Table 1. Conditional probabilities $P(l|S)$ to detect the idler photon in state $l$ given detection of the signal photon in state $S$, at the point of maximum correlation for $\Delta t = 100$ ns delay between read and write pulses; all the errors are based on counting statistics of coincidence events.

| Basis | $P(H|H^\dagger)$ | $P(V|H^\dagger)$ | $P(V|V^\dagger)$ | $P(H|V^\dagger)$ |
|-------|----------------|----------------|----------------|----------------|
| 0°    | 0.92 ± 0.02   | 0.08 ± 0.02   | 0.88 ± 0.03   | 0.12 ± 0.03   |
| 45°   | 0.75 ± 0.02   | 0.25 ± 0.02   | 0.81 ± 0.02   | 0.19 ± 0.02   |

Fig. 4. Time-dependent entanglement fidelity of the signal and the idler $F_t$; circles for $\Delta t = 100$ ns, diamonds for $\Delta t = 200$ ns.

We have realized a quantum node by combining the entanglement of atomic and photonic qubits with the atom-photon quantum state transfer. By implementing the second node at a different location and performing a joint detection of the signal photons from the two nodes, the quantum repeater protocol $(II)$, as well as distant teleportation of an atomic qubit, may be realized. Based on this work, we estimate the rate for these protocols to be $R_2 = (\beta^{\pi/2})^2 R = 3 \times 10^{-2} s^{-1}$. However, improvements in $\beta$ that are based on increasing the optical thickness of atomic samples $(16)$, as well as elimination of transmission losses, could provide several orders of magnitude increase in $R_2$. Our results also demonstrate the possibility of realizing quantum nodes consisting of multiple atomic qubits by using multiple beams of light. This approach shows promise for implementation of distributed quantum computation $(20, 21)$.

**References and Notes**


Electric Field Effect in Atomically Thin Carbon Films

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We describe monocrystalline graphitic films, which are a few atoms thick but are nonetheless stable under ambient conditions, metallic, and of remarkably high quality. The films are found to be a two-dimensional semimetal with a tiny overlap between valence and conduction bands, and they exhibit a strong ambipolar electric field effect such that electrons and holes in concentrations up to $10^{13}$ per square centimeter and with room-temperature mobilities of $\sim 10,000$ square centimeters per volt-second can be induced by applying gate voltage.

The ability to control electronic properties of a material by externally applied voltage is at the heart of modern electronics. In many cases, it is the electric field effect that allows one to vary the carrier concentration in a semiconductor device and, consequently, change an electric current through it. As the semiconductor industry is nearing the limits of performance improvements for the current technologies dominated by silicon, there is a constant search for new, nontraditional materials whose properties can be controlled by the electric field. The most notable recent examples of such materials are organic conductors $(1)$ and carbon nanotubes $(2)$. It has long been tempting to extend the use of the field effect to metals [e.g., to develop all-metallic transistors that could be scaled down to much smaller sizes and would consume less energy and operate at higher frequencies]

than traditional semiconducting devices $(3)$. However, this would require atomically thin metal films, because the electric field is screened at extremely short distances $(\sim 1 \text{ nm})$ and bulk carrier concentrations in metals are large compared to the surface charge that can be induced by the field effect. Films so thin tend to be thermodynamically unstable, becoming discontinuous at thicknesses of several nanometers; so far, this has proved to be an insurmountable obstacle to metallic electronics, and no metal or semimetal has been shown to exhibit any notable $(>1\%)$ field effect $(4)$.

We report the observation of the electric field effect in a naturally occurring two-dimensional $(2D)$ material referred to as few-layer graphene $(FLG)$. Graphene is the name given to a single layer of carbon atoms densely packed into a benzene-ring structure, and is widely used to describe properties of many carbon-based materials, including graphite, large fullerens, nanotubes, etc. (e.g., carbon nanotubes are usually thought of as graphene sheets rolled up into nanometer-sized cylinders) $(5–7)$. Planar graphene itself has been presumed not to exist in the free state, being unstable with respect to the formation of curved structures such as soot, fullerens, and nanotubes $(5–14)$.
We have been able to prepare graphitic sheets of thicknesses down to a few atomic layers (including single-layer graphene), to fabricate devices from them, and to study their electronic properties. Despite being atomically thin, the films remain of high quality, so that 2D electronic transport is ballistic at submicrometer distances. No other film of similar thickness is known to be even poorly metallic or continuous under ambient conditions. Using FLG, we demonstrate a metallic field-effect transistor in which the conducting channel can be switched between 2D electron and hole gases by changing the gate voltage.

