Supplementary materials

Partial Hydrogenation of Soybean and Waste Cooking Oil Biodiesel over Recyclable Polymer Supported Pd and Ni Nanoparticles

Ambra Maria Fiore, Giuseppe Romanazzi, Cristina Leonelli, Piero Mastrorilli and Maria Michela Dell'Anna*

Contents

1S. Characterization of FAMEs: GC-MS analyses and Mass Spectra .....pag 2

2S. STEM analyses *Ni-pol*..... pag 5

3S. TEM analyses *Pd-pol*..... pag 8

1S. Characterization of FAMEs

FAME composition (%wt) was determined by GC-FID analyses with the internal standard method (methyl eptadecanoate).

The average molar mass (AMM) of biodiesel was calculated on the base of the FAME composition (%wt), by the formula: $AMM = \Sigma (\chi_i \cdot MM_i)$, where χ_I and MM_i are the molar mass and the molar fraction of the *i*-FAME, respectively.

Identification and characterization of FAMEs was achieved by GC-MS analyses by comparing NIST database literature data and authentic samples.

Methyl Palmitate (C16:0)
MS m/z (%): 270 (10, M^+); 227 (9); 143 (12); 87 (62); 74 (100).

Methyl Stearate (C18:0)
MS m/z (%): 298 (9, M^+); 255 (9); 199 (12); 87 (66); 74 (100).

Methyl Oleate (C18:1)
MS m/z (%): 296 (9, M^+); 264 (18); 222 (15); 97 (61); 69 (80); 55 (100).

Methyl Linoleate (C18:2)
MS m/z (%): 294 (12, M^+); 263 (10); 109 (30); 95 (60); 81 (90); 67 (100).

Methyl Linolenate (C18:3)
MS m/z (%): 292 (5, M^+); 236 (5); 121 (20); 95 (50); 79 (100).

Methyl Arachidate (C20:0)
MS m/z (%): 326 (25, M^+); 283 (12); 87 (55); 74 (100).

