

Supplementary Information

Mechanochemical activation and patterning of an adhesive surface toward nanoparticle deposition

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Section 1. Instrumentation

XPS spectra shown on Figure S2 were recorded on an Omicron ESCA XPS spectrometer equipped with EA125 energy analyzer. Photoemission was stimulated by a monochromatic Al κ alpha radiation (1486.6 eV) with the operating power of 300 W. Survey scans and high-resolution scans were collected using pass energies of 70 eV and 26 eV, respectively. Analyzer substrate angle was 45°. Binding energies in the spectra were referenced to the C1s binding energy set at 285 eV. At least three different measurements were performed for each sample. For the data displayed in Figure S10, XPS spectrometer (ThermoFisher Scientific) with a monochromatized Al κ alpha X-ray source was used.

AFM images were obtained on a Bruker Dimension Icon AFM microscope. For quantitative measurement of mechanical properties, PeakForce QNM software was used which gave DMT moduli data as direct maps, taking PDMS standard sample with modulus of 7.10 MPa. Tap525A tips (spring constant, $k = 149$ N/m) were used in QNM measurements. For magnetic force microscopy (MFM) measurements, MESP tips (resonance frequency, $f = 80$ Hz) were used. AFM, KFM and MFM images were simultaneously recorded by using lift mode.

NPs were investigated using a transmission electron microscope (TEM) (Tecnai G2-F30, FEI). The absorption spectra were recorded using a Cary 300 UV-Visible spectrophotometer from Agilent. X-ray diffraction (XRD) spectra were taken using an X'Pert Pro (Panalytical).

Section 2. Further experimental detail and figures

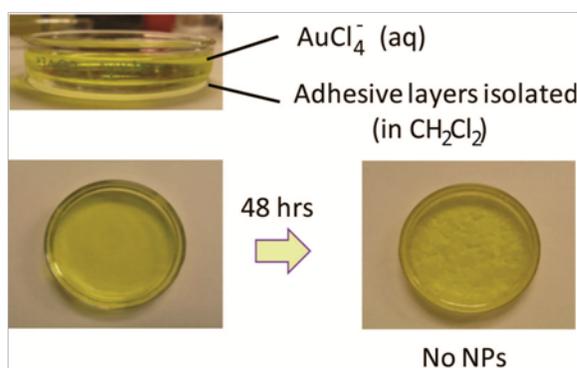


Figure S1. Isolation of the polyacrylate (sticky) polymer from the adhesive tape by soaking the tape in pure toluene or dichloromethane. Yellow colored HAuCl_4 (aq) was added to the isolated polyacrylate and left for 48 hrs – even after several weeks no reduced metal NPs were observed.