Our graphene films were prepared by mechanical exfoliation (repeated peeling) of small mesas of highly oriented pyrolytic graphite (15). This approach was found to be highly reliable and allowed us to prepare FLG films up to 10 μm in size. Thicker films (d ≥ 3 nm) were up to 100 μm across and visible by the naked eye. Figure 1 shows examples of the prepared films, including single-layer graphene [see also (15)]. To study their electronic properties, we processed the films into multiterminal Hall bar devices placed on top of an oxidized Si substrate so that a gate voltage $V_g$ could be applied. We have studied more than 60 devices with $d < 10$ nm. We focus on the electronic properties of our thinnest (FLG) devices, which contained just one, two, or three atomic layers (15). All FLG devices exhibited essentially identical electronic properties characteristic for a 2D semimetal, which differed from a more complex (2D plus 3D) behavior observed for thicker, multilayer graphene (15) as well as from the properties of 3D graphite.

In FLG, the typical dependence of its sheet resistivity $\rho$ on gate voltage $V_g$ (Fig. 2) exhibits a sharp peak to a value of several kilohms and decays to ~100 ohms at high $V_g$ (note that 2D resistivity is given in units of ohms rather than ohms × cm as in the 3D case). Its conductivity $\sigma = 1/\rho$ increases linearly with $V_g$ on both sides of the resistivity peak (Fig. 2B). At the same $V_g$ where $\rho$ has its peak, the Hall coefficient $R_H$ exhibits a sharp reversal of its sign (Fig. 2C). The observed behavior resembles the ambipolar field effect in semiconductors, but there is no zero-conductance region associated with the Fermi level being pinned inside the band gap.

Our measurements can be explained quantitatively by a model of a 2D metal with a small overlap $\delta\epsilon$ between conduction and valence bands (15). The gate voltage induces a surface charge density $n = \epsilon_0\delta\epsilon V_g / \epsilon e$ and, accordingly, shifts the position of the Fermi energy $\epsilon_F$. Here, $\epsilon_0$ and $\epsilon$ are the permittivities of free space and SiO$_2$, respectively; $e$ is the electron charge; and $t$ is the thickness of our SiO$_2$ layer (300 nm). For typical $V_g = 100$ V, the formula yields $n \approx 7.2 \times 10^{12}$ cm$^{-2}$. The electric field doping transforms the shallow-overlap semimetal into either completely electron or completely hole conductor through a mixed state where both electrons and holes are present (Fig. 2). The three regions of electric field doping are clearly seen on both experimental and theoretical curves. For the regions with only electrons or holes left, $R_H$ decreases with increasing carrier concentration in the usual way, as $1/ne$. The resistivity also follows the standard dependence $\rho^{-1} = \sigma = ne\mu$ (where $\mu$ is carrier mobility). In the mixed state, $\sigma$ changes little with $V_g$, indicating the substitution of one type of carrier with another, while the Hall coefficient reverses its sign, reflecting the fact that $R_H$ is proportional to $1/n$.
the difference between electron and hole concentrations.

Without electric field doping (at zero $V_g$), FLG was found to be a metal, which is seen as a shift of the peak in $\rho$ to large positive $V_g$. However, this shift is attributed to an unintentional doping of the films by absorbed water (16, 17). Indeed, we found that it was possible to change the position of the peak by annealing our devices in vacuum, which usually resulted in shifting of the peak close to zero voltages. Exposure of the annealed films to either water vapor or NH$_3$ led to their p- and n-doping, respectively (15). Therefore, we believe that intrinsic FLG is a mixed-carrier material.

Carrier mobilities in FLG were determined from field-effect and magnetoresistance measurements as $\mu = e\nu/\rho$ and $\mu = R_{xx}/\rho$, respectively. In both cases, we obtained the same values of $\mu$, which varied from sample to sample between 3000 and 10,000 cm$^2$/V·s. The mobilities were practically independent of absolute temperature $T$, indicating that they were still limited by scattering on defects. For $\mu = 10,000$ cm$^2$/V·s and our typical $n \approx 5 \times 10^{12}$ cm$^{-2}$, the mean free path is $\sim 0.4$ μm, which is surprising given that the 2D gas is at most a few Å away from the interfaces. However, our findings are in agreement with earlier high $\mu$ observed for intercalated graphite (5), where charged dopants are located next to graphene sheets. Carbon nanotubes also exhibit a very high $\mu$, but this is commonly attributed to the suppression of scattering in the 1D case. Note that for multilayer graphene, we observed mobilities up to $\sim 15,000$ cm$^2$/V·s at 300 K and $\sim 60,000$ cm$^2$/V·s at 4 K.

