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Permalink
https://escholarship.org/uc/item/4435j17d

Journal
Nature communications, 9(1)

ISSN
2041-1723

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Publication Date
2018-08-03

DOI
10.1038/s41467-018-05352-9

Peer reviewed
In situ formation of catalytically active graphene in ethylene photo-epoxidation

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Ethylene epoxidation is used to produce $2 \times 10^7$ ton per year of ethylene oxide, a major feedstock for commodity chemicals and plastics. While high pressures and temperatures are required for the reaction, plasmonic photoexcitation of the Ag catalyst enables epoxidation at near-ambient conditions. Here, we use surface-enhanced Raman scattering to monitor the plasmon excitation-assisted reaction on individual sites of a Ag nanoparticle catalyst. We uncover an unconventional mechanism, wherein the primary step is the photosynthesis of graphene on the Ag surface. Epoxidation of ethylene is then promoted by this photogenerated graphene. Density functional theory simulations point to edge defects on the graphene as the sites for epoxidation. Guided by this insight, we synthesize a composite graphene/Ag/α-Al₂O₃ catalyst, which accomplishes ethylene photo-epoxidation under ambient conditions at which the conventional Ag/α-Al₂O₃ catalyst shows negligible activity. Our finding of in situ photogeneration of catalytically active graphene may apply to other photocatalytic hydrocarbon transformations.

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Heterogeneous catalysts facilitate the economical production of commodity and fine chemicals, but their workings are often complex and shrouded in mystery\(^1,2\). Although the nature of the active site of the catalyst is often deducible from electronic structure simulations or ultrahigh vacuum single-crystal studies, but under realistic working conditions, the catalyst can be appreciably different in structure and mechanism from the idealization. Moreover, under reaction conditions, the catalytically active phase can involve a dynamically changing surface structure and/or composition, which is not reflected in a steady-state picture. In situ studies under working conditions are therefore of central importance in atomic-level elucidation, design, and optimization of industrially relevant catalysts.

The epoxidation of ethylene (C\(_2\)H\(_4\)) to ethylene oxide (EO), a major feedstock for several organic chemicals and plastics, is practiced on a massive scale of \(-2 \times 10^9\) tons\(^3\) and tens of billions of dollars worth of annual production\(^4\). The epoxidation reaction is catalyzed by an \(\alpha\)-Al\(_2\)O\(_3\)-supported Ag-based catalyst under high pressure (10–30 bar) and high temperature (200–300 °C) conditions\(^5\), a process that accomplishes high selectivity for EO in the face of the competing full oxidation of C\(_2\)H\(_4\) to CO\(_2\). However, accomplishment of C\(_2\)H\(_4\) epoxidation at moderate pressures and temperatures is desirable\(^6,7\) from the point of view of reducing heat energy input, enhancing energy efficiency, mitigating thermal damage and deactivation of the catalyst, and further enhancing EO selectivity by reducing high-temperature-favored processes such as isomerization of EO to acetaldehyde\(^8\) and full oxidation to CO\(_2\). Recently, visible-light photos excitation of plasmon-resonant Ag nanoparticles (NPs) has been shown to be effective at achieving C\(_2\)H\(_4\) epoxidation at less elevated temperatures and pressures\(^6,7,9\).

With the aim of understanding how C\(_2\)H\(_4\) epoxidation is catalyzed under visible-light excitation and ambient atmosphere conditions, we monitor the process on a supported Ag NP photocatalyst. Using in situ surface-enhanced Raman scattering (SERS), we interrogate surface chemical events occurring in real time on individual domains of the photocatalyst. The interrogation reveals an active phase and working mechanism of the photocatalyst deviating markedly from the presupposed picture of a pristine metal surface. The primary step in the photocatalysis is the dynamic photosynthesis of graphenic carbon from the C\(_2\)H\(_4\) precursor. The in situ photogenerated graphene serves to actively promote further C\(_2\)H\(_4\) epoxidation. Armed with the insight that the active photocatalytic phase involves graphenic carbon and not just the pristine metal surface, we prepare a composite graphene/Ag/\(\alpha\)-Al\(_2\)O\(_3\) photocatalyst. This composite photocatalyst accomplishes epoxidation at ambient temperature and pressure conditions, where a conventional Ag/\(\alpha\)-Al\(_2\)O\(_3\) photocatalyst shows low activity. Our study provides an example of how realistic knowledge of the active form of the photocatalyst can lead to advances in an industrially important chemical process.

**Results and discussion**

SERS monitoring of photocatalytic C\(_2\)H\(_4\) epoxidation on Ag NPs. The SERS monitoring was performed in a home-made reaction flow cell (Fig. 1a). The catalyst consisted of Ag NPs (Supplementary Figs. 1, 2) immobilized at a low area density on the SiO\(_2\) surface of the cell (Supplementary Fig. 3). A visible-wavelength laser served as the source for both photoactivation and SERS. SERS from individual emitters was monitored in real time with sub-second resolution under reaction conditions (C\(_2\)H\(_4\) + ambient air + 514.5 nm laser excitation). Here, an emitter

![Fig. 1](image_url)
refers to a discrete light-absorbing, light-scattering domain, consisting of one or a few Ag NPs (Supplementary Fig. 3). The single-domain spatial resolution and high sensitivity of SERS allowed us to capture reactants, intermediates, and products stochastically formed on the catalyst surface (Fig. 1), which are otherwise undetectable in spatially averaged measurements, due to their short lifetimes on the surface and/or low steady-state concentrations.

Prior to the introduction of C₂H₄, no distinct SERS bands are seen from individual emitters (Fig. 1d, e), confirming the surface cleanliness of the catalyst. After C₂H₄ is introduced, distinct SERS bands are seen to emerge (Fig. 1d, e and Supplementary Fig. 4) in some cases, following an induction period. Nearly 40% of all individual emitters monitored (Fig. 1b) showed such dynamic chemical activity. The remaining ~60% of the emitters show non-responsive SERS spectra under C₂H₄ flow (Fig. 1c, f), possibly due to the absence of an electromagnetic field hotspot for ample SERS amplification (e.g., single Ag NPs in Supplementary Fig. 3) or due to a significantly oxidized, inactive Ag surface. We did not study this non-responsive class of emitters further, instead focusing our attention on the responsive sub-population.

The SERS bands observed under reaction conditions (i.e., C₂H₄ flow) are well-defined with peak maxima at ~1340 and ~1570 cm⁻¹, which can be assigned, respectively, to the D and G bands of graphitic carbon. The presence of vibrational overtones at 2650 cm⁻¹ (2D mode), 2890 cm⁻¹ (D + G mode), and 3160 cm⁻¹ (2G mode) further confirms the assignment of the SERS spectrum (Fig. 1g and Supplementary Fig. 5) to graphitic carbon. High-resolution transmission electron microscopy (HRTEM) characterization, discussed later, provides visual evidence of the formed graphene. We confirm that C₂H₄ acts as the direct precursor for graphene generation from the results shown in Fig. 1d, e, where the emergence of graphene features is observed to be correlated with the introduction of C₂H₄. Thus, it appears that the condensation of C₂H₄ to graphene on the Ag surface is a primary step under the photo-epoxidation conditions.

