge of the locked portion of the Main Himalayan Thrust (MHT) fault, along which the Himalayan wedge is thrust

over India (5). The earthquake nucleated ~80 km northwest of Kathmandu and ruptured a 140-kmlong segment of the fault (Fig. 1A), with a hypocentral depth of ~15 km and a dip angle of 7° to 12° (5, 6). The MHT accommodates most of the convergence between India and southern Tibet, with a convergence rate between 17 and 21 mm/year (7). For the 2015 event, which resulted in over 8000 deaths (mostly in Kathmandu and adjacent districts), modified Mercalli intensities (MMIs) reported by the National Society for Earthquake Technology-Nepal (NSET) (8) reached up to IX (violent shaking) and exceeded VI (strong shaking) over an area 170 km by 40 km. Kathmandu has been struck by repeated earthquakes in the past, with major destruction [MMI > X (extreme shaking)] in the years 1255, 1344, 1408, 1681, 1833, and 1934 (9-11). These earthquakes all occurred close to Kathmandu and have been