Fermi energies ($E_F = -0.17$ to $-0.43$ eV). We observe that the carrier density ($n_e$) changes linearly with $V_g$ (Fig. 2C) and graphene has an intrinsic doping $E_D = -0.17$ eV produced by charge transfer from the silica. Next, the analytic model is used to retrieve the protein permittivity from experimental results by adjusting a Lorentzian permittivity

$$\varepsilon_p(\omega) = n_f^2 + \frac{S_k^2}{\omega_k^2 - \omega^2 - i\Gamma_k}$$

Good agreement is observed between experimental and calculated spectra (Fig. 2B) for the protein Lorentzian parameters upon least-squares fitting. The extracted permittivity has a nondispersive term $n_f^2 = 2.08$ and shows two absorption peaks at 1608 and 1532 cm$^{-1}$, matching the amide I and II bands, respectively (Fig. 2D). The fitted permittivity is also in good agreement with independent protein permittivity measurements from ellipsometry for $n_f^2$ and IR reflection absorption spectroscopy (IRRAS) for $S_k$ and $\Gamma_k$ (20). There is, however, a small discrepancy, which we attribute to a slight overestimate of plasmon-protein coupling in the theoretical model. These results indicate that the proposed graphene biosensor combines refractive index sensing, so far a prerogative of visible plasmonic sensors, with the unique chemical specificity of mid-IR spectroscopy, together with the extra degree of freedom enabled by the graphene electro-optical tunability. The characteristics of our graphene biosensor become more evident by comparing its spectral response to that of a state-of-the-art metallic localized surface plasmon resonance (LSPR) sensor composed of a gold dipole-antenna array (Fig. 3). Both devices are first operated in a spectral range free of protein vibrational modes by setting graphene at $V_g = -20$ V and designing a gold dipole length $L = 2.6 \mu$m (Fig. 3A). Upon protein immobilization, we detect a resonance shift of 160 cm$^{-1}$ for graphene, which is approximately 6 times the 27 cm$^{-1}$ shift obtained with gold. Next, the operation spectrum is moved toward the protein amide I and II bands at $V_g = -120$ V and using a different gold sensor with $L = 2.1 \mu$m (Fig. 3B). Clearly, dynamic tunability of graphene is one of its main advantages over gold for surface-enhanced IR absorption (SEIRA), enabling sensing over a broad spectrum with a single device. In addition, for the SEIRA signal corresponding to the amide I band, the graphene sensor features a signal modulation of 127%, which is almost 3 times that observed with the gold sensor (11%). The large spectral shifts and absorption signals confirm the unprecedented sensitivity of our graphene biosensor to the complex refractive index of the target molecule. For similar IR-frequency plasmons, the graphene atomic thickness leads to a higher confinement, resulting in a much larger spatial overlap between the mid-IR plasmonic field and the analyte. Figure 3C shows the nearfield distribution of LSPR modes in graphene nanoribbons and gold dipole arrays calculated with a finite-element method. The field hotspots are located at the endpoints of the gold dipole and along the edges of the graphene nanoribbon. By computing the percentage of near-field intensity confined within a given distance $d$ from the structure (Fig. 3D), we observe that 90% of the mode energy is confined within 15 nm from the graphene surface, whereas the same percentage is spread over a distance 500 nm away from the gold surface, thus confirming the tighter field confinement of graphene in the mid-IR. As the biosensing signal comes only from the field inside the target volume, we also calculate the field overlap with an 8-nm-thick protein bilayer, which is 29% for graphene and only 4% for gold. The near-field intensity overlap can be experimentally extracted as the ratio of the relative resonance shift ($\Delta \omega/\omega$) and the permittivity variation ($\varepsilon_p - \varepsilon_p$) (24). This estimate yields 26% and 5% field overlap for graphene and gold, in good agreement with simulations (see above). These results demonstrate the ability of graphene to provide stronger light-protein interactions beyond state-of-the-art metallic plasmonic sensors; further improvement in the graphene structure should lead to even better sensitivity and spectral resolution.

REFERENCES AND NOTES
1. A. N. Grigorenko, M. Polini, K. S. Novoselov, Nat. Photonics 6, 749–756 (2012).
2. F. J. García de Abajo, Science 339, 917–918 (2013).
3. A. Vakil, N. Engheta, Science 323, 1291–1294 (2011).
4. M. Jablan, H. Buljan, M. Soljačić, Phys. Rev. E 80, 245435 (2009).
5. I. Ju et al., Nanotechnol. 6, 630–634 (2005).
6. H. Yan et al., Nat. Photonics 7, 394–399 (2013).
7. A. Weisssner et al., Nat. Mater. 14, 421–425 (2015).
8. Z. Fang et al., ACS Nano 7, 2388–2395 (2013).
9. V. W. Brar et al., Nano Lett. 13, 2541–2547 (2013).
10. Z. Fei et al., Nature 487, 82–85 (2012).
11. V. G. Kohners et al., Nano Lett. 11, 3370–3377 (2011).