As per recent reports, C₂H₄ monomers can undergo condensation reactions at high temperatures (e.g., 770–970 K) on transition metal surfaces (e.g., Rh (111) to form extended graphene). In the present case, the ambient temperature formation of graphenic carbon appears to be photoactivated by visible-light excitation of the plasmon-resonant Ag NPs. The graphene is formed from condensation of C₂H₄ monomers via a photo-driven process on the Ag NP surface. On the basis of recent plasmon-assisted bond-dissociation reactions, we propose that the plasmon-exicted Ag NP surface and/or surface-adsorbed O₂ is involved in hot electron-assisted hydride abstraction from the C₂H₄. The resulting carbene species can polymerize to form graphene.

Such photosynthesis of graphene at ambient temperature ought to be contrasted from the formation of amorphous carbon or coking of catalyst surfaces known in high-temperature catalytic cracking processes. In the latter processes, hydrocarbon reactants and/or products, particularly of the aromatic kind, strongly adsorb on the catalyst surface, where they gradually accumulate followed by chemical reactions to produce amorphous carbon deposits of low volatility, resulting in poisoning of the catalyst. Whereas surface carbon formation or coking is known to contaminate or poison the metal catalyst; the in situ generated graphenic carbon in our case appears to promote C₂H₄ photo-epoxidation, as described in the next section.

The 2D band of the in situ generated graphene (Fig. 1g and Supplementary Fig. 5) is significantly weaker in intensity compared to that for free-standing, pristine graphene (Supplementary Fig. 6). It is known that a suppressed 2D band is a signature of disruption in the electronic structure of graphene, like those caused by molecular adsorbates, lattice defects, and/or graphene–metal substrate electronic interactions. Based on this known characteristic, the weak 2D band appears to be an indicator of the electronic contact of the in situ generated graphene fragment with the Ag NP surface, n-doping of the graphene by Ag, and/or unterminated bonds of the fragments. Also, it must be noted that the graphenic carbon bands (Supplementary Table 1) can be assigned either to graphene or to graphene oxide, which can inter-change with each other under laser irradiation in ambient air: graphene can photo-oxidize into graphene oxide, and the latter can be reduced back to graphene by laser excitation, assisted by the light-absorbing Ag NP. The graphenic carbon bands show intermittency (Fig. 2a and Supplementary Figs. 4, 7), which may signify dynamic formation/breakdown of graphenic carbon fragments under laser excitation.

![Fig. 2 Graphenic carbon formed in situ catalyzes C₂H₄ epoxidation.](image-url)

**Fig. 2** Graphenic carbon formed in situ catalyzes C₂H₄ epoxidation. a) Digital reaction trajectory (presence of a reaction species vs. time) for a representative single Ag NP emitter under photocatalytic C₂H₄ oxidation conditions corresponding to the data in Fig. 1e. The SERS monitoring was carried out under the flow of C₂H₄ in air, which serves as the source of oxygen. The trajectories, shown stacked, demonstrate the correlation between the presence of graphenic carbon and the formation and detection of C₂H₄ oxidation reaction species, as also shown by additional examples in Supplementary Fig. 5. b) Time series of SERS spectra, shown by a waterfall plot, for a single graphene-covered Ag NP emitter. Continuous SERS spectra were taken at a rate of 0.2 s per frame and are shown normalized. The instant when C₂H₄ flow was introduced is labeled as on. c) Selected time slices from in situ SERS study of the single graphene-covered Ag NP emitter in (b). The SERS spectrum before start of C₂H₄ flow (black curve, t = 40 s slice) shows D, G, 2D, and D + G modes of graphene. The SERS spectra under C₂H₄ epoxidation conditions (red curve, t = 372 s and blue curve, t = 181.2 s) show formation of EO. Spectra are shown normalized and stacked with the key vibrational modes labeled with the peak wavenumbers indicated in cm⁻¹.
Photogenerated graphene promotes C2H4 photo-epoxidation.

Of the emitters that exhibit in situ formed graphene, nearly 40% (equivalent to 17% of the entire population, Fig. 1b) exhibit the formation of reaction species associated with C2H4 oxidation (Fig. 1e). As shown by the representative example in Fig. 1h and several others in Supplementary Fig. 5, selected SERS spectral frames show sharp peaks (labeled in Fig. 1h) co-existing with the graphenic carbon D and G bands. Based on literature (Supplementary Table 1) as well as our density functional theory (DFT) calculations (Table 1), these observed SERS peaks are found to be vibrational modes of reactive intermediates and products EO.

### Table 1 Raman mode frequencies computed for reaction products and selected intermediates from reaction schemes in Fig. 4

| Products          | Vibrational mode | V1 (cm⁻¹) | IX (cm⁻¹) |
|-------------------|------------------|-----------|-----------|
| CH2 wag           | 1025             | 1023, 1216|
| Ring stretch      | 1125, 1147       | 1126, 1151|
| CH2 wag and ring stretch | 1170           | 1171       |
| Ring stretch      | 1279             | 1278       |
| CH2 scissor       | 1517, 1539       | 1536, 1553|
| C-H stretch       | 3116, 3147, 3231 | 3155, 3162, 3254|
| H2O related       | NA               | 1654, 3373, 3749|
| Graphene related  | 1344, 1586, 1662 | 1363, 1584, 1652|

| Intermediates     | Vibrational mode | IV (cm⁻¹) | V (cm⁻¹) | VII (cm⁻¹) |
|-------------------|------------------|-----------|---------|-----------|
| C-/C-C-O stretch  | 1106             | 1040      | 897, 1056|
| CH2 wag           | 1157             | 1133, 1165| 1093, 1226|
| CH2 wag           | 1306, 1401       | 1264, 1286| 1151, 1204|
| CH2 scissor       | 1475             | 1415      | 1489     |
| C-H stretch       | 3023, 3160       | 3030, 3058| 3065, 3176|
|                  | 3295             | 3103      | 3333     |
| Graphene related  | 1340, 1576       | 1349, 1580| 1365, 1581|
|                  | 1653             | 1657      | 1664     |

Those modes observed in situ SERS studies are shown in bold.