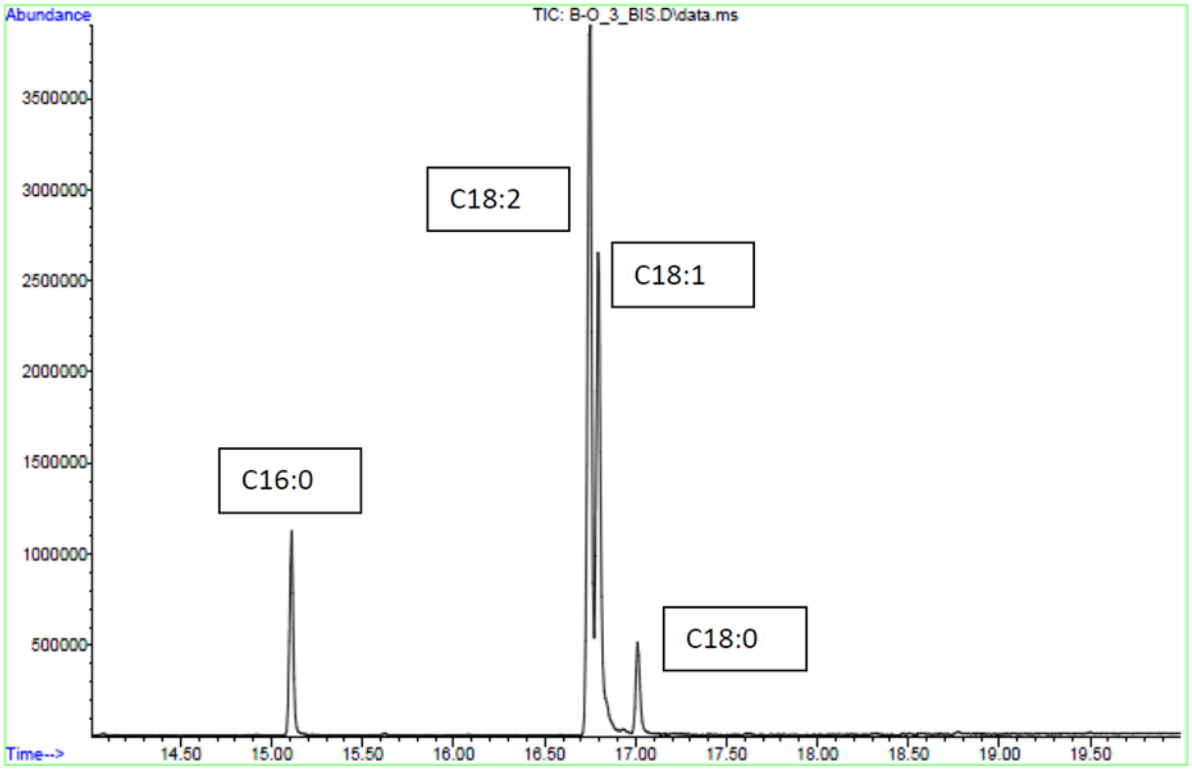

Figure S1. Chromatogram of FAMEs obtained from waste cooking oil using GC-MS instrument. C18:3 is partially overlapped by C18:1 peak. C20:0 gives a small peak at retention time = 18.79 min.

