Supplementary Information

Raman Tweezers for Tire and Road Wear Micro- and Nanoparticles Analysis

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This electronic supplementary information was updated on 08.07.2022 to add movies ESI Movie S1, ESI Movie S2, ESI Movie S3 and ESI Movie S4, which were missing at time of first publication

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Note S1

Optical forces calculations on absorbing particles. For particles larger than the wavelength of the incident photons, we can make use of the geometrical optics approximation to calculate the optical forces.[1,2] In this approximation, the optical field is split in a collection of rays, each of them carrying *N* photons, a total linear momentum $N\vec{p} = N\,\hbar\vec{k}$ and a total energy $N\,\hbar\omega$. Here $\hbar$ is the reduced Planck's constant, $\vec{k} = (2\pi/\lambda)\,\hat{u}$ is the wavevector of the ray moving along the unit vector $\hat{u}$, and ω is the angular frequency of the photons. In a homogeneous, transparent medium, the rays propagate in a straight line with a speed given by c/n_m, where c is the speed of light in vacuum and n_m is the refractive index of the medium. When a light ray impinges from a medium (refractive index n_m) on a dielectric particle surface (refractive index n_p), it is partially transmitted inside the particle and partially reflected back in the medium, according to the Snell's law.

For the case of a strongly absorbing particle, we assume no field inside. The incident ray will only be reflected by the surface, with attenuated intensity. The momentum transferred by the ray to the particle can be calculated as $\Delta\vec{p} = \vec{p}_{\mathrm{inc}} - \vec{p}_{\mathrm{ref}}$, i.e. the difference between the momentum of the incident ray $\vec{p}_{\mathrm{inc}} = N_{\mathrm{inc}}\,\hbar\vec{k}_{\mathrm{inc}}$ and that of the reflected one $\vec{p}_{\mathrm{ref}} = N_{\mathrm{ref}}\,\hbar\vec{k}_{\mathrm{ref}}$. Here we have indicated with $N_{\mathrm{inc\,(ref)}}$ the number of photons in the incident (reflected ray), and with $\vec{k}_{\mathrm{inc\,(ref)}} = (2\pi/\lambda)\,\hat{u}_{\mathrm{inc\,(ref)}}$ the wavevector of the incident (reflected) photon. The momentum transfer is thus a result of the incident ray deflection ($\hat{u}_{\mathrm{ref}} \neq \hat{u}_{\mathrm{inc}}$) and power attenuation ($N_{\mathrm{ref}} < N_{\mathrm{inc}}$). The optical force is calculated as the rate of momentum transfer per unit time, i.e. $\vec{F} = \Delta\vec{p}/\Delta t$. Recalling that in a medium of dielectric constant n_{m} we have $2\pi/\lambda = n_{\mathrm{m}}\,\omega/c$ and that $N_{\mathrm{inc\,(ref)}}\,\hbar\omega/\Delta t$ is the power (energy per unit time) of the incident (reflected) ray, the optical force will be:

$$\vec{F} = (n_{\mathrm{m}}P_{\mathrm{inc}}/c)\,\hat{u}_{\mathrm{inc}} - (n_{\mathrm{m}}P_{\mathrm{ref}}/c)\,\hat{u}_{\mathrm{ref}}$$

Since the power of the reflected ray is $P_{\mathrm{ref}} = R \cdot P_{\mathrm{inc}}$, with R the reflectivity coefficient, finally, we find:

$$\vec{F} = (n_{\mathrm{m}}P_{\mathrm{inc}}/c)\,(\hat{u}_{\mathrm{inc}} - R\,\hat{u}_{\mathrm{ref}})$$

Summing over the all the *k*-th optical rays we obtain

$$\vec{F} = \sum_k \frac{n_{\mathrm{m}} P_{\mathrm{inc}}^{(k)}}{c} \left[\hat{u}_{\mathrm{inc}}^{(k)} - \mathrm{R}\ \mathrm{u}_{\mathrm{ref}}^{(k)} \right]$$

Movie S1

Optical pushing of car tire particles when the laser beam is focused on the surface. The movie shows an elongated particle (350 nm) intercepting the light beam and pushed away from the focal region by the scattering forces. A second, Mickey Mouse shaped, particle (~ 1 μm) is pushed when the laser is positioned over it and instantly switched on. A similar pushing effect is observed when the laser intercepts the side of a larger agglomerate (~ 10 μm size). The action is shown twice: at normal speed and at slow motion.