Graphene/Ag/Al2O3 catalyst for C2H4 photo-epoxidation. The insight about the involvement of graphenic carbon in the active form of the photocatalyst has utility for practical catalyst design. As a demonstration, we prepared a composite catalyst consisting of graphene-functionalized Ag NPs supported on α-Al2O3 (G-Ag/Al2O3). We compared the photocatalytic C2H4 epoxidation performance (Fig. 3a and Supplementary Figs. 13–15) of this composite to the more conventional form of the catalyst consisting of Ag NPs supported on α-Al2O3 (Ag/Al2O3). The Ag loading (~20 wt%) was identical in the two cases. Both catalysts (G-Ag/Al2O3 and Ag/Al2O3) have an absorbance band spanning from ca. 400 nm extending out across the visible region of the spectrum (Fig. 3c). This visible absorbance is the contribution from the plasmonic absorption of Ag NPs and coupled NP aggregates, as ascertained from the lack of such absorbance in G-Al2O3 powder (Fig. 3c).

The reaction was carried out in a glass reactor filled with 15 mg of the solid catalyst powder, C2H4, and ambient air under continuous-wave excitation by a 0.5 W, 514.5 nm laser. As shown in Supplementary Fig. 15, G-Ag/Al2O3 showed relatively high and sustained activity towards photocatalytic epoxidation, as determined from EO generated in the reactor headspace measured by.
gas chromatography (GC). The average TOF for EO formation (Supplementary Note 1) was found to be 262 NP$^{-1}$s$^{-1}$ (Fig. 3a) under the visible-light photoexcitation conditions employed. While this epoxidation activity is not comparable to that of thermal C$_2$H$_4$ epoxidation under industrial conditions, the accomplishment of epoxidation under ambient conditions is noteworthy. The quantum yield of the photoreaction is estimated to be 5.75 × 10$^{-5}$ EO molecules generated per photon (Supplementary Note 2).

A control test in which G-Ag/Al$_2$O$_3$ was excited by the 514.5 nm laser in air atmosphere in the absence of C$_2$H$_4$ yielded no EO (Supplementary Fig. 13), confirming that EO was an epoxidation product and not an outcome of graphene photodegradation. G/Al$_2$O$_3$ itself exhibited no activity (Supplementary Fig. 13), confirming that the Ag NPs are required as a light absorber in the photocatalytic reaction. In contrast to the high activity of the composite catalyst (G-Ag/Al$_2$O$_3$), as-prepared Ag/Al$_2$O$_3$ showed low activity for photo-epoxidation (Fig. 3a and Supplementary Figs. 14, 15), despite its significant light absorption at 514.5 nm (Fig. 3c). Thus, we confirmed that for visible-light-driven C$_2$H$_4$ epoxidation at ambient conditions, the photocatalyst requires both graphene and Ag NPs. Interestingly, we found that the as-prepared Ag/Al$_2$O$_3$ could be activated under visible-light irradiation in C$_2$H$_4$ atmosphere. The activated catalyst (A-Ag/Al$_2$O$_3$) obtained from 14 h of such irradiation exhibited a photo-epoxidation performance much higher than Ag/Al$_2$O$_3$ and one approaching that of G-Ag/Al$_2$O$_3$ (Fig. 3a and Supplementary Fig. 15). Naturally, we conjectured that the activation process is tantamount to the in situ formation of graphenic carbon on the surfaces of Ag NPs. The latter was indeed the case as seen from SERS spectra of A-Ag/Al$_2$O$_3$ showing distinct D and G bands (Fig. 3b). Naturally, we conjectured that for visible-light-driven C$_2$H$_4$ epoxidation, the activation process is tantamount to the in situ formation of graphenic carbon on the surfaces of Ag NPs.

HRTEM imaging (Fig. 3d, e and Supplementary Fig. 16) provided additional characterization of the in situ formed graphenic carbon/Ag NP composite. The as-received Ag NPs are quasi-spherical in shape. Their crystallinity is evident from lattice spacings of 0.24 and 0.21 nm, corresponding to {111} and {200} planes of metallic Ag (Supplementary Fig. 16a-c). Occasionally, we observe a lattice spacing of 0.28 nm corresponding to the {111} planes of Ag$_2$O$_3$ (Fig. 3d-f) indicate no obvious structural or morphological changes resulting from solely laser irradiation. However, Ag NPs subjected to 514.5 nm laser irradiation in C$_2$H$_4$ atmosphere (similar to in situ SERS and photocatalytic reaction conditions) show on their surface the presence of graphenic carbon nanofragments, with an interlayer spacing of 0.34 nm (Fig. 3d).

This signature interlayer spacing of 0.34 nm is confirmed from HRTEM images of Ag NPs covered with commercially available graphene flakes (Supplementary Fig. 16g-i). The {002} planes of graphene with a lattice spacing of 0.32 nm are also seen in...
HRTEM of the graphenic carbon fragments formed on Ag NPs by irradiation in C2H4 (Fig. 3e). Defective or partially oxidized graphene with an interlayer spacing of 0.54 nm is also observed in HRTEM (Supplementary Fig.17). These bulk photocatalytic and HRTEM studies verify that the in situ formation of graphenic carbon (depicted in Fig.3f) is a primary step of the photocatalytic reaction, and the graphene/metal composite acts as the active phase of the photocatalyst under reaction conditions. Graphenic carbon catalytically promotes C2H4 photo-epoxidation, which is in striking contrast to the accepted role of carbon as an innocent support or a deactivator in conventional catalysis. Although these mechanistic findings may not apply to the industrial epoxidation reaction, which is conducted at significantly elevated temperatures and pressures, the formation of graphene and its role as a catalytic promoter may be relevant to other photocatalytic hydrocarbon transformations performed under ambient conditions.

DFT insights into role of graphene in catalytic promotion. The possible mechanism/s by which graphene nanofragments promote C2H4 epoxidation was investigated using DFT simulations. We focused our attention on unterminated bonds of the graphene nanofragments, which are likely highly active sites for chemisorption. Note that pristine graphene flakes can form such active nanofragments under laser excitation, with assistance from the light-absorbing Ag NP (Supplementary Figs. 4, 6). DFT computations of free energies show that both C2H4 and O2 can be chemisorbed at unterminated bonds of a graphene nanofragment with high energetic favorability (Fig.4 and Supplementary Figs. 8 and 9). Such chemisorption can be a first step in C2H4 epoxidation.

Figure 4 shows a possible pathway starting from O2 chemisorption at an edge defect lacking H termination (I → II). Following O2 incorporation, a photogenerated hot electron transfers from Agn to trigger the scission of the O–O bond. The 1.92 eV cost of this dissociation reaction can be compensated by the excess energy (relative to the Ag Fermi level) of the hot electron. One of the dangling O atoms can further react with a C2H4 molecule from the gas phase, while the other O atom is involved in a structural reorganization to a ketone. The C=O vibrational mode (1720–1740 cm−1) observed in in situ SERS (Supplementary Fig. 5j) may be a signifier of such ketone formation. This step (III → IV) requires a free energy of 1.36 eV, posing an activation barrier for the reaction. The anion intermediate (IV) can release EO by one of two possible reaction pathways. Reaction of the anion intermediate with the hole leftover in the Agn and an H˙ atom generates an EO molecule and a ketone and H termination at the defect (Fig. 4, Pathway A). Alternatively, the anion can react with the hole...
leftover in the Ag$_{\text{NP}}$, and four H$^-$ atoms to result in an EO molecule, a water molecule, and H termination at the defect (Fig. 4, Pathway B). Ag NP-photocatalyzed scission of C–H bonds in CH$_4$ (during the condensation reaction) or in graphene can serve as the source of H$^-$ atoms, which can then adsorb to the Ag surface. Although we present two of possibly many pathways, they highlight the ability of graphene nanofragments to facilitate the C-H$_4$ photo-epoxidation reaction in synergy with photogenerated carriers available from the plasmonically excited Ag NP.