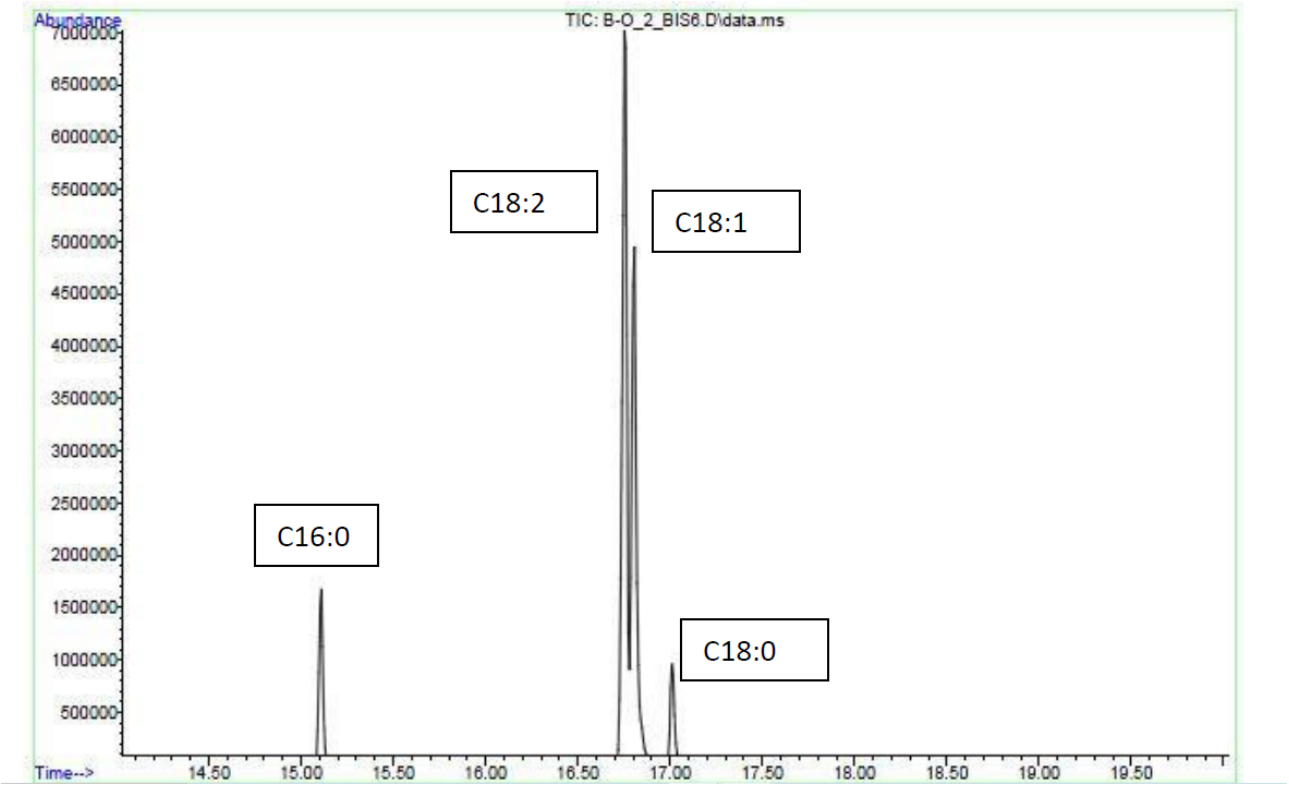

Figure S2. Chromatogram of FAMEs obtained from soybean oil using GC-MS instrument. C18:3 is partially overlapped by C18:1 peak. C20:0 gives a small peak at retention time = 18.79 min.

2S. STEM analyses of *Ni-pol*

Scanning Transmission Electron Microscopy (STEM) analyses were performed by Nova NanoSEM 450 manufactured by FEI Company, USA. TEM copper grids were used for samples, that were gold-palladium sputtered (K550, Emitech Ltd, UnitedKingdom). Scanning Transmission Electron Microscopy (STEM) Detector allowed transmission images to be taken at 30 keV. Resolution limits of this microscope were:1.4 nm @ 1 kV in high vacuum mode.