Movie S2

2D trapping of car tire particles. When the laser is off, TPs freely float due to Brownian motion. By defocusing the objective in the vertical position, we can place the laser spot slightly outside the top glass cell surface. When this condition is met, particles intercepting the laser beam are pushed and trapped against the glass cell surface. An example of 2D trapping is shown here for a particle of 850 nm. The trapped particle appears blurred as a consequence of the defocusing needed to achieve 2D trapping. Due to its asymmetric shape the particle is subject to an in-plane rotation, due to angular momentum exchange.

Movie S3

Fragmentation of TPs by laser irradiation. A laser beam is focused on the bottom surface of the glass cell, in proximity of a precipitated aggregate of TPs. Moving the TPs towards the laser spot produces a progressive disaggregation of the mass into its constituent particles. These latter are pushed by the scattering forces and dispersed into the liquid.

Movie S4

Thermophoretic trapping. Bubbling is shown when focusing the laser beam on an isolated particle stuck on the glass surface, as a consequence of intense heating. The thermal gradients generate convective fluxes inside the liquid medium. Particles located in the surrounding are dragged towards the focal region.

Figure S1

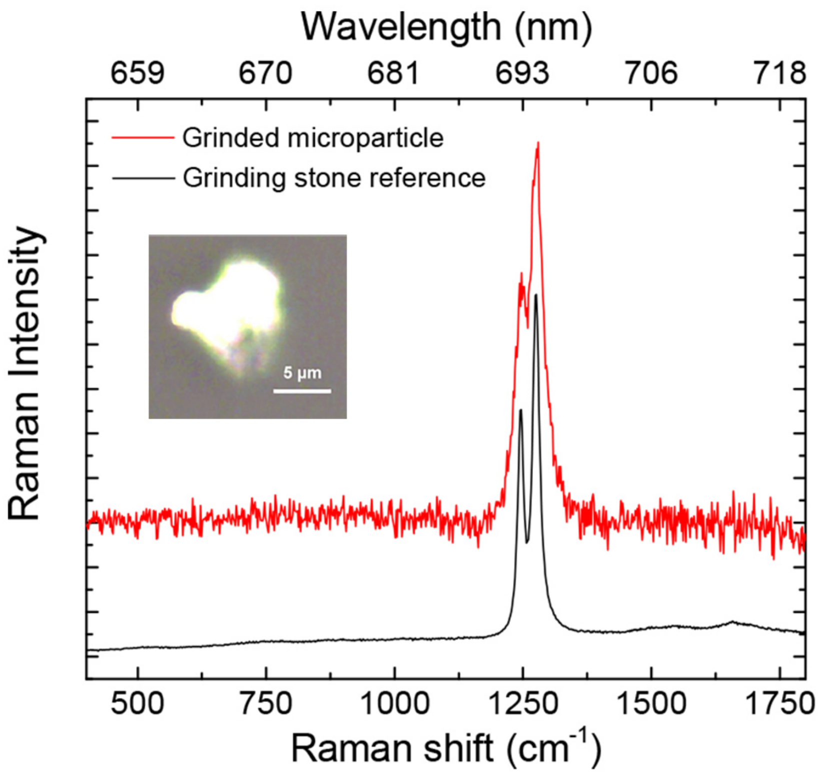

Figure S1: Raman analysis of the grinding stone. Black line: typical micro-Raman spectrum of the grinding stone. The spectrum has been acquired with a 10X objective, excitation wavelength 638nm, on an area of ~ 3 µm diameter. Red line: micro-Raman spectrum of an alumina micro particle (picture in the inset) released during the scrub of a tire fragment (100X objective, excitation wavelength 638nm, probed area diameter ~ 850 nm).