The addition of reactant species (CH$_4$, or O$_2$) to high energy defects of a graphene fragment can effectively passivate them, resulting in the termination of their participation in catalyst. Yet, sustained photo-epoxidation activity is exhibited by graphene-containing photocatalysts (G-Ag/AlO$_x$ and A-Ag/AlO$_x$), with no observed deactivation (Supplementary Fig. 15), which points to the regenerability of catalytic graphene sites. Visible-light activation can promote continuous regeneration of active graphene defect sites through multiple photo-mediated scission reactions and/or the photo-assisted condensation of new graphene moieties with unsaturated edges. Such a proposal is supported by the dynamic formation and breakdown of graphenic carbon fragments observed in SERS monitoring (Fig. 2a and Supplementary Figs. 4, 6).

We computed Raman spectra of the reaction intermediates and products of the two reaction pathways. As shown by the calculated Raman frequencies (Table 1) and spectra (Supplementary Fig. 11), in both pathways, the formation of EO contributes modes at 1023, 1145, 1170, 1216, and 1277 cm$^{-1}$, which reproduce the SERS bands observed experimentally (Figs. 1h, 2c and Supplementary Fig. 5). Adsorption free energy calculations (Supplementary Table S2) suggest that EO generated at a defect site can adsorb to the Ag NP surface ($\Delta G_{\text{ads}} = -0.53$ eV) for a timescale long enough to be detected by SERS. Scissoring modes of CH$_3$ in the reaction intermediates contribute to computed vibrational modes at 1415 and 1470 cm$^{-1}$, which also correspond to bands in experimental SERS spectra (Figs. 1h, 2c and Supplementary Fig. 5). Note that vibrational modes in a similar range (1432 and 1484 cm$^{-1}$) have been reported in the literature and were assigned to an oxametallacycle intermediate formed on the Ag surface in thermal C-H$_4$ epoxidation.

In conclusion, using SERS performed in an ensemble-averaging-free manner, we captured and identified the dynamic formation of graphenic carbon fragments on the surface of an Ag catalyst, which constitutes a primary step in photocatalytic C-H$_4$ epoxidation. The composite of this in situ formed graphenic carbon with the plasmonic Ag NP constitutes the catalytically active phase of the photocatalyst. This atomic-level insight coupled with DFT simulations sheds light into an unconventional role of crystalline carbon as a promoter in the photocatalysis and also allows us to engineer an improved photocatalyst for ambient-condition C-H$_4$ epoxidation. The findings highlight the central importance of in situ studies of photocatalysts, where the pristine metal surface may not solely be the active phase of the photocatalyst under reaction conditions.

**Methods**

**Flow cell preparation.** An optical microscopy-compatible flow cell was constructed from a glass slide and a glass coverslip. Glass coverslips (VWR SuperSlips, No.1, 24 x 60 mm$^2$) and glass slides (VWR, 1 mm thick, 75 x 25 mm$^2$) were cleaned by etching away the top silica surface by heating in 2 M KOH for 30 min (~ 85 °C), followed by washing first with distilled water, and then with Nanopure water. The glass slides and coverslips were sonicated in Nanopure water for 15 min. Further again, the coverslip was washed with Nanopure water and sonicated again in fresh Nanopure water for 30 min. A 1 mm (diameter) and a 2.5 mm hole were drilled at a distance of 1 cm, respectively, from the left and right edges of a glass slide using a diamond-coated drill bit operated at ~15,000 rpm, immersed in water.

The sample was prepared from PELCO$^\text{TM}$ NanoXact$^\text{TM}$ citrate-capped Ag NP colloidal (Ted Pella, Item no. 84050-60), unless otherwise specified. TEM images of these colloids (Supplementary Figs. 1a–c) show quasi-spherical NPs of average size 52.5 ± 5.5 nm and consisting of metallic Ag. Ten microliters of this colloid, which has a localized surface plasmon resonance (LSPR) absorption band maximum at ~432 nm (see Supplementary Fig. 2), were diluted with 40 μL of Nanopure water. The mixture was sonicated for a few minutes. The precleaned coverslip was blow dried with N$_2$ gas. Then, 10 μL of the diluted NP dispersion was drop-cast onto the clean Ag slip and allowed to dry in air for at least 15 min. The Ag NP emitters were found to be free of background SERS signal from citrate. The coverslip was incorporated into the flow cell. Briefly, a precleaned glass slide was blow dried with N$_2$ gas. A polyethylene tube (Instech laboratories, 0.076 cm inner diameter) was inserted into the 1 mm hole (the inlet of the flow cell) and glued using 5 min Locite epoxy. The epoxy was allowed to polymerize for 20 min after mixing. The 2.5 mm hole was left unsealed to serve as the outlet for the flow cell. Epoxy glue was applied on the inner edge of glass slide, to which the NP-coated coverslip was attached. Tens of μm-thick double-sided tape served as a spacer between the coverslip and the glass slide.

**Ag NP monolayer preparation.** Some SERS experiments were carried out on Ag NP monolayers (Fig. 1). In a typical procedure, a precleaned coverslip was immersed in a 1% (v/v) solution of 3-aminopropyltriethoxysilane in ethanol for 1 h. Following this aminosilanization procedure, the coverslip was thoroughly washed with ethanol, then with Nanopure water, followed by drying with N$_2$. A successfully prepared aminosilanized coverslip exhibits strong hydrophobicity, which is clearly observed by water beading up on the coverslip surface. The coverslip was then placed in a Ag NP dispersion for at least 16 h to allow the amine-terminated surface to be coated with a monolayer of Ag NPs. The initially trans parent coverslip turned greenish following the coating of Ag NPs. To remove citrate ligands from the surfaces of the NPs and remaining aminosilane, the coverslip was washed with Nanopure water followed by drying under under N$_2$ and then placed for 30 min in a freshly prepared 50 mM aqueous solution of NaBH$_4$, which was followed by thorough washing with Nanopure water. This NaBH$_4$ treatment was repeated three times. For ensuring more complete cleaning, the sample-coated coverslip was irradiated with ultraviolet (UV) light from a mercury lamp (46 W) for photooxidative removal of citrate ligands. The duration of the pretreatment varied from one sample to another, but generally a 10 min exposure was sufficient to yield Ag NP emitters with no SERS backgrounds. Note that this method can cause some oxidation of the Ag NP surface; however, we found the SERS response to be qualitatively consistent with samples cleaned by vacuum baking. The monolayer-coated coverslip was then assembled into a flow cell for in situ SERS measurements.