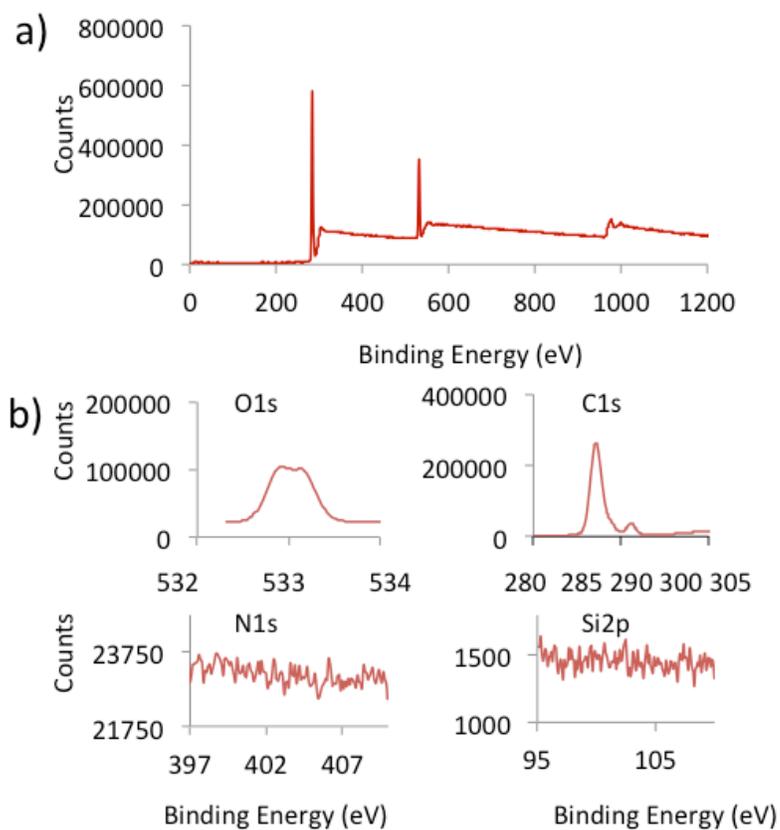


Figure S2. XPS spectra of the adhesive side of the sticky tape used in the study. a) Survey scan and b) Hires spectra at O1s, C1s, N1s, and Si2p regions. There is no silicon or nitrogen-containing additive on the sticky side.

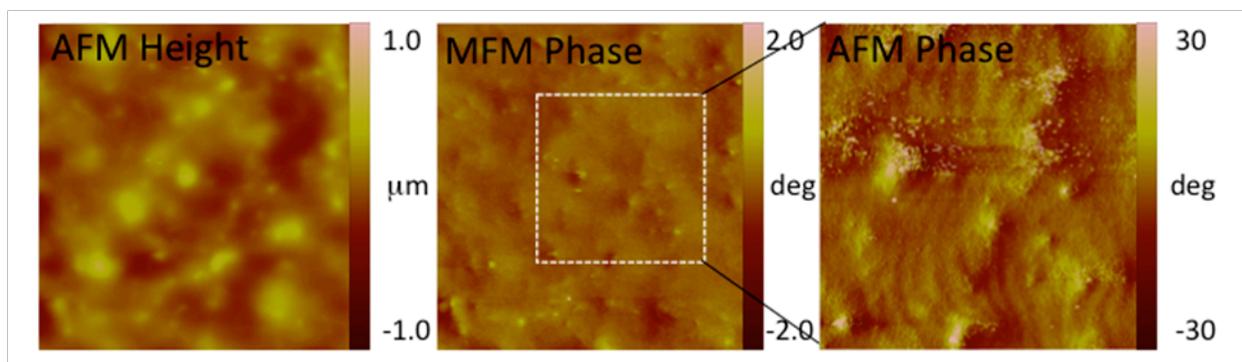
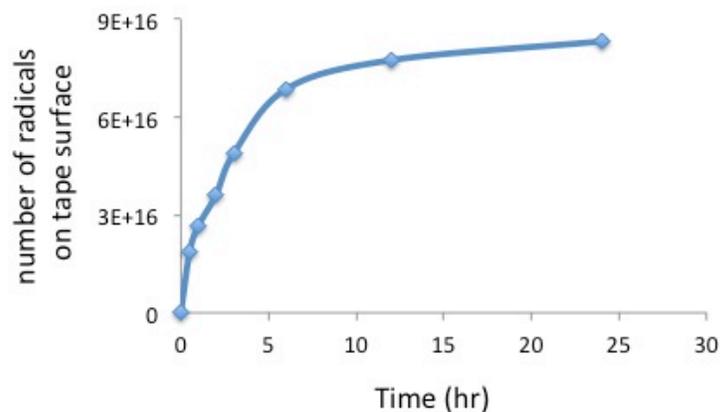


Figure S3. AFM height, MFM phase and AFM phase images of the non-sticky side of the adhesive tape showing no significant bond-breaking and no radicals. Image sizes are (from left to right) 50 μm , 50 μm and 20 μm



time (hr)	0	0.5	1	2	3	6	12	24
delta Abs	0	0.036	0.051	0.069	0.093	0.131	0.148	0.159
Conc (DPPH) consumed*	0	3.13043E-06	4.43E-06	0.000006	8.09E-06	1.14E-05	1.29E-05	1.38E-05
volume of dye solution	0	0.01	0.01	0.01	0.01	0.01	0.01	0.01
mol of dye consumed	0	3.13043E-08	4.43E-08	6E-08	8.09E-08	1.14E-07	1.29E-07	1.38E-07
mol of radicals	0	3.13043E-08	4.43E-08	6E-08	8.09E-08	1.14E-07	1.29E-07	1.38E-07
number of radicals on tape surface	0	1.88452E+16	2.67E+16	3.61E+16	4.87E+16	6.86E+16	7.75E+16	8.32E+16