Figure S2

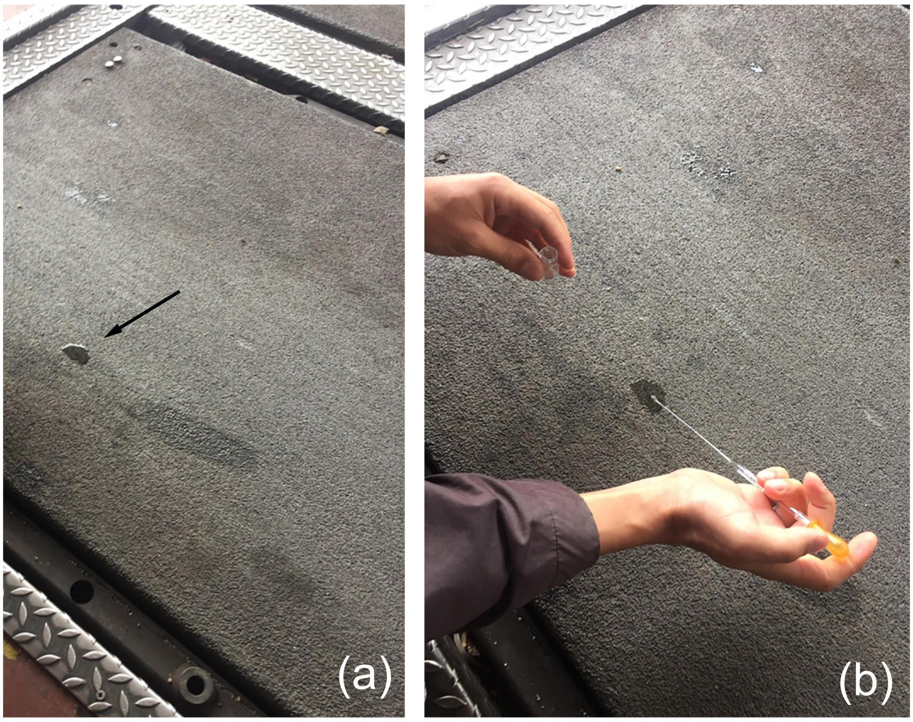

Figure S2: Extraction of natural TWRPs from a brake test platform. (a) 10 mL of distilled water were casted on the platform surface and gently mixed. (b) After few minutes, a pipette was used to collect the liquid and decant it in a glass vial, which was then immediately sealed in order to avoid contamination from airborne particles.

Figure S3

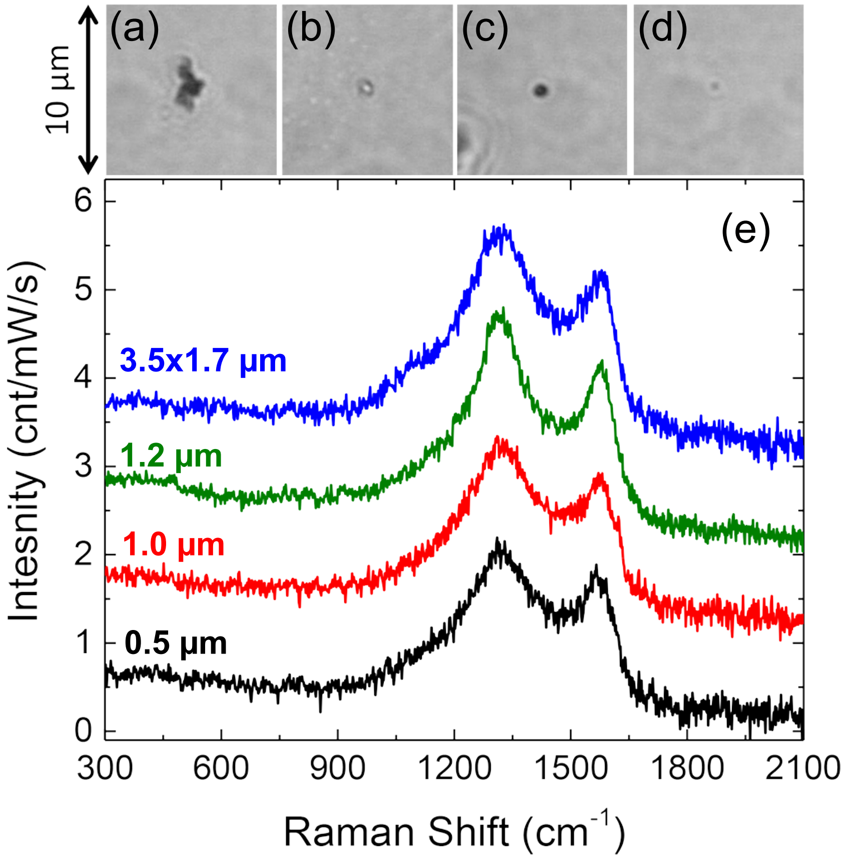

Figure S3: Raman spectra of trapped tire particles in sea water. The top images (a-d) are acquired keeping the particle in focus, with the laser off, just after Raman spectroscopy. Raman spectra (e) are acquired in 2D trapping conditions with a defocused laser. Each particle exhibits the spectrum typical of carbon black. Particles sizes are: (a) 3.5x1.7 µm, (b) 1.2 µm, (c) 1.0 µm and (d) 0.5 µm. Acquisition time: 60s two acquisitions. Spectra are offset for clarity.