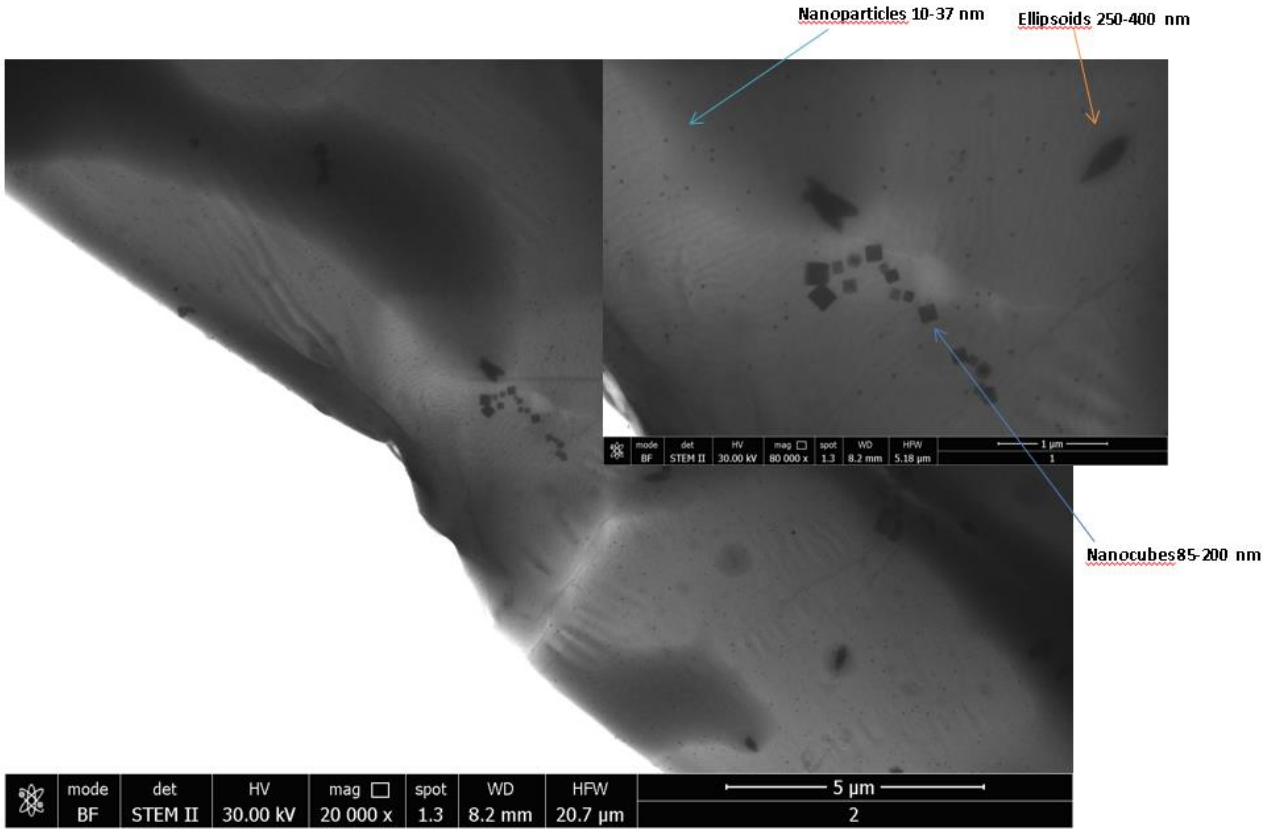

Figure S3: STEM image of *Ni-pol* before use in catalysis.

After calcination, Ni nanoparticles formed on Ni-pol surface. Figure S3 shows the presence of small metal nanoparticles of diameter size ranging from 10 to 37 nm, nanocubes with size ranging from 85 to 200 nm and ellipsoids with major diameter comprises between 250 and 400 nm.

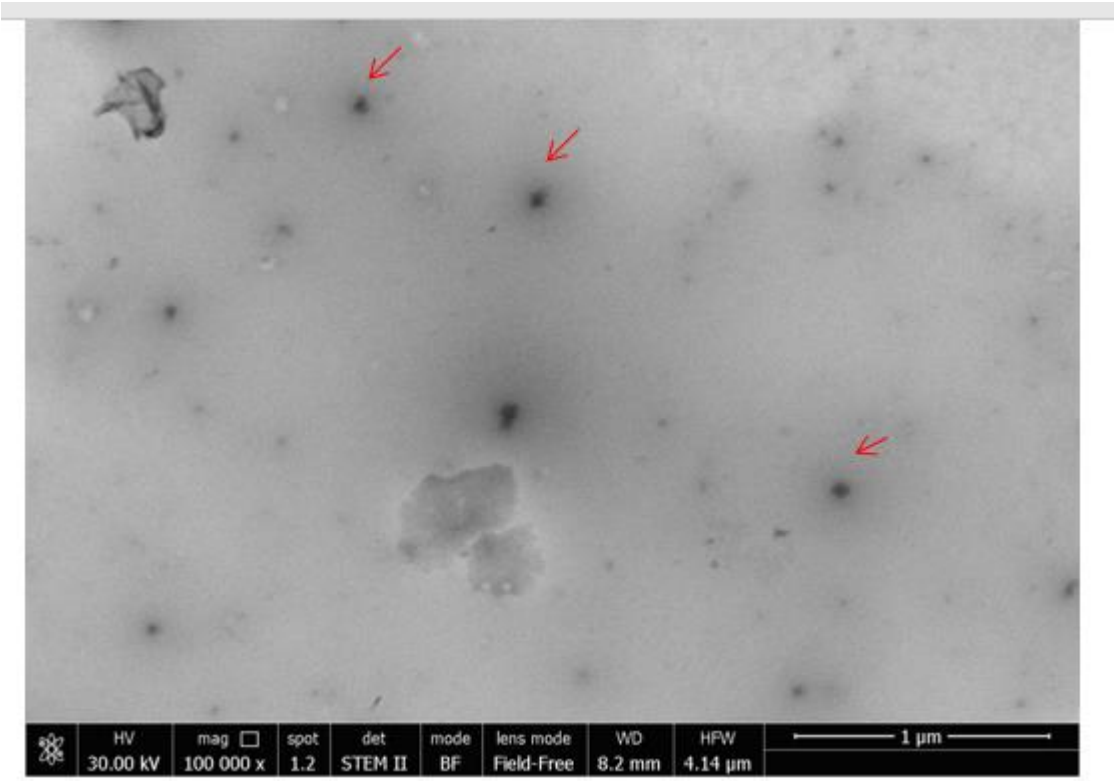

Figure S4a: STEM image of *Ni-pol* recovered after five cycles. Red arrows indicate some nanoparticles as in the pristine catalyst.