Despite being essentially gigantic fullerene molecules and unprotected from the environment, FLG films exhibit pronounced Shubnikov–de Haas (ShdH) oscillations in both longitudinal resistivity $\rho_{xx}$ and Hall resistivity $\rho_{xy}$ (Fig. 3A), serving as another indicator of the quality and homogeneity of the experimental system. Studies of ShdH oscillations confirmed that electronic transport in FLG was strictly 2D, as one could reasonably expect, and allowed us to fully characterize its charge carriers. First, we carried out the standard test and measured ShdH oscillations for various angles $\theta$ between the magnetic field and the graphene films. The oscillations depended only on the perpendicular component of the magnetic field $B \cos \theta$, as expected for a 2D system. More important, however, we found a linear dependence of ShdH oscillations’ frequencies $B_\nu$ on $V_g$ (Fig. 3B), indicating that the Fermi energies $\epsilon_\nu$ of holes and electrons were proportional to their concentrations $n$. This dependence is qualitatively different from the 3D dependence $\epsilon_\nu \propto n^{2/3}$ and proves the 2D nature of charge carriers in FLG. Further analysis (15) of ShdH oscillations showed that only a single spatially quantized 2D subband was occupied up to the maximum concentrations achieved in our experiments ($\sim 3 \times 10^{13}$ cm$^{-2}$). It could be populated either by electrons with mass $m_e \approx 0.06m_0$ (where $m_0$ is the free electron mass) located in two equivalent valleys, or by light and heavy holes with masses of $\sim 0.03m_0$ and $\sim 0.1m_0$, and the double-valley degeneracy. These properties were found to be the same for all FLG films studied and are notably different from the electronic structure of both multilayer graphene (15) and bulk graphite (5–7). Note that graphene is expected (5–7) to have the linear energy dispersion and carriers with zero mass, and the reason why the observed behavior is so well described by the simplest free-electron model remains to be understood (15).

We also determined the band overlap $\delta_e$ in FLG, which varied from 4 to 20 meV for different samples, presumably indicating a different number of graphene layers involved (18). To this end, we first used a peak value $\rho_{xx}$ of resistivity to calculate typical carrier concentrations in the mixed state, $n_g$ (e.g., at low $T$ for the sample in Fig. 2, A to C, with $\rho_{xx} \approx 4000$ cm$^2$/V·s and $\rho_{xy} \approx 8$ kilohms, $n_g$ was $\sim 2 \times 10^{11}$ cm$^{-2}$). Then, $\delta_e$ can be estimated as $n_g/D$, where $D = 2m_e/\hbar^2$ is the 2D density of electron states and $\hbar$ is Planck’s constant divided by $2\pi$. For the discussed sample, this yields $\delta_e \approx 4$ meV [i.e., much smaller than the overlap in 3D graphite ($\sim 40$ meV)]. Alternatively, $\delta_e$ could be calculated from the temperature dependence of $n_g$, which characterizes relative contributions of intrinsic and thermally excited carriers. For a 2D semimetal, $n_g(T)$ varies as $n_g(0K)/f(T) = f(T)$, where $f = 2\alpha/\hbar T/\delta e$ and $\alpha$ is Boltzmann’s constant; Fig. 2D shows the best fit to this dependence, which yields $\delta_e \approx 6$ meV. Different FLG devices were found to exhibit a ratio of $n_g(300K)/n_g(0)$ between 2.5 and 7, whereas for multilayer graphene it was only $\sim 1.5$ (Fig. 2D). This clearly shows that $\delta_e$ decreases with decreasing number of graphene layers. The observed major reduction of $\delta_e$ is in agreement with the fact that single-layer graphene is in theory a zero-gap semiconductor (5, 18).

Graphene may be the best possible metal for metallic transistor applications. In addition to the scalability to true nanometer sizes envisaged for metallic transistors, graphene also offers ballistic transport, linear current-voltage ($I$-$V$) characteristics, and huge sustainable currents ($\sim 10^8$ A/cm$^2$) (15). Graphene transistors show a rather modest on-off resistance ratio (less than 30 at 300 K; limited because
of thermally excited carriers), but this is a fundamental limitation for any material without a band gap exceeding $k_BT$. Nonetheless, such on-off ratios are considered sufficient for logic circuits (19), and it is feasible to increase the ratio further by, for example, using p-n junctions, local gates (3), or the point contact geometry. However, by analogy to carbon nanotubes (2), other, nontransistor applications of this atomically thin material ultimately may prove to be the most exciting.

References and Notes
11. Other methods of preparing thin graphitic layers exist. The closest analogs of FLG are nanometer-sized patches of graphene on top of pyrolytic graphite (12), carbon films grown on single-crystal metal substrates (14), and mesoscopic graphitic disks with thickness down to ~60 graphene layers (8, 9).
15. See supporting data on Science Online.