Figure S4

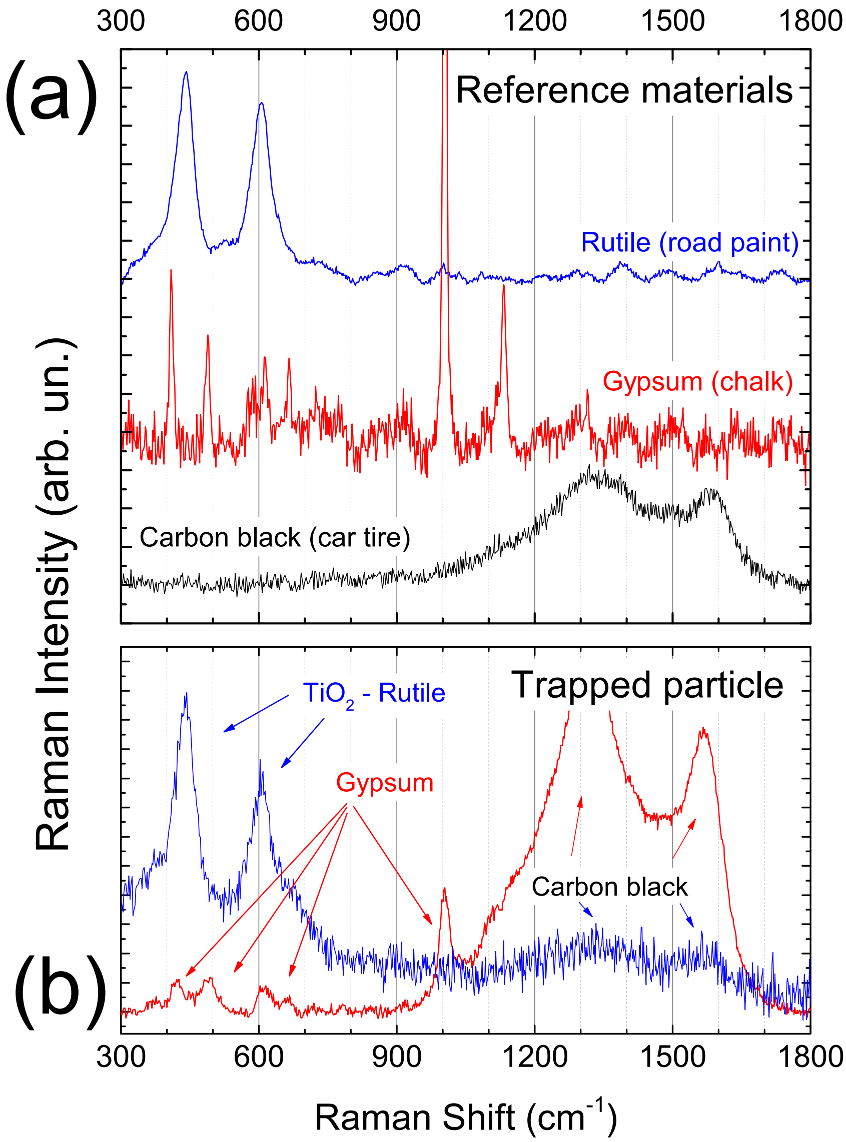

Figure S4: Raman spectra of reference materials (a) superposed to those of trapped tire particles (b). Gypsum (a, red line) was extracted from a piece of chalk, rutile (a, blue line) from a piece of road paint, carbon (a, black line) from the interior part of a piece of tire cut with a knife, which has not been in contact with the road dust. Carbon black has bands centered at 1344 and 1585 cm^{-1}. Gypsum has peaks at 409, 489, 614, 666, 1004 and 1134 cm^{-1}. Rutile has peaks at 442 and 607 cm^{-1}. Spectra on the reference materials are acquired with a standard micro-Raman setup, with excitation at 638nm. In (a) spectra are offset for clarity. Spectra of the trapped particles are the same displayed in Figure 8d in the main text.