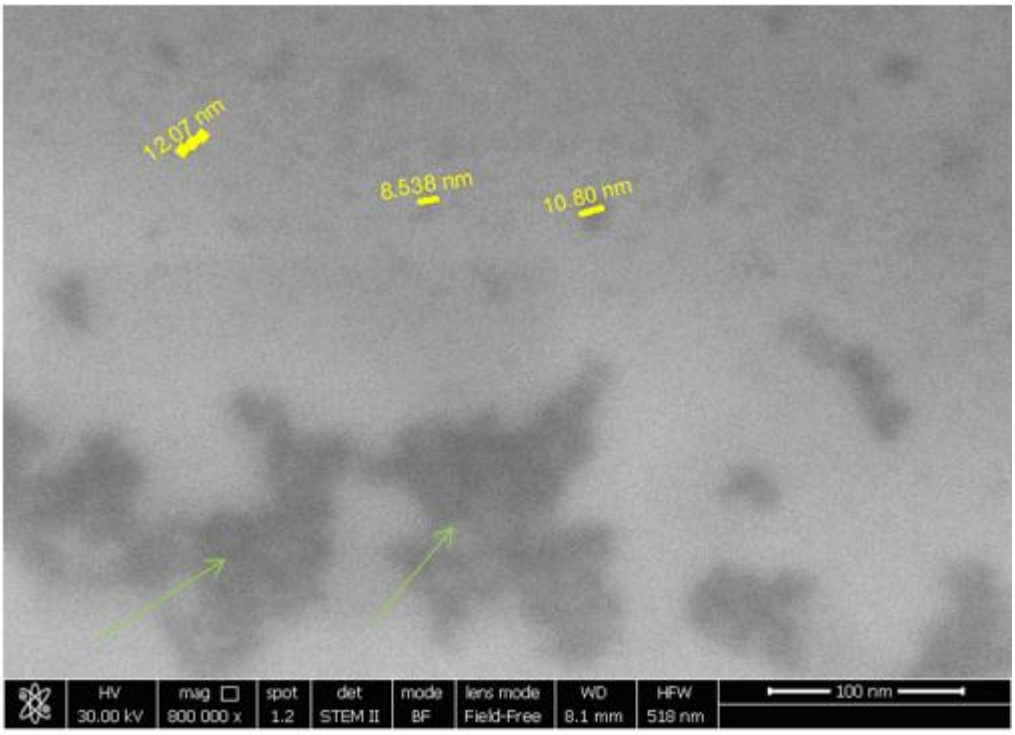

Figure S4b: STEM image of *Ni-pol* recovered after five cycles. Smaller nanoparticles (8-10 nm) are more evident than in the pristine *Ni-pol*. Some large particles aggregate at the polymer surface (green arrows)

STEM images of Ni-pol recovered after five catalytic runs show the presence of Ni nanoparticles already found in the pristine catalyst (Figure S4a), besides new small metal nanoparticles (8-10 nm in size, Figure S4b) presumably formed under reaction conditions and particles aggregates (green arrows, Figure S4b)

3S. TEM analyses of *Pd-pol*

Transmission Electron Microscopy (TEM) observations were carried out by TEM instrument Model JEM 2010, Jeol, Akishima Tokyo, Japan, equipped with X-ray energy dispersive spectroscopy (EDS), at acceleration voltage of 200 kV. Samples were prepared by dispersing powders in distilled water using an ultrasonic stirrer and then placing a drop of suspension on a copper grid covered with a transparent polymer film, followed by drying and carbon coating.