Hydrated Electron Dynamics: From Clusters to Bulk

The electronic relaxation dynamics of size-selected ($\text{H}_2\text{O})_n^-/(\text{D}_2\text{O})_n^- [25 \leq n \leq 50]$ clusters have been studied with time-resolved photoelectron imaging. The excess electron ($e_\text{aq}^-$) was excited through the $e_\text{aq}^-(p) \leftrightarrow e_\text{aq}^+(s)$ transition with an ultrafast laser pulse, with subsequent evolution of the excited state monitored with photodetachment and photoelectron imaging. All clusters exhibited p-state population decay with concomitant s-state repopulation (internal conversion) on time scales ranging from 180 to 130 femtoseconds for ($\text{H}_2\text{O})_n^-$ and 400 to 225 femtoseconds for ($\text{D}_2\text{O})_n^-$; the lifetimes decrease with increasing cluster sizes. Our results support the “nonadiabatic relaxation” mechanism for the bulk hydrated electron ($e_\text{aq}^-$), which invokes a 50-femtosecond $e_\text{aq}^-(p) \rightarrow e_\text{aq}^+(s)$ internal conversion lifetime.

A free electron introduced into a polar solvent, such as water (1) or ammonia (2), may be trapped by locally oriented solvent molecules. In water, an “equilibrated” hydrated electron ($e_\text{aq}^-(s)$) can be transiently confined within a roughly spherical cavity defined by six OH bonds oriented toward the negative charge distribution in the so-called Kevan geometry (3–5). The hydrated electron is an important reagent in condensed-phase chemistry and molecular biology, as it participates in radiation chemistry, electron transfer, and charge-induced reactivity. Thus, research investigating the dynamics of this species, whether in the presence or absence of other reagents, has attracted considerable attention in the theoretical and experimental physical chemistry communities. Here, we present time-resolved results on the electronic relaxation dynamics of anionic clusters of water that lend profound insight to the elucidation of hydrated electron dynamics in the bulk.

The electronic energetics of a hydrated electron are characterized by three types of states (Fig. 1A): a localized $e_\text{aq}^-(s)$ ground state; three localized, near-degenerate $e_\text{aq}^+(p)$ excited states; and a delocalized conduction band (CB) characterized by a charge distribution spread across hundreds of molecules in the solvent “network.” The visible absorption spectrum of the equilibrium hydrated electron, a broad band peaking at 720 nm (1), is well understood as an excitation from the occupied $e_\text{aq}^-(s)$ state to the vacant $e_\text{aq}^+(p)$ states (4, 5). The electron-solvent dynamics subsequent to $e_\text{aq}^-(p) \leftrightarrow e_\text{aq}^+(s)$ excitation are more controversial, however, in spite of considerable experimental (6–12) and theoretical (13, 14) effort devoted to this problem.

Transient absorption measurements made with femtosecond (fs) laser pulses as short as 5 fs (12) show a near infrared (NIR) absorption band beyond 900 nm developing on a 40- to 50-fs time scale after $e_\text{aq}^-(p) \leftrightarrow e_\text{aq}^+(s)$ excitation. This broad feature shifts back to shorter wavelengths on a time scale of several hundred fs, with recovery of the original $e_\text{aq}^-(s)$ absorption spectrum largely complete within ~1 picosecond (ps). Deuteration of the solvent (8, 12) appears only to affect the fastest measured time scale (i.e., the build-up time of the transient NIR absorption), with $T_{\text{pD}_2\text{O}/\text{H}_2\text{O}} = 1.4$ to 1.6. As described by Yokoyama et al. (8), two rather different energy relaxation mechanisms have been proposed to account for these observations. In the “adiabatic solvation” scheme (13, 14), the infrared transient at the earliest times is attributed to absorption of the $e_\text{aq}^-(p)$ electron, which is solvated on the upper state within 50 fs (process x in Fig. 1A). The excited electron then undergoes internal conversion (IC) to the ground state (y) on a 400-fs time scale, generating ground-state electrons that further relax on the ~1-ps time scale by dissipating energy to the solvent. In contrast, the “nonadiabatic relaxation” mechanism (7, 9, 12) invokes much more rapid IC, on a 50-fs time scale, and attributes the transient NIR band at early times to absorption of the ground-state electron in a vibrationally excited solvent environment. In this model, subsequent dynamics are assigned to reorganization of the local (~400 fs) and extended (~1 ps) solvent network following the electronic decay.

We present an alternative and complementary approach to assessing the relaxation dynamics of the hydrated electron through time-resolved photoelectron imaging (TRPEI) studies (15) of electron dynamics in size-selected water cluster anions, ($\text{H}_2\text{O})_n^-$ and ($\text{D}_2\text{O})_n^-$, with $25 \leq n \leq 50$. Water cluster anions were first detected mass spectromet-