Figure S5

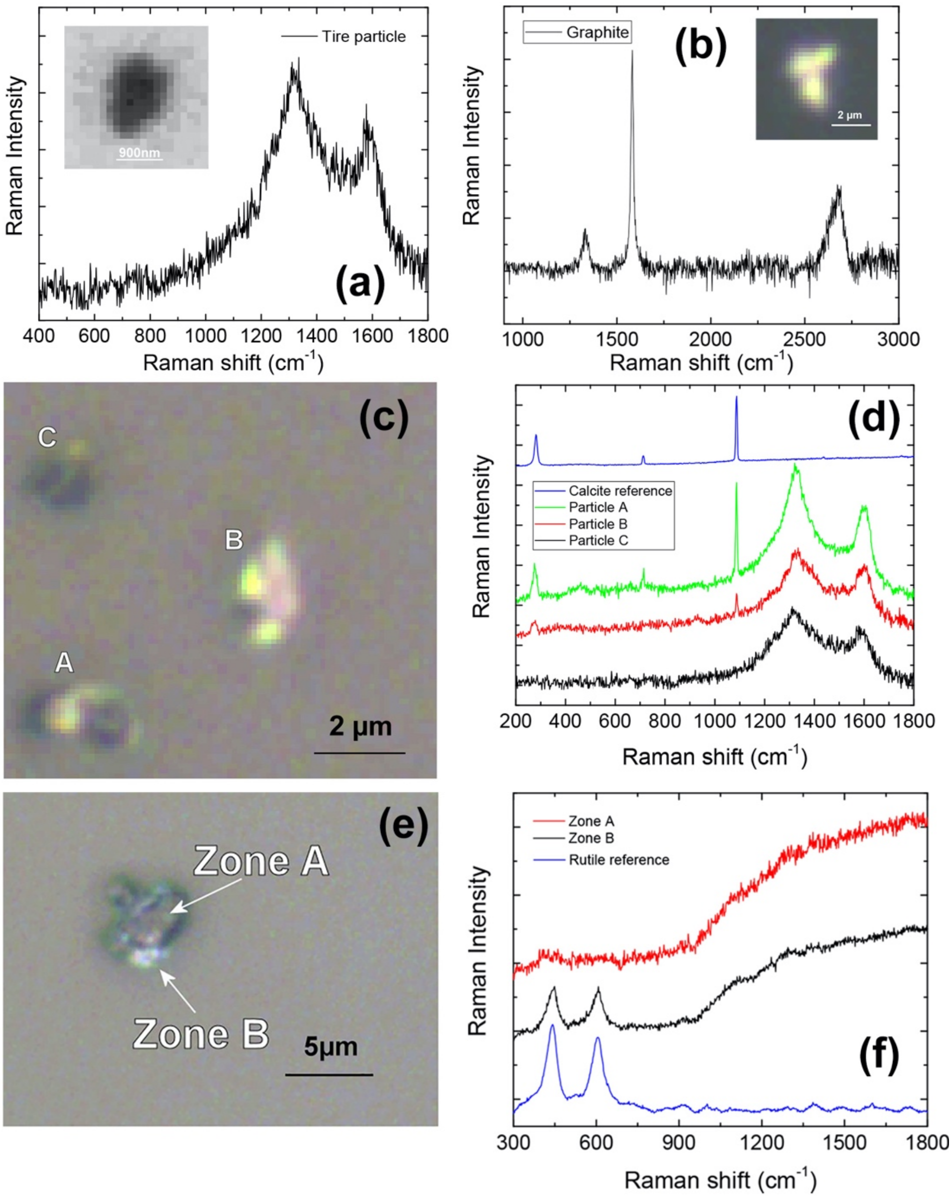

Figure S5: Standard micro-Raman analysis of grinded car tires microparticles. (a) Raman spectrum and optical image (inset) of a car tire sub-micron particle. (b) Raman spectrum and optical image (inset) of a micrometric graphitic particle, characterized by sharp bands at 1332 and 1582 cm^{-1} and by an asymmetric band at 2692 cm^{-1}). Optical image (c) and Raman spectra (d) of three microparticles. Particles A and B are composed of carbon and calcite in different relative amounts (d, green and red lines). Particle C is made of only carbon (d, black line). A reference spectrum on calcite powder (d, blue line) is also shown, showing peaks at 280, 710 and 1088 cm^{-1}. Optical image (e) and Raman spectra (f) of a heterogeneous microparticle containing rutile in zone B (f, black line) together with a fluorescent specie that spreads all around in zone A (f, red line). A reference spectrum of rutile (f, blue line) is also shown. All spectra are acquired with excitation at 638nm, using a 100X objective in air. In (d) and (f) spectra are offset for clarity.