ACKNOWLEDGMENTS
Supported by European Commission grants FP7-IEF-2013-625673-GRYPHON, Graphene Flagship CNECT-ICT-604391, and FP7-ICT-2013-613024-GRASP, the Spanish Ministry of Economy and Competitiveness (MINECO) “Fondo Europeo de Desarrollo Regional” (FEDER) through grant TEC2013-46568-R: NATO’s Public Diplomacy Division in the framework of “Science for Peace”; European Union’s Horizon 2020 research and innovation program under grant agreement No 644956, the Swiss National Science Foundation through project 133583, and Fundació Privada Cellex, the Severo Ochoa Program, and the Ramón y Cajal fellowship program. We also acknowledge École Polytechnique Fédérale de Lausanne and Center of MicroNano Technology for financial support and nanofabrication. This paper is dedicated to the memory of our friend and colleague, Julien Perrinseau-Barrier.

SUPPLEMENTARY MATERIALS
www.sciencemag.org/content/349/6244/165/suppl/DC1
Materials and Methods
Supplementary Text Figs. S1 to S3 Reference (25, 26)
12. B. validation et al. J. Appl. Phys. 113, 013110 (2013).
13. Y. Li et al., Nano Lett. 14, 1573–1577 (2014).
14. P. Li et al., Nano Lett. 14, 4400–4405 (2014).
15. P. R. Griffiths, J. A. De Haseth, Fourier Transform Infrared Spectrometry (Wiley, New York, 2007).
16. F. Neubrech et al., Phys. Rev. Lett. 101, 157403 (2008).
17. R. Adato, H. Altug, Nat. Commun. 4, 2154 (2013).
18. C. Wu et al., Nat. Mater. 11, 69–75 (2012).
19. Y. Zhong et al., J. Nanophotonics 9, 035791 (2015).
20. See supplementary materials on Science Online.
21. R. Adato et al., Nano Lett. 13, 2584–2591 (2013).
22. F. J. García de Abajo, ACS Photonics 1, 135–152 (2014).
23. E. D. Palik, Handbook of Optical Constants of Solids (Academic Press, New York, 1998).
24. J. D. Joannopoulos et al., Photonic Crystals: Molding the Flow of Light (Princeton Univ. Press, Princeton, NJ, 2011).

GALAXY EVOLUTION

An over-massive black hole in a typical star-forming galaxy, 2 billion years after the Big Bang

Benny Trakhtenbrot,1,6 C. Megan Urry,2,3,4 Francesca Civano,3,5 David J. Rosario,6 Martin Elvis,1 Kevin Schawinski,1 Hyewon Suh,5,7 Angelo Bongiorno,8 Brooke D. Simmons9

Supermassive black holes (SMBHs) and their host galaxies are generally thought to coevolve, so that the SMBH achieves up to about 0.2 to 0.5% of the host galaxy mass in the present day. The radiation emitted from the growing SMBH is expected to affect star formation throughout the host galaxy. The relevance of this scenario at early cosmic epochs is not yet established. We present spectroscopic observations of a galaxy at redshift $z = 3.328$, which hosts an actively accreting, extremely massive BH, in its final stages of growth. The SMBH mass is roughly one-tenth the mass of the entire host galaxy, suggesting that it has grown much more efficiently than the host, contrary to models of synchronized coevolution. The host galaxy is forming stars at an intense rate, despite the presence of a SMBH-driven gas outflow.