* Molar absorptivity of DPPH in CH₃CN is 11500 cm⁻¹ M⁻¹

Figure S4. Estimation of the number of radicals that bleached DPPH in the solution outside of the adhesive tape. After peeling, adhesive tape was immersed in 10 mL of DPPH solution (10.0 μ M in CH₃CN) for 24 hrs. The radicals reaching the surface of the polymer reacted with the surrounding DPPH solution and bleached it from purple to yellow (cf. Fig. 4b in the main text).

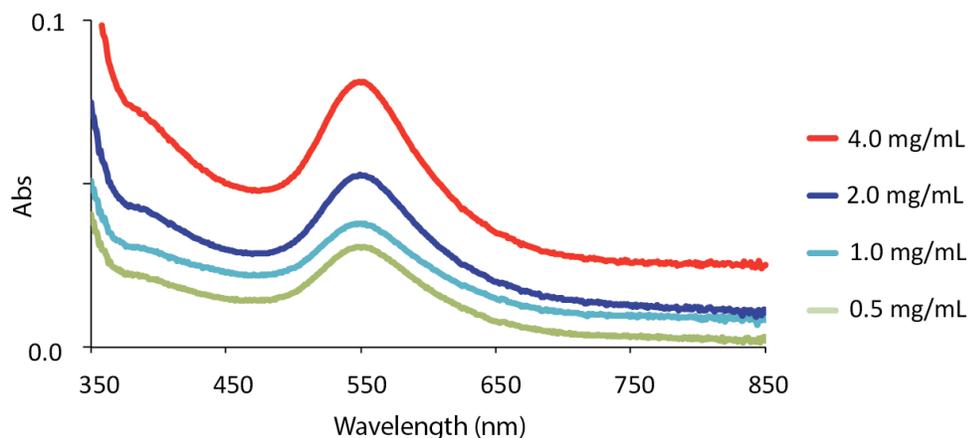


Figure S5. Formation of AuNPs on adhesive tapes at different concentrations of salt solution, monitored by UV-Vis spectroscopy. Immersion time 24 hrs.

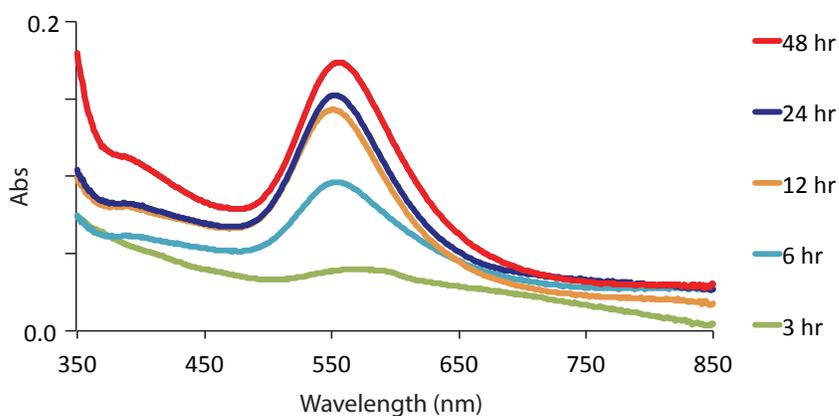


Figure S6. Formation of AuNP on adhesive tapes with time, monitored by UV-Vis spectroscopy. $[\text{HAuCl}_4] = 4 \text{ mg / mL}$.