**Graphene-covered Ag NPs for in situ SERS measurement.** First, 10 μL of Ag NP colloidal, diluted 5× with Nanopure water, was drop-cast onto a precleaned coverslip and subjected to a ligand cleaning procedure described above. A 10 μL ethanolic solution of graphene in 0.1 mg mL$^{-1}$, (Electron Microscopy Sciences) was then drop cast onto the Ag NP-coated coverslip and dried by heating at 60 °C in a vacuum desiccator for 2 h. The sample-bearing coverslip was then assembled into a flow cell. The in situ SERS experiments on the Ag NP sample were carried out in a manner similar to that for the Ag NP sample.

**Dark-field scattering imaging of Ag NP emitters.** The flow cell was mounted in an inverted Olympus microscope with the coverslip side facing down towards the microscope objective. The Ag NP-coated surface was illuminated with an Olympus U-LH100-3 100 W halogen lamp focused through an Olympus U-DCW 1.2–1.4 NA oil immersion dark-field condenser. Light scattered from the Ag NPs was collected in dark-field mode using an Olympus UPlanApo 0.5–1.35 NA ×100 oil immersion objective. For dark-field imaging, the focus of the condenser and that of the objective was set to the surface bearing the Ag NPs. Ag NP emitters were visualized in the wide-field image due to their strong LSPR scattering. Selected emitters were then aligned with a spectrometer slit, and a spectrometer slit mounted on the back of the microscope for in situ SERS spectroscopy. For the Ag NP monolayer, similar dark-field imaging was carried out. The colored dark-field images (Fig. 1i and Supplementary Fig. 3c, d) were taken using a top-view camera (AmScope MUC035) mounted on the microscope and ×100 dark-field objective.

**In situ SERS studies.** The flow cell was mounted in an inverted Olympus microscope with the coverslip side facing down towards the microscope objective. The Ag NP-coated surface of the flow cell was excited by an Ar laser beam (Stabline 2017, 314.5 nm, 5 mW) focused to a spot (full-width half-maximum (fwhm) = 2.56 μm$^2$) using an Olympus UPlanApo ×60 water immersion objective. The backscattered light was collected by the same objective and detected in the form of a spectrum using a Princeton Instruments Acton SP-2358 spectrograph equipped with a 300 lines per mm, 500 nm blaze grating and a Pylon 100B charge-coupled device (CCD) camera. A selected Ag NP emitter identified in the wide-field image was aligned with the spectrometer slit mounted on the exit port of the microscope.
Prior to the introduction of C₂H₄, SERS spectra were continuously recorded for the selected emitter for hundreds of frames with an acquisition time of 0.2 s per frame and the spectrograph centered at 660 nm. The absence of any background SERS bands, say from ligands, was ensured prior to further study of the selected emitter. Following this control run, pure C₂H₄ was allowed to flow from a balloon into the flow cell inlets and allowed to exit through the open outlet. Air, which serves as the source of oxygen, was not excluded from the flow cell. Typically, the introduction of the gas causes a pressure rise inside the flow cell, leading the cell to slightly buckle and move the Ag NP emitter out of focus. The objective lens had to be slightly readjusted to regain focus. Under C₂H₄ flow, SERS spectra were recorded continuously with an acquisition time of 0.2 s per frame and the spectrograph centered at 660 nm. The start of the experiment is set as t = 0 s in plotted time series. Typically, after acquiring 1000–2000 frames of the spectrum, the C₂H₄ flow was turned off. Another suitable emitter was identified and aligned with the spectrograph slit and subject to a similar control run, followed by in situ SERS spectroscopy in C₂H₄.

Data analysis. Hand in hand with the single-molecule-level sensitivity of SERS, spectra acquired with single NP spatial resolution and sub-second time resolution naturally reflect spatial and temporal heterogeneity of the surface. In these cases, a single-frame SERS spectrum is selected from the continuous time series for analyzing representative behavior. In these cases, the spectrum was first subject to manual baseline subtraction in Origin and plotted with or without normalization from 0 to 1. SERS peaks were identified manually and labeled with their wavenumber maxima. SERS peaks were assigned to known vibrational modes tabulated in Table S1. Spectral frames were made from series of spectra, with each spectrum normalized from 0 to 1. In specific cases, a single-frame SERS spectrum is selected from the continuous time series for analyzing representative behavior. In these cases, the spectrum was first subject to manual baseline subtraction in Origin and plotted with or without normalization from 0 to 1. SERS peaks were identified manually and labeled with their wavenumber maxima. SERS peaks were assigned manually to known vibrational modes tabulated in Table S1 and Table 1.

For some representative cases, digital trajectories were generated for each of the key reaction species: EO, CO₂, and graphene. A time series of SERS spectra was analyzed frame by frame by an automated Matlab code. Spectra were first smoothed and peaks were located by a first-derivative algorithm. If a spectrum contained three or more vibrational modes corresponding to EO (1025, 1147, 1289, 1415, 1475, and 1530 cm⁻¹ with a ±20 cm⁻¹ tolerance), then EO was assigned to be present in that frame. CO₂ was assigned to be present if either both signature modes (1289 and 1380 cm⁻¹ with a ±20 cm⁻¹ tolerance) were found in a spectrum. Graphenic carbon was assigned to be present if either 1330 and 1560 cm⁻¹ bands (with a ±30 cm⁻¹ tolerance) were present. Spectral frames with SERS modes from the specific reaction species were assigned a value of 1. Frames where modes from the species were absent were assigned a value of 0. The presence of the species (assigned a value of 0 or 1) was plotted as a function of time, with t = 0 s set to the start of the experiment.

DFT simulations. DFT calculations were performed using Gaussian 09 installed on a supercomputer cluster. Input geometries of reaction species (gas phase, unless noted otherwise) and model Ag clusters were created in Gaussian View or Avogadro softwares. According to our TEM study (Supplementary Fig. 16), Ag (111) is the most prevalent surface facet on the Ag NPs. Therefore, the Ag surface was modeled by the (111) surface of a 2 × 2 × 3 slab of Ag, consisting of a total of 15 atoms [78]. The Ag and O atom clusters were generated using VESTA (version 3.3.2) software using reference crystal structure information from Springer Materials (http://materials.springer.com/). Crystal structures were exported from VESTA in the form of xyz files, which were converted into Gaussian input files using Avogadro. All other input geometries were built using Gaussian View.

Thermodynamic parameters were extracted from the vibrational mode calculation at 298 K and 1 atm, which are default settings. The free energy of a reaction was calculated as:

$$\Delta G = \sum (\varepsilon_i + G \text{corr})_{} \text{products} - \sum (\varepsilon_i + G \text{corr})_{} \text{reactants}$$  

where ($\varepsilon_i + G \text{corr}$) represents the sum of electronic and corrected thermal free energies. Optimized geometries were plotted in Gauss View or Avogadro. Details of energy calculations are provided in the Supplementary Notes.