Figure S6

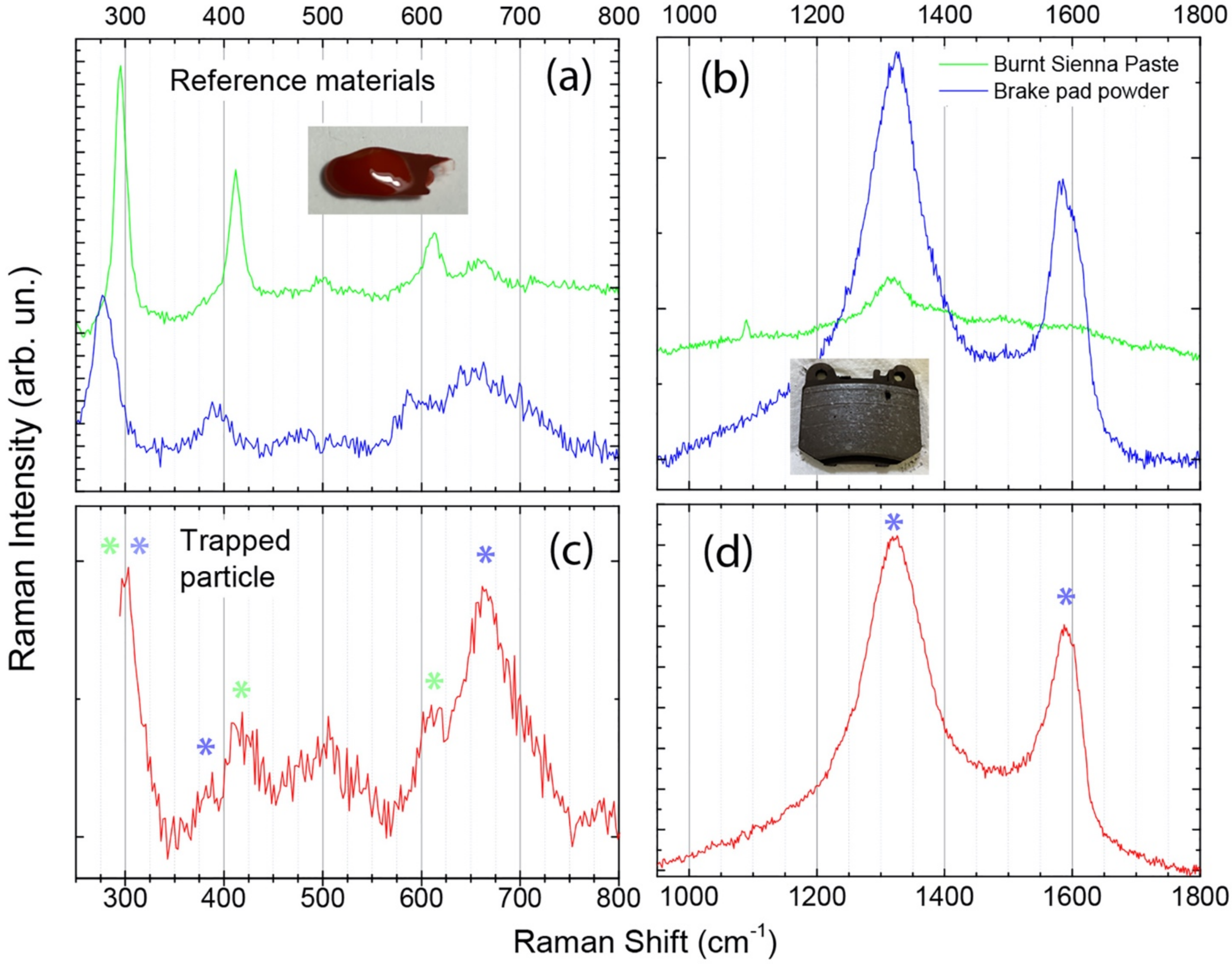

Figure S6: (a, b) Raman spectra of reference Burnt Sienna paste (green lines) and of the surface of a brake pad (blue lines), superposed to the signal from a trapped microparticle extracted from a brake test platform (c, d). Spectra are visualized in two windows: 250 – 800 cm^{-1} (a, c) and 975 – 1800 cm^{-1} (b, d) for clarity. Asterisks in (c, d) are used to highlight the correspondence of the Raman modes of the trapped particle with Burnt Sienna (green) and brake pad (blue). Pictures of the investigated samples are shown in the insets. Reference spectra in (a, b) are acquired with excitation at 638nm, using a 10X objective. The spectrum of the trapped particle is the same shown in the inset of Figure 9e (black line).

References

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2 A. Callegari, M. Mijalkov, A. B. Gököz and G. Volpe, *JOSA B*, 2015, **32**, B11–B19.