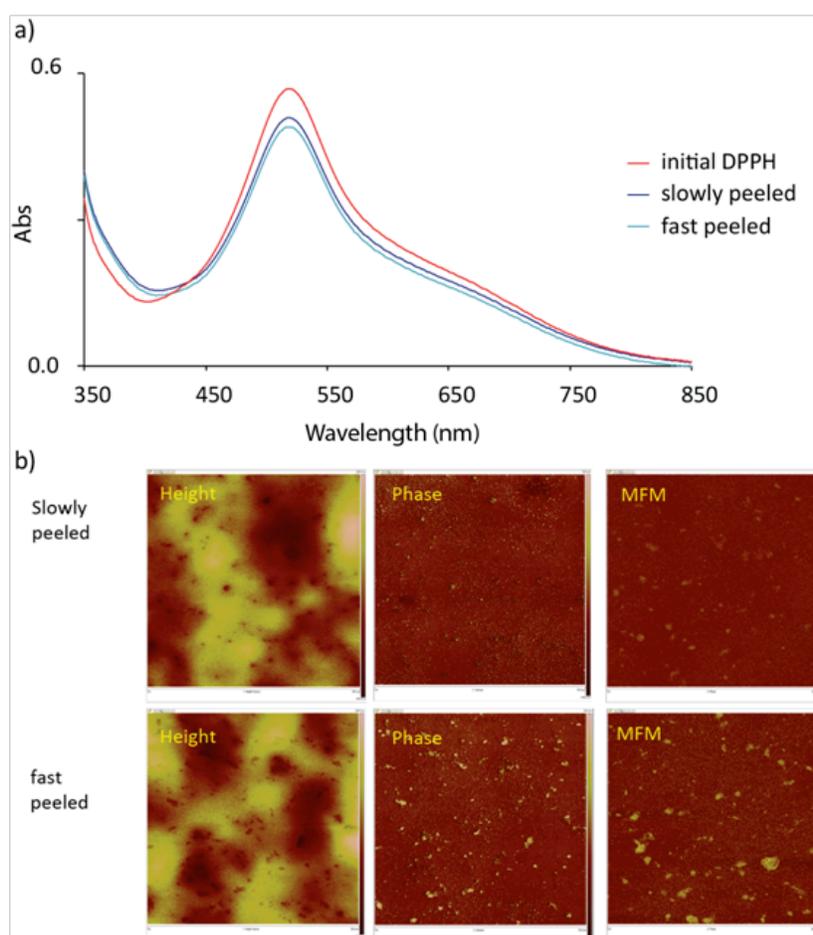


Figure S7. a) Formation of AuNPs on rapidly (50 cm/s) and slowly (0.2 cm/s) peeled adhesive tapes, monitored by UV-Vis spectroscopy. **b)** AFM height, phase and MFM images of the slowly and rapidly peeled tapes. MFM image shows higher contrast for rapidly peeled tapes indicating more radicals are forming, Image size = 50 micron.

Particle size determination:

From TEM imaging: TEM analyses of the AuNPs on the sticky tape after 24 hours of deposition time show that the average particle size is ca. 100 nm, which is in good agreement with the UV-Vis absorption maximum (570 nm) vs. particle size correlation found by others¹ for similar UV-Vis spectroscopic analyses of spherical AuNPs. Interestingly, the deposited material also contains some nanotriangles and nanorods of gold.

From the XRD analyses: Using Scherrer equation, we determined the particle sizes as follows; $\tau = \kappa\lambda / (\beta \cos\theta)$, where τ is the mean size of the crystalline nanoparticles, κ is the shape factor, which is taken as 0.94 for spherical crystallites with cubic symmetry, λ is the X-ray wavelength (1.5404 Å), β is the line broadening (full width at maximum height), after subtracting the instrumental line broadening (radians), and θ is the Bragg angle (the 111 plane appears at $\theta = 38.18^\circ$ for AuNP, and at $\theta = 37.87^\circ$ for AgNP). We found out the average particle size as 41 nm for AuNP, and 45 nm for AgNP, which are smaller than the values determined by TEM and UV-Vis spectroscopy. While the XRD confirms the metallic structure of the deposited metal, we believe the size determination by TEM is more accurate since it does not require additional parameters (like in the Scherrer formula).