Several lines of observational evidence, spanning a wide range of cosmic epochs, have led to a commonly accepted picture wherein supermassive black holes (SMBHs, $M_{\text{BH}} > 10^6 M_\odot$; $M_\odot$ is the solar mass) coevolve with their host galaxies (1–4). Moreover, energy- and/or momentum-driven “feedback” from accreting SMBHs (Active Galactic Nuclei; AGN) is thought to quench star formation in the host galaxy (5). To directly test the relevance of such scenarios
early cosmic epochs (high redshifts, z) requires the most basic properties of SMBHs and their hosts, including masses and growth rates, to be observed. Several observational studies found that at z ≥ 2 (more than 3.3 billion years after the Big Bang), the typical BH-to-stellar mass ratio, MBH/M∗, increases toward higher redshifts (6–8), suggesting that some SMBHs were able to gather mass more efficiently, or faster, than the stellar populations in their hosts. To date, measurements of MBH at earlier epochs (z > 2) have only been conducted for small samples of extremely luminous objects [L_{bol} > 10^{46} \text{ erg s}^{-1}, (9–12)] representing a rare subset of all accreting SMBHs, with number densities on the order of 1 to 10 per Gpc^{3} [i.e., ∼10^{−10} to ∼10^{−8} Mpc^{−3}; (13)]. Moreover, the high AGN luminosities in such sources overwhelm the host galaxy emission and prohibit a reliable determination of M∗, and therefore of MBH/M∗. We initiated an observational campaign aimed at estimating MBH in x-ray-selected, unobscured z ∼ 3 to 4 AGN within the Cosmic Evolution Survey field (COSMOS; (14)). Such sources have lower AGN luminosities and are more abundant than the aforementioned luminous sources by factors of 10 to 1000 [e.g., (13, 15)] and thus form a more representative subset of the general AGN population. Moreover, the fainter AGN luminosities and rich multiwavelength coverage of AGN within the COSMOS field enable reliable measurements of the mass and growth rate of the stellar populations in the host galaxies (M∗ and star-formation rate, SFR).

COSMOS—947 is an x-ray-selected, unobscured AGN at z = 3.328, detected in both XMM-Newton and Chandra x-ray imaging data of the COSMOS field [see fig. S4 and sections S2 and S4 in the supplementary materials (16)]. We obtained a near-infrared (IR) K-band spectrum of COSMOS—947 using the MOSFIRE instrument at the W. M. Keck telescope, at which z = 3.328 covers the hydrogen Hβ broad emission line (see details in section S1 in the supplementary materials). The calibrated spectrum shows a very broad Hβ emission line, among other features (Fig. 1). Our spectral analysis indicates that the monochromatic AGN luminosity at rest-frame 5100 Å is L_{5100} = 3.58_{−0.08}^{+0.06} \times 10^{12} \text{ ergs s}^{-1}. The typical line-of-sight velocity (i.e., the full-width at half-maximum of the line) is 11,330_{−800}^{+800} \text{ km s}^{-1} (see section S1.2 in the supplementary materials). By combining this line width with the observed L_{5100} and relying on an empirically calibrated estimator for MBH based on the virial motion of ionized gas near the SMBH (17), we obtain MBH = 6.9_{−1.2}^{+0.8} \times 10^{9} M_{\odot}. All the reported measurement-related uncertainties are derived by a series of simulations and represent the 16th and 84th quantiles of the resulting distributions. These simulations indicate a SMBH mass larger than 3.6 \times 10^{9} M_{\odot} at the 99% confidence level (see sections S1.2 and S3 in the supplementary materials for more details). Determinations of MBH from single Epoch spectra of the Hβ emission line are known to also be affected by significant systematic uncertainties, of up to ∼0.3 to 0.4 dex. For a detailed discussion of some of the systematics and related issues, see section S3 in the supplementary materials. This high MBH is comparable with some of the most massive BHs known to date in the local universe (18) or with the masses of the biggest BHs in the much rarer, more luminous AGN at z ∼ 2 to 4 [e.g., (9)]. The bolometric luminosity of COSMOS—947 is in the range L_{bol} = (1.1 to 2.2) \times 10^{46} \text{ erg s}^{-1}, estimated either from the observed optical luminosity or the multwavelength spectral energy distribution. Combined with the measured MBH, we derive a normalized accretion rate of L_{bol}/MBH = 0.01 to 0.02. This value is lower, by at least an order of magnitude, than the accretion rates of known SMBHs at z ∼ 3.5 [e.g., (9, 10)]. Furthermore, assuming a standard radiative efficiency of 10%, we obtain an e-folding time scale for the SMBH mass of at least 2.1 \times 10^{9} \text{ years} (Gy) (see section S3 in the supplementary materials), which is longer than the age of the universe at z = 3.328. By contrast, even the most extreme models for the emergence of “seed” BHs predict masses no larger than M_{seed} ∼ 10^{5} M_{\odot} at z ∼ 10 to 20 [e.g., (19)]. Therefore, the SMBH powering CID—947 had to grow at much higher accretion rates and at a high duty cycle in the past, to account for the high observed MBH only 1.7 Gy after z = 20. CID—947 could have evolved from a parent population similar to the fast-growing SMBHs observed in z ≥ 5 quasars, which have L_{bol}/MBH > 0.5 and MBH = 10^{9} M_{\odot} (e.g., (11, 12)). The requirement for a high accretion rate in the very recent past is supported by the clear presence of a high-velocity outflow of ionized gas, observed in the rest-frame ultraviolet spectrum of the source (fig. S4). The broad absorption features of C IV 15489 and Si IV 13400 have maximal velocities of v_{max} = 12,000 \text{ km s}^{-1}. Assuming that this outflow is driven by radiation pressure, these velocities require an accretion rate of L_{bol}/MBH ≥ 0.1, as recently as 10^{5} to 10^{6} \text{ years} before the observed epoch (see section S4 in the supplementary materials). We conclude that the SMBH powering CID—947 is in the final stages of growth and that we are witnessing the shut-down of accretion onto one of the most massive BHs known to date.

