Lin et al. characterized Au/TiO₂ films by surface enhanced Raman scattering, observing red-shift in the extinction spectrum with increasing TiO₂ film thickness. We investigate a similar Au/TiO₂ structure by analytical electron microscopy. A TiO₂ film was deposited on an optical microscope glass slide at 200°C, by 417 cycles of atomic layer deposition (ALD) using tetrakisdimethylamido titanium and H₂O. An Au layer ~3 nm thick was then deposited on the TiO₂ film surface by thermal evaporation. The specimen was reinforced with carbon and Pt layers. Analytical EM was performed using a JEM-2100F UHR STEM. TEM images (Figs. 1a and 1b) reveal that the Au film was composed of round particles with diameters of ~15 nm or less. The thickness of TiO₂ layer was 11 nm though the nominal thickness was 19 nm. On this glass substrate, the sticking probability for the TiO₂ ALD was poor and the TiO₂ layer was amorphous. Figs. 1d and 1e. This thin specimen with a mean thickness of t < 0.31λ warrants the accuracy of the EELS analysis. Composite EFTEM map (Fig. 1f) indicates the TiO₂ layer and the reinforcement of C. Figs. 2b-2f show EDS analysis of the Au/TiO₂ microstructure in HAADF image (Fig. 2a). Figs. 2b and 2e show that the substrate was common soda lime glass containing Ca atoms. Fig. 2f indicates the TiO₂ layer. However, the EDS maps in Figs. 2b, 2c, and 2e exhibit artifact contrasts (in blue circles) due to the higher background of X-rays stimulated by strong emissions form Au particle. EELS maps in Figs. 2g-2l do not exhibit any artifact in the gold region, confirming the existence of TiO₂ layer. Ca atoms could diffuse into an area in less than a few nanometers from the substrate surface. When the amorphous TiO₂ layer was thin, voids on its surface might been occupied by diffused Ca atoms, and the deposited Au atoms migrated easily on the surface and formed more Au nuclei, accordingly. This explains the difference in growth behavior among Au films reported in ref. (1).
Fig. 1: Au/TiO₂ structure on the glass sheet. Conventional (a) and HR-TEM images (b), EFTEM thickness map (t/λ) (c), Zero-loss (0.5 eV) (d) and conventional EFTEM images (e), and composite EDS map (f).

Fig. 2: HAADF image (a), EDS (b-f) and EELS maps (g-j), O-K map with energy-loss near-edge structure for Ti-O (k), and composite EELS map (Ca:red, Ti:green and C:blue).