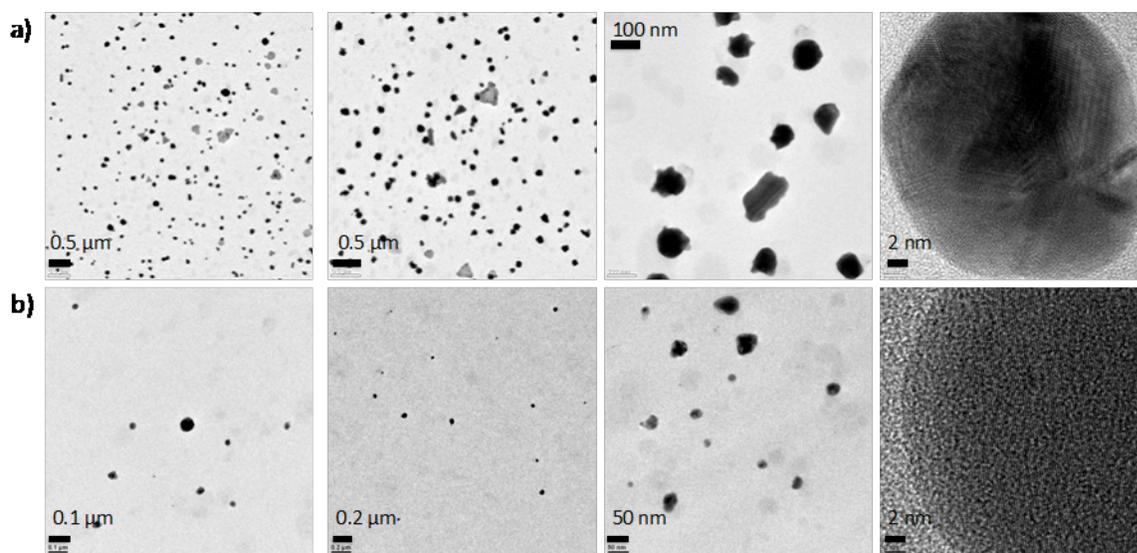


Figure S8. TEM images of a) gold and b) silver nanoparticles formed on the adhesive tapes. Nanoparticle-sticky tape composite was analyzed after isolation of the polyacrylate (sticky) polymer from the adhesive tape by soaking the tape in pure dichloromethane.