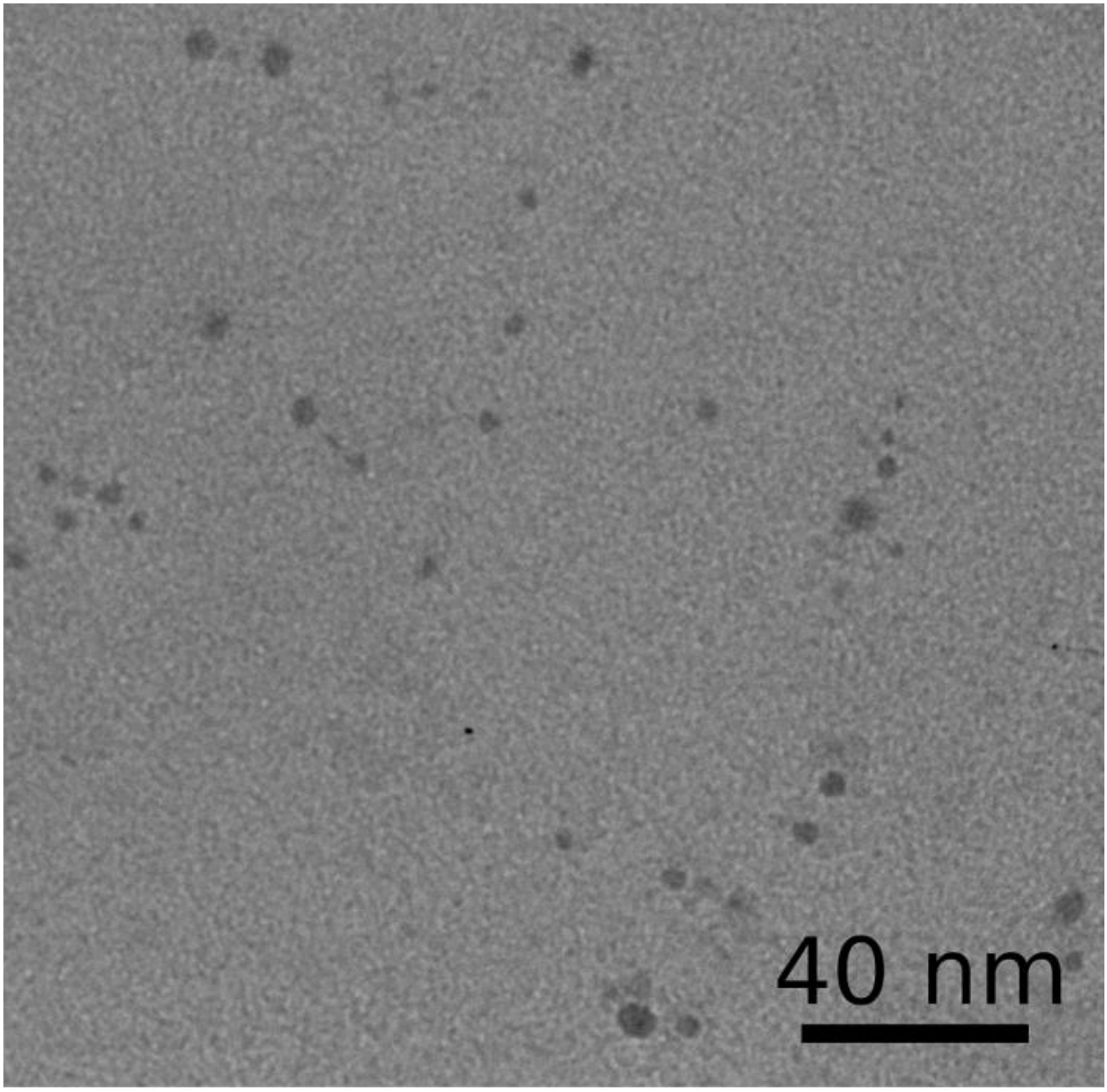

Figure S5: TEM image of *Pd-pol* before use in catalysis.