Synthesis of Ag/Al₂O₃. Citrate-capped Ag NPs were synthesized using the Lee and Meisel method52. Briefly, 45 mg of AgNO₃ was dissolved in 250 mL of Nanopure water and the solution was brought to boiling. Five milliliters of 1 wt% aqueous sodium citrate solution was then injected and the solution was kept boiling for 1 h. The brownish as-synthesized Ag NP colloids were centrifuged at 6300 × g followed by washing with Nanopure water 3X and redispersed in ~30 mL of Nanopure water. The LSPR maximum of this colloids was found from UV–Vis absorbance spectroscopy to be at ~409 nm (Fig. S2).

Assuming 100% of the AgNO₃ precursor in the synthesis was converted into Ag NPs, the colloidal contained ~25 mg of Ag by weight. To this suspension, 100 mg of a commercially added, following 1 mL of ethanol at 298 K and 1 atm, which are default settings. The free energy of a reaction was calculated as:

$$\Delta G = \sum (\varepsilon_i + G \text{corr})_{} \text{products} - \sum (\varepsilon_i + G \text{corr})_{} \text{reactants}$$  

where ($\varepsilon_i + G \text{corr}$) represents the sum of electronic and corrected thermal free energies. Optimized geometries were plotted in Gauss View or Avogadro. Details of energy calculations are provided in the Supplementary Notes.

Synthesis of G/Al₂O₃. Fifty-six milligrams of Al₂O₃ powder was dispersed in 20 mL of ethanol under sonication. Then, a 280 μL solution of graphene in ethanol was added to the dispersion, followed by sonication for 20 min. The solution was heated at 50 °C under stirring until the ethanol fully evaporated. The powder left behind was recovered and dried in a vacuum desiccator overnight under heating at 60 °C.

Activation of Ag/Al₂O₃. The Ag/Al₂O₃ powder was placed in a glass vial, which was then flushed with pure C₂H₄ for 30 min. The powder was then irradiated by a 514.5 nm laser (1 W, 1 cm beam diameter) for 14 h. This activation process, the product of which was referred to as A-Ag/Al₂O₃, was carried out prior to a photocatalytic reaction. For each powder sample, a diffuse-reflectance absorption spectrum was obtained. Two kinks in the spectra resulting from detector/light source change at 348 and 800 nm were removed, followed by normalization of the spectra from 0 to 1, prior to plotting.

Bulk photocatalysis studies. Photocatalytic reaction studies for G/Al₂O₃, Ag/ Al₂O₃, G-Ag/Al₂O₃, and A-Ag/Al₂O₃ powders were carried out in batch mode in a glass tube reactor (9 mL volume), with the light-absorbing catalyst lying at the bottom of the tube. The reactor was sealed with a rubber septum fastened by a copper wire. Ambient air was used as the source of molecular oxygen (O₂). Prior to reaction, the reactor containing the catalyst was flushed with house air for 30 min, after which the reactor contains 9 cm³ of air, equivalent to ca. 1.89 cm³ of O₂. Then, 2 cm³ of C₂H₄ at atmospheric pressure was injected into the reactor and mixed well using the gas needle. The catalyst was irradiated with a laser (514.5 nm, 0.5 W, 2 mm beam diameter) to initiate the photocatalytic reaction. The amount of catalyst (15 mg) loaded into the reactor was more than sufficient to cover the laser beam area, in order to ensure complete light absorption. The reaction was paused at 2.5-min intervals by blocking the laser and reaction products in the reactor headspace were analyzed by GC. An Agilent 6890 GC with an HP-Plot Q capillary column equipped with a flame ionization detector (FID) was used to assay the reaction mixture. The GC column was held at 50 °C for 4.5 min, then raised to 60 °C at the rate of 20 °C min⁻¹, where it was maintained for 3 min, followed by ramping of the temperature to 100 °C at the rate of 20 °C min⁻¹, where it was maintained for 5 min. Finally, the oven was ramped to 160 °C at a rate of 20 °C min⁻¹ and held for 10 min. Helium was used as the carrier gas at a flow rate of 1 mL min⁻¹. The injector and the detector temperatures were set at 150 and 200 °C, respectively. C₂H₄ and EO peaks were identified based on retention times, which were measured to be around 3.4 and 13.9 min, respectively, from GC of C₂H₄ and EO standards. The peak area corresponding to EO was integrated in GC Chemstation software. We ran 3–4 trials for each catalyst to account for batch-to-batch variability in activity. We also ran two trials of control photo-reactions (in the absence of C₂H₄ but with 9 cm³ air) for Ag/Al₂O₃ and G-Ag/Al₂O₃. We also ran two trials of a control photo-reaction for G/Al₂O₃ in a reactor filled with 9 cm³ air and 2 cm³ C₂H₄.

The EO for the standard run was synthesized using a wet chemistry method53, whereby a mixture of 3 mL of 14.9 M 2-chloroethanol (Sigma Aldrich, USA) and
7.5 mL of 6 M aq. KOH solution (Fisher Scientific, USA) was gently heated in an oil bath at ~80 °C. The EO gas generated in the reaction (Cl-CH₂CH₂-OH → KCl + H₂O) was collected by a balloon. Standard GC runs were also conducted for a hydrocarbon mixture and acetaldehyde.

Photocatalytic reaction studies for Ag/Al₂O₃, G/Ag/Al₂O₃, and A-Ag/Al₂O₃ were also performed under quasi-state conditions by adapting the above procedure as follows. First, 15 mg of the catalyst powder was loaded into a glass reactor. The reactor was sealed and flushed with house air (10 scm) for 20 min, after which the reactor contains 9 cm³ of air. Then 2 cm³ of pure CH₄ gas was injected into the reactor and mixed well using a syringe. The catalyst powder was irradiated in the C₂H₄ and air atmosphere by a 0.5 W, 514.5 nm laser. After 2 min of photoreaction, 100 μL of the headspace vapor of the reactor was sampled and subject to GC-FID analysis. After this, the reactor was opened and evacuated by subjecting it to vacuum for 10 min at room temperature. After evacuation, the reactor was sealed and filled with air and CH₄ using the aforementioned procedure. The catalyst powder in the gas atmosphere was then subject to a 2-min photoreaction and GC-FID analysis. A 90-min (cumulative) long photocatalytic reaction was conducted in such a cyclic manner, the results of which are presented in Supplementary Fig. 15.

The amount of EO generated in each cycle was quantified using the integrated area measured for the EO peak (14 min retention time) in the gas chromatogram. For this quantification, a calibration was separately carried out using pure EO gas of a known concentration (100 ppm in N₂, Cal Gas Direct, Inc.). Estimation of TOF of EO generation is described in the Supplementary Notes.