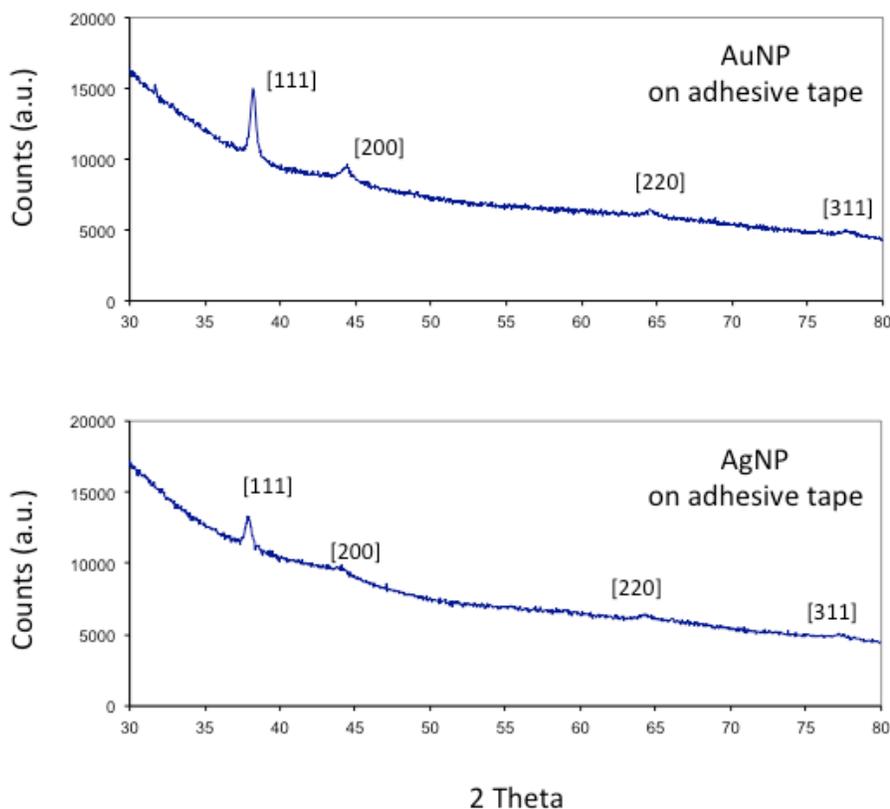


Figure S9. XRD patterns of prepared AuNP and AgNP (from HAuCl_4 , AgNO_3 solutions each 4 mg/mL in H_2O , tape immersion time: 24 hrs) The observed peaks are for [111], [200], [311], and [222] at $2\theta = 38.0, 44.4, 64.7, \text{ and } 77.7$ for AuNPs showing the metallic crystalline lattice structure (fcc) of the deposited material. AgNP have similar values since AgNP have the same lattice structure (fcc) and the radii of silver atoms are very close to that of gold atoms.

XPS analysis:

The XPS analyses summarized in Fig. S10 evidences that the deposited Ag or Au is, indeed, in the metallic state (for the silver, the $3d_{5/2}$ peak). For PdNPs, the deposition is usually less than the other metals likely due to the poor solubility of PdCl_2 precursor in water.² However, the deposition can still be readily detected visually (brownish color) and also instrumentally via the UV-Vis spectral changes (Figure 2b). While it is more challenging to obtain a HIREX XPS spectrum, we managed to do so – we provide an XPS spectrum to show only palladium, oxygen, and carbon; the absence of chlorine (with binding energy 201 eV) indicating that the deposited material does not contain any chloride. HIREX XPS spectrum of palladium shows two signals with binding energy 336.5 eV for Pd $3d_{5/2}$ and 342.0 eV for Pd $3d_{3/2}$.³ For copper nanoparticles (CuNPs), the HIREX XPS spectra show two signals for Cu $2p_{1/2}$ at 951.8 eV and Cu $2p_{3/2}$ 931.8 eV.⁴ (We also note that the copper nanoparticles may contain an oxide layer of Cu(I), which is hard to differentiate from Cu(0) with XPS analysis).⁵ Nevertheless, the spectrum does not contain any Cu $^{2+}$, which would appear around 945 eV as an intense signal.⁴