The rich collection of ancillary COSMOS multicolor multiwavelength data available for CID—947 enables us to study the basic properties of its host galaxy (see details in section S2 in the supplementary materials). A previously published analysis of the observed spectral energy distribution of the emission from the source reveals an appreciable stellar emission component, originating from 5.6_{−0.5}^{+0.8} \times 10^{10} M_{\odot} in stars (20). Our own analysis provides a yet lower stellar mass, of M∗ = 4.4_{−0.4}^{+0.3} \times 10^{10} M_{\odot}. However, we focus on
the previously determined, higher stellar mass, as a conservative estimate. The source is also detected at far-IR and (sub)millimeter wavelengths, which allows us to constrain the SFR in the host galaxy to about 400 M⊙ year⁻¹. The stellar mass of the host galaxy is consistent with the typical value for star-forming galaxies at z ≈ 3 to 4 [i.e., the “break” in the mass function of galaxies; (21)]. Similarly, the combination of M∗ and SFR is consistent with the typical values observed at z ≈ 3 to 4, which appear to follow the so-called main sequence of star-forming galaxies (22). Thus, the host galaxy of CID-947 is a typical star-forming galaxy for its redshift, representing a population with a number density of about 5 × 10⁻³ Mpc⁻³ [e.g., (21)]. This suggests that neither the intense, ionizing radiation that emerged during the fast SMBH growth, nor the AGN-driven outflow, have quenched star formation in the host galaxy. The relatively high stellar mass and SFR of the host galaxy further suggest that it is unlikely that the AGN affected the host in yet earlier epochs. That is, even in this case of extreme SMBH growth, there is no sign of AGN-driven suppression of star formation in the host.

Our analysis indicates that the BH-to-stellar mass ratio for CID-947 is MBH/M∗ ≈ 1/8. In comparison, most local (dormant) high-mass BHs typically have MBH/M∗ ≈ 1/700 to 1/500 [see Fig. 2 and, e.g., (4, 29)]. The MBH/M∗ value that we find for CID-947 is thus far higher than typically observed in high-mass systems in the local universe, by at least an order of magnitude and more probably by a factor of about 50. The only local system with a comparable extreme mass ratio is the galaxy NGC 1277, which was reported to have MBH/M∗ ≈ 1/7 [with MBH = 1.7 × 10⁹ M⊙ ≈ 2.5 × 10⁹ M⊙ (CID-947); see (24), but also (25)]. At earlier epochs (still z < 2), the general trend is for MBH/M∗ to increase slightly with redshift, but typically not beyond MBH/M∗ ≈ 1/100 (see Fig. 3). Only a few systems with reliable estimates of MBH show MBH/M∗ reaching as high as 1/30 [e.g., (6–8)].

Given the high masses of both the SMBH and stellar population in CID-947, we expect this system to retain an extreme MBH/M∗ throughout its evolution, from z = 3.328 to the present-day universe. Because the M∗ that we find is already comparable to the most massive BHs known, it is unlikely that the SMBH will experience any further appreciable growth (i.e., beyond MBH ≈ 10²⁸ M⊙). Indeed, if the SMBH accretes at the observed rate through z = 2, it will reach the extreme value of ~10⁻¹⁰ M⊙, and by z = 1 it will have a final mass of ~2.5 × 10³⁰ M⊙.