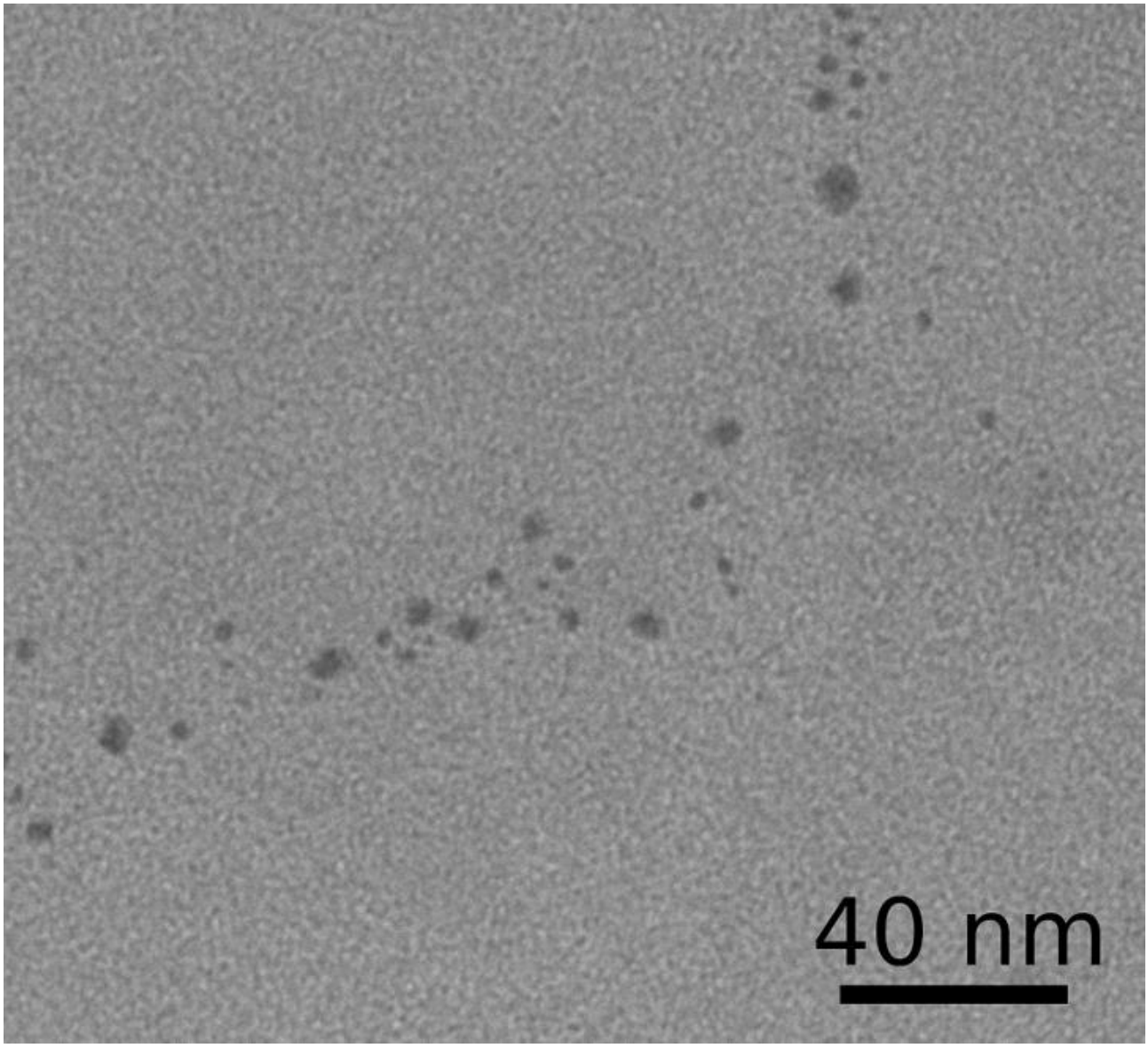

Figure S6: TEM image of *Pd-pol* recovered after five cycles.