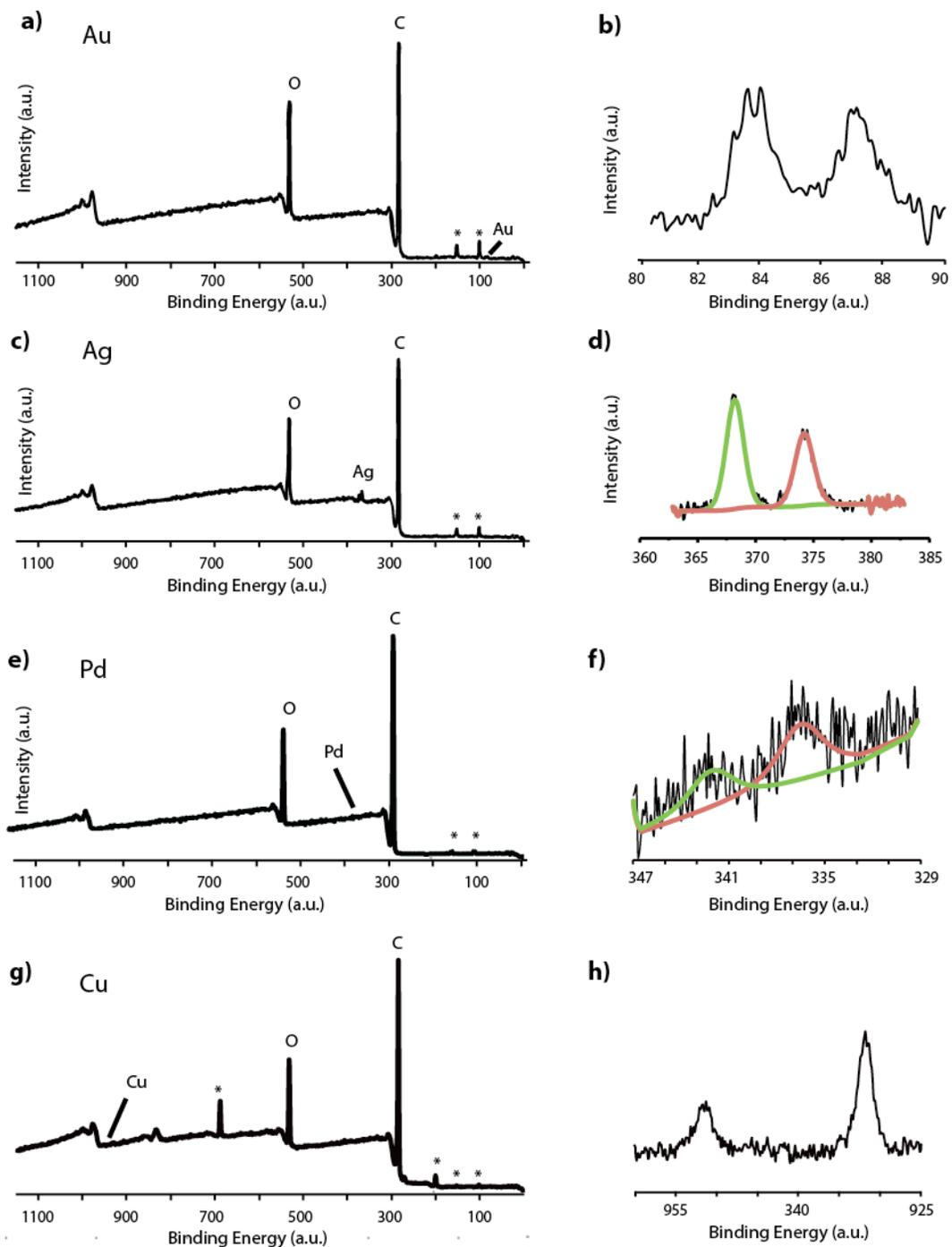


Figure S10. XPS spectra of adhesive tapes with (from top to bottom) Au, Ag, Pd, and Cu nanoparticles deposited. On the left are the survey scans, and on the right are the corresponding high resolution scans. (* indicates elements from the substrates, on which the tapes were placed for XPS analyses.)