SERS spectra of G-Ag/Al₂O₃ and A-Ag/Al₂O₃ G-Ag/Al₂O₃ or A-Ag/Al₂O₃ powder was dispersed in Nanopure water to a level of dilution where no clumping of the powder is seen. The dispersion was subsequently drop cast onto a precleared coverslip, followed by drying with N₂. The sample-bearing coverslip was mounted on a glass slide, followed by drying with N₂. The sample-bearing coverslip was mounted on a glass slide, followed by drying with N₂.

**TEM sample preparation and imaging** Ten microliters of PELCO® NanoXact™ 60 nm citrate-coated Ag NPs (Ted Pella, Inc.) were sonicated for 5 min and drop-cast onto a TEM grid (ultrathin carbon coverslip, followed by drying with N₂). The solution was allowed to dry in air for 1 h and then heated in a vacuum desiccator at 90 °C for 5 h. In addition to the as-received Ag NPs, three other samples were subject to TEM:

(i) A sample of Ag NPs prepared on a TEM grid, as above, was attached using double-sided tape to a precleaned glass slide with sample facing away from the flow cell. The sample-bearing coverslip was mounted on a glass slide, followed by drying with N₂.

(ii) A sample of Ag NPs prepared on a TEM grid was subjected to a similar procedure as (i), except the irradiation was carried out in an atmosphere of C₂H₄. Air was not excluded from the flow cell.

(iii) A sample of Ag NPs prepared on a TEM grid, as above, was then covered with commercially available graphene. Ten microliters of ethanolic solution of graphene (1 mg mL⁻¹) was drop-cast onto the Ag NP-bearing grid and allowed to dry in air.

TEM and HRTEM imaging was performed on a Hitachi 9500 microscope operating at 200 kV with a spot size of 0.1 μm. The beam was focused on the central region of the TEM grid, which had been laser-treated. Micrographs were acquired by an Orius CCD camera with an exposure time of 0.1 s and an acquisition time of 1 s. Micrographs were analyzed in ImageJ or Digital Micrograph software. Fast-Fourier transforms of selected regions were performed to obtain lattice fringe distances. Scale bars were also included in ImageJ.

**Data availability** Data supporting the findings of this manuscript, Matlab codes, and computational input files are available from the corresponding authors upon reasonable request.

**Received:** 20 March 2018 **Accepted:** 30 June 2018

**Published online:** 03 August 2018

**References**

1. Ertl, G., Knozinger, H., Schuth, F. & Weitkamp, J. *Handbook of Heterogeneous Catalysis* (Wiley-VCH, Weinheim, 2008).

2. Somorjai, G. A. & Li, Y. M. *Introduction to Surface Chemistry and Catalysis* 2nd edn (Wiley, New York, 2010).

3. Van den Reijen, J. E. & et al. Preparation and particle size effects of Ag/a-Al₂O₃ catalysts for ethylene epoxidation. *J. Catal.* 356, 65–74 (2017).

4. Stegelmann, C., Schindt, N. C., Campbell, C. T. & Stoltze, P. Microkinetic modeling of ethylene oxidation over silver. *J. Catal.* 221, 630–649 (2004).

5. Bocklein, S., Gunther, S. & Wintterlin, J. High-pressure scanning tunneling microscopy of a silver surface during catalytic formation of ethylene oxide. *Angew. Chem. Int. Ed.* 52, 5518–5521 (2013).

6. Christopher, P., Xin, H. L. & Linic, S. Visible-light-enzanced catalytic oxidation reactions on plasmonic silver nanostructures. *Nat. Chem.* 3, 467–472 (2011).

7. Christopher, P., Xin, H. L., Marinimuthu, A. & Linic, S. Singular characteristics and unique chemical bond activation mechanisms of photocatalytic reactions on plasmonic nanostructures for efficient conversion of solar to chemical energy. *Nat. Mater.* 10, 911–921 (2011).

8. Ferrari, A. C. & Basko, D. M. Raman spectroscopy as a versatile tool for studying the properties of graphene. *Nat. Nanotechnol.* 8, 235–246 (2013).

9. Liu, H. T. et al. Photochemical reactivity of graphene. *J. Am. Chem. Soc.* 131, 17099–17101 (2009).

10. Li, Z. T. et al. Effect of airborne contaminants on the wettability of supported graphene and graphite. *Nat. Mater.* 12, 925–931 (2013).

11. Wang, B. et al. Ethene to graphene: surface catalyzed chemical pathways, intermediates, and assembly. *J. Phys. Chem. C* 121, 9413–9423 (2017).

12. Bradford, M. C. J. & Fuentes, D. X. A possible role for surface carbon during acetaldehyde oxidation over silver catalysts. *Catal. Commun.* 3, 51–60 (2002).

13. Eberly, P. E., Kimberly, C., Miller, W. H. & Drushel, H. V. Coke formation on silica-alumina cracking catalysts. *Ind. Eng. Chem. Process. Des. Dev.* 5, 193–198 (1966).

14. Voggu, R., Das, B., Rout, C. S. & Rao, C. N. R. Effects of charge transfer interaction of graphene with electron donor and acceptor molecules examined using Raman spectroscopy and cognate techniques. *J. Phys. Condens. Matter* 20, 472204 (2008).

15. Das, A. et al. Monitoring dopants by Raman scattering in an electrochemically top-gated graphene transistor. *Nat. Nanotechnol.* 3, 210–215 (2008).

16. Giovanniatti, G. et al. Doping graphene with metal contacts. *Phys. Rev. Lett.* 101, 026803 (2008).

17. Dong, X. C. et al. Symmetry breaking of graphene monolayers by molecular decoration. *Phys. Rev. Lett.* 102, 135501 (2009).

18. Lee, J., Novoselov, K. S. & Shin, H. S. Interaction between metal and graphene: Dependence on the layer number of graphene. *ACS Nano* 5, 608–612 (2011).

19. Auneman, J., Johansson, A., Herranen, O., Myllyperkio, P. & Petterson, M. Local photo-oxidation of individual single walled carbon nanotubes probed by femtosecond four wave mixing imaging. *Phys. Chem. Chem. Phys.* 17, 209–216 (2015).

20. Sokolov, D. A. et al. Direct observation of single layer graphene oxide reduction through spatially resolved, single sheet absorption/emission microscopy. *Nano. Lett.* 14, 3172–3179 (2014).

21. Wang, C. B., Diao, G. & Wachs, I. E. Interaction of polycrystalline silver with oxygen, water, carbon dioxide, ethylene, and methanol: in situ Raman and catalytic studies. *J. Phys. Chem. B* 103, 5645–5656 (1999).