As for the host galaxy, we can constrain its subsequent growth following several different assumptions. First, if one simply assumes that the galaxy will become as massive as the most massive galaxies in the local universe [M∗ = 10¹² M⊙; (26)], then the implied final mass ratio is on the order of MBH/M∗ ≈ 1/100. Alternatively, we consider more realistic scenarios for the future growth of the stellar population, relying on the observed mass (M∗) and growth rate (SFR). Our calculations involve different scenarios for the decay of star formation in the galaxy (see section S5 in the supplementary materials) and predict final stellar masses in the range M∗(z = 0) = (2 to 7) × 10¹³ M⊙, which is about an order of magnitude higher than the observed mass at z = 3.328. The
inferred final mass ratio is $M_{\text{BH}}/M_* \sim 1/50$. This growth can only occur if star formation continues for a relatively long period ($\sim 1$ Gyr) and at a high rate ($>50 M_\odot$ year$^{-1}$). This would require the presence of a substantial reservoir, or the accretion of cold gas, which, however, could not increase the SMBH mass by much. Finally, in the most extreme scenario, the star formation shuts down almost immediately (i.e., due to the AGN-driven outflow), and the system remains “frozen” at $M_{\text{BH}}/M_* \sim 1/10$ throughout cosmic time. If the SMBH does indeed grow more (i.e., beyond $10^{10} M_\odot$), this would imply yet higher $M_{\text{BH}}/M_*$. Thus, the inferred final BH-to-stellar mass ratio for CID-947 is, in the most extreme scenarios, about $M_{\text{BH}}/M_* \sim 1/100$, and probably much higher (see Fig. 2).

CID-947 therefore represents a progenitor of the most extreme, high-mass systems in the local universe, like NGC 1277. Such systems are not detected in large numbers, perhaps due to observational selection biases. The above considerations indicate that the local relics of systems like CID-947 are galaxies with at least $M_* \sim 5 \times 10^{10} M_\odot$. Such systems are predominantly quiescent (i.e., with low star-formation rates, SFR $< 1 M_\odot$ year$^{-1}$) and relatively rare in the local universe, with typical number densities on the order of $10^{-6}$ Mpc$^{-3}$ (26). We conclude that CID-947 provides direct evidence that at least some of the most massive BHs, with $M_{\text{BH}} \gtrsim 10^9 M_\odot$, already in place just 2 Gyr after the Big Bang, did not shut down star formation in their host galaxies. The host galaxies may experience appreciable mass growth in later epochs, without much further black hole growth, resulting in very high stellar masses but still relatively high $M_{\text{BH}}/M_*$. Lower-mass systems may follow markedly different coevolutionary paths. However, systems with $M_{\text{BH}}/M_*$, as high as in CID-947 may be not as rare as previously thought, as they can be consistently observed among populations with number densities on the order of $10^{-5}$ Mpc$^{-3}$, both at $z > 3$ and in the local universe, and not just among the rarest, most luminous quasars.

REFERENCES AND NOTES

1. L. Ferrarese, D. Merritt, Astrophys. J. 539, L9–L12 (2000).
2. K. Gebhardt et al., Astrophys. J. 539, L13–L16 (2000).
3. Z. Z. Zheng et al., Astrophys. J. 707, 1566–1577 (2009).
4. J. Kormendy, L. C. Ho, Annu. Rev. Astron. Astrophys. 51, 531–653 (2013).
5. A. C. Fabian, Annu. Rev. Astron. Astrophys. 50, 455–489 (2012).
6. A. Merloni et al., Astrophys. J. 708, 137–157 (2010).
7. R. Decarli et al., Mon. Not. R. Astron. Soc. 402, 2463–2463 (2012).
8. V. N. Bennert, M. W. Auger, T. Treu, J.-H. Woo, M. A. Malkan, Astrophys. J. 742, 107 (2011).
9. O. Shenker et al., Astrophys. J. 641, 547–557 (2004).
10. H. Netzer, P. P. Li, A. Trakhtenbrot, O. Shenker, I. Gury, Astrophys. J. 671, 1256–1263 (2007).
11. G. De Rosa et al., Astrophys. J. 739, 56 (2011).
12. B. Trakhtenbrot, H. Netzer, P. Li, O. Shenker, Astronom. J. 730, 7 (2011).
13. D. Masters et al., Astrophys. J. 755, 169 (2012).
14. N. Z. Scoville et al., Astrophys. J. Suppl. Ser. 172, 1–8 (2007).
15. F. Civano et al., Astrophys. J. 741, 91 (2011).
16. Data and methods: supplementary text, figures and tables are available on Science Online.
17. Y. Shen, Bull. Astron. Soc. Ind. 41, 61 (2013).
18. N. J. McConnell et al., Astrophys. J. 756, 193 (2012).
19. M. Volonteri, Astron. Astrophys. Rev. 18, 279–310 (2010).
20. A. Borgonovi et al., Mon. Not. R. Astron. Soc. 427, 3103–3133 (2012).