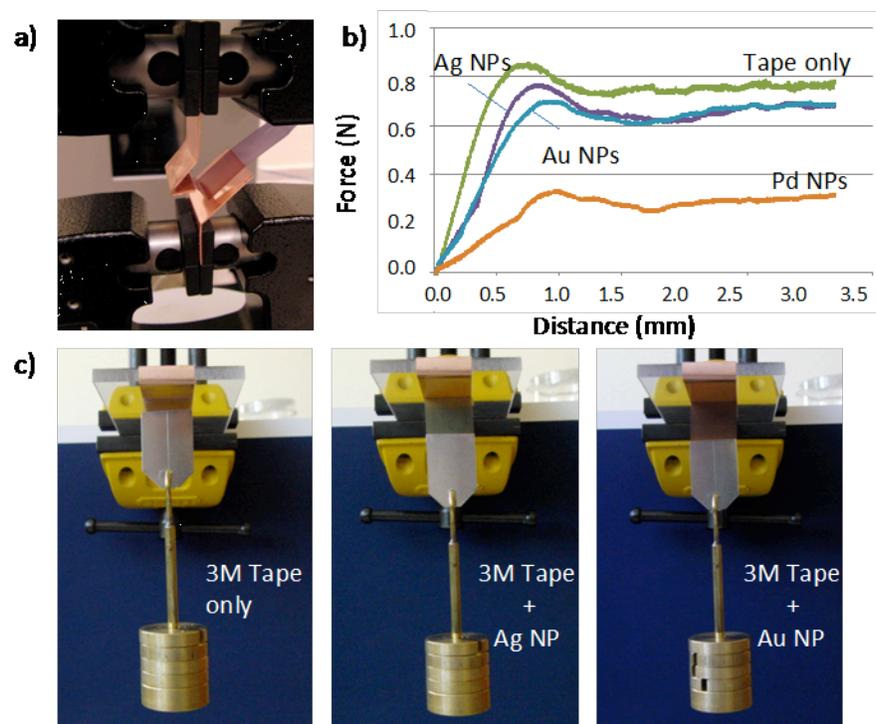


Figure S11. Adhesiveness test on 3M tapes with and without nanoparticles. a) experimental setup; peeling tests were done on a polished copper plate at an angle of 45°, b) Force vs distance curves upon peeling. Nanoparticle deposited tapes need a smaller force compared to that of tape without nanoparticles, and c) photos showing the adhesiveness of the tapes with a load of 1.3 N.

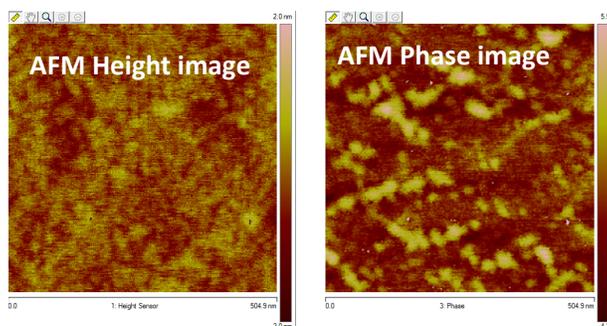


Figure S12. AFM images of the adhesive polymer with gold nanoparticles, image size 500 nm (immersion time 24 hrs, $[\text{HAuCl}_4] = 2\text{mg/mL}$)

Section 3. Antibacterial effect of AgNP adhesive tapes

E. coli (ATCC 25922) was grown on Mueller-Hinton Agar plates (Hardy Diagnostics) at 37 °C for 16 hrs. Single colonies were isolated from this culture and were used to inoculate Mueller-Hinto broth and grown overnight at 37 °C for 16 hrs. After the incubation, bacterial concentrations were determined to be 2.08×10^9 cfu/mL using the serial dilution method. As described previously, the Kirby-Bauer disk diffusion test was used to measure the antibacterial effect of the coatings (References 15 and 16 in the main text). Mueller-Hinton Agar plates were inoculated with freshly grown bacteria and left to stand for

2-3 minutes in a sterile condition. Adhesive polymers with newly formed AgNP coatings were then placed directly on top of the plates before they were incubated at 37 °C for 16 hrs. The plates were imaged using 10X objective and the Zone of Inhibition (ZOI) was measured using Bitplane[®].

¹ Haiss, W.; Thanh, N. T. K.; Aveyard, J.; Fernig, D. G. *Anal. Chem.* **2007**, *79*, 4215.

² Zhang, X.-X.; Harris, M. C.; Sadighi, J. P.; Buchwald, S. L. *Can. J. Chem.* **2001**, *79*, 1799.

³ a) Lu, L.; Wang, H.; Xi, S.; Zhang, H. *J. Mater. Chem.* **2002**, *12*, 156. b) Yang, S.; Dong, J.; Yao, Z.; Shen, C.; Shi, X.; Tian, Y.; Lin, S.; Zhang, X. *Scientific Reports* **2014**, *4*, 4501, 1.

⁴ Abdulla-Al-Mamun, M.; Kusumoto, Y.; Muruganandham, M. *Mater. Lett.* **2009**, *63*, 2007.

⁵ Gonzalez-Arellano, C.; Luquez, R.; Macquarrie, D. J. *Chem. Commun.* **2009**, 4581.