22. Millar, G. J., Metson, J. B., Bowmaker, G. A. & Cooney, R. P. In-situ Raman studies of the selective oxidation of methanol to formaldehyde and ethene to ethylene-oxide on a polycrystalline silver catalyst. *J. Chem. Soc. Faraday Trans. 91, 4149–4159 (1995).*

23. Boghosian, S., Bebelis, S., Vayenas, C. G. & Patapheodorou, G. N. Insitu high-temperature SERS study of Ag catalysts and electrodes during ethylene epoxidation. *J. Catal.* 117, 561–565 (1999).

24. Nowobilski, P. J. Silver Catalyzed Ethylene Epoxidation: Novel Approaches to Mechanistic Studies (Surface Enhanced Raman Scopactscopy). PhD thesis, Purdue University (1986).

25. McBreen, P. H. & Moskovits, M. A surface-enhanced Raman study of ethylene and oxygen interacting with supported silver catalysts. *J. Catal.* 103, 188–199 (1987).

26. Bukkanikar, V. I. et al. Combined in situ XPS and PTRMS study of ethylene epoxidation over silver. *J. Catal.* 238, 260–269 (2005).

27. Linic, S. & Bartheau, M. A. Formation of a stable surface oxametallacycle that produces ethylene oxide. *J. Am. Chem. Soc.* 124, 310–317 (2002).

28. Jones, G. S., Majrikkas, M., Bartheau, M. A. & Vols, J. M. First synthesis, experimental and theoretical vibrational spectra of an oxametallacycle on a metal surface. *J. Am. Chem. Soc.* 120, 3196–3204 (1998).
31. Thrall, E. S., Crowther, A. C., Yu, Z. H. & Brus, L. E. R6G on graphene: high Raman detection sensitivity, yet decreased Raman cross-section. Nano. Lett. 12, 1571–1577 (2012).
32. Li, J. F. et al. Shell-isolated nanoparticle-enhanced Raman spectroscopy. Nature 464, 392–395 (2010).
33. Kang, L. L., Chu, J. Y., Zhao, H. T., Xu, P. & Sun, M. T. Recent progress in the applications of graphene in surface-enhanced Raman scattering and plasmon-induced catalytic reactions. J. Mater. Chem. C 3, 9024–9037 (2015).
34. Zhang, N., Tong, L. M. & Zhang, J. Graphene-based enhanced Raman scattering toward analytical applications. Chem. Mater. 28, 6426–6435 (2016).
35. Xu, W. G. et al. Graphene-veiled gold substrate for surface-enhanced Raman spectroscopy. Adv. Mater. 25, 928–933 (2013).
36. Liu, G. L. et al. Delineating the pathways for the site-directed synthesis of individual nanoparticles on surfaces. Proc. Natl Acad. Sci. USA 110, 887–891 (2013).
37. Scholl, J. A., Koh, A. L. & Dionne, J. A. Quantum plasmon resonances of individual metallic nanoparticles. Nature 483, 421–427 (2012).
38. Wu, Y. M. A. et al. Visualizing redox dynamics of a single Ag/AgCl heterogenous nanocatalyst at atomic resolution. ACS Nano 10, 3738–3746 (2016).
39. Mangalyarksai, D. et al. Large area multi-color changes induced by femtosecond laser pulses in soda-lime silicate glass embedded with Ag nanoparticles. J. Non Cryst. Solids 351, 3156–3159 (2005).
40. Dong, Y. Q. et al. Carbon-based dots co-doped with nitrogen and sulfur for high quantum yield and excitation-independent emission. Angew. Chem. Int. Ed. 52, 7800–7804 (2013).
41. Zhou, J. et al. An electrochemical avenue to blue luminescent nanocrystals from multiwalled carbon nanotubes (MWCNTs). J. Am. Chem. Soc. 129, 744–745 (2007).
42. Baker, S. N. & Baker, G. A. Luminescent carbon nanodots: emergent nanolights. Angew. Chem. Int. Ed. 49, 6726–6744 (2010).
43. Tang, L. et al. Deep ultraviolet photoluminescence of water-soluble self-passivated graphene quantum dots. ACS Nano 6, 5102–5110 (2012).
44. Liu, J. J. et al. Facile fabrication of carboxymethyl cellulose sodium/graphene hydrogel microparticles for water purification. RSC Adv. 6, 50061–50069 (2016).
45. Tiwari, S. K., Huczkó, A., Oraon, R., De Adhikari, A. & Nayak, G. C. A time efficient reduction strategy for bulk production of reduced graphene oxide using selenium powder as a reducing agent. J. Mater. Sci. 51, 6156–6165 (2016).
46. Jana, D., Matti, C., He, J. & Sagle, L. Capping agent-free gold nanostars show greatly increased versatility and sensitivity for biosensing. Anal. Chem. 87, 3964–3972 (2015).
47. Mohan, V. & Jain, P. K. Spectral heterogeneity of hybrid lead halide perovskites demystified by spatially resolved emission. J. Phys. Chem. C 121, 19392–19400 (2017).
48. Bernardo, C. & Gomes, J. The adsorption of ethylene on the (110) surfaces of copper, silver and platinum: a DFT study. J. Mol. Struct. Theocmum 582, 159–169 (2002).
49. Hay, P. J. & Wadt, W. R. Ab initio effective core potentials for molecular calculations. Potentials for the transition-metal atoms Sc to Hg. J. Chem. Phys. 82, 270–283 (1985).
50. Becke, A. D. A new mixing of Hartree–Fock and local density-functional theories. J. Chem. Phys. 98, 1372–1377 (1993).
51. Lee, C. T., Yang, W. T. & Parr, R. G. Development of the Colle–Salvetti correlation-energy formula into a functional of the electron-density. Phys. Rev. B 37, 785–789 (1988).
52. Lee, P. C. & Meisel, D. Adsorption and surface-enhanced Raman of dyes on silver and gold sols. J. Phys. Chem. 86, 3391–3395 (1982).
53. Swain, C. G., Ketley, A. D. & Bader, R. F. W. The mechanism of ethylene oxide formation from 2-chloroethanol. J. Am. Chem. Soc. 81, 2353–2359 (1959).

Acknowledgements
This research was supported by the Arnold and Mabel Beckman Foundation through a Young Investigator Award to P.K.J. This work was conducted in part at the Frederick Seitz Materials Research Laboratory. X.Z. acknowledges help from Andrew Wilson and Tobias Blickhan, who provided methods and codes for data analysis, from Sungiu Yu and Alex Kurzhals with GC measurements, from Phuong Thao Nguyen for discussions on DFT calculations, and from Julio Soares with the measurement of diffuse-reflectance spectra.

Author contributions
X.Z. designed and conducted experiments, performed data analysis and modeling, and co-wrote paper. G.K. helped with in situ SERS study and DFT calculations. J.H. conducted TEM characterization. P.K.J. conceived project, designed experiments, developed DFT calculations, and from Julio Soares with the measurement of diffuse-refectance spectra.

Additional information
Supplementary Information accompanies this paper at https://doi.org/10.1038/s41467-018-05352-9.

Competing interests: The authors declare no competing interests.

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