Supporting Information

Activity improvement of gold yolk-shell catalysts for CO oxidation by doping with TiO_2

Robert Güttel, Michael Paul, Ferdi Schüth*

Max-Planck-Institut für Kohlenforschung, Department of Heterogeneous Catalysis,
Kaiser-Wilhelm-Platz 1, 45470 Mülheim an der Ruhr, Germany.

Chemicals

In all preparation steps millipore water (18.2 MΩ cm^{-2}) or absolute ethanol (99.9 %, LiChrosolv®, Merck) were used as solvents. The $HAuCl_4$ solution was produced by dissolving gold in boiling aqua regia. Other chemicals used are: sodium citrate (citric acid trisodium salt dihydrate, 99 %, ACROS organics), polyvinylpyrrolidone (K 15, Fluka), ammonia solution (28-30 % NH_3 in water, Merck), TEOS (tetraethyl orthosilicate, 98 %, ACROS organics), lutensol AO5 (BASF), zirconium butoxide (80 wt% in butanol, Aldrich), titanium butoxide (80 wt% in butanol, Aldrich), titanium(IV)-propoxide (98 %, Aldrich), NaOH (97 %, pellets, Merck) and MTBE (99.9 %, Biesterfeld).

Au/TiO_2, @ZrO_2

The Au@SiO_2 intermediate material was prepared according to our previous method.[1] Millipore water was refluxed under stirring and 25 mL of a $HAuCl_4$ (2.54×10^{-3} M) solution was added, followed by addition 12.5 mL of a sodium citrate solution (10 mg mL^{-1}). The resulting solution was refluxed for 30 min and finally cooled to room temperature. Subsequently, 0.325 mL of an aqueous polyvinylpyrrolidone solution (12.8 mg mL^{-1}) was added and the resulting mixture was stirred overnight to allow complete adsorption of the polymer on the gold surface. The solution was than centrifuged (10000 rpm, 50 min) to remove the supernatant. The volume of the concentrated colloid was adjusted to 6 mL by dilution with water and vigorously stirred for 5 min. The doping with titania was achieved by adding up to 3 mL titania precursor solution (0.1 ml titanium(IV)-propoxide, Aldrich, in 8 g EtOH) to the concentrated gold colloid solution under stirring for 30 min. The titania precursor was intended to adsorb and form a thin layer on the gold nanoparticle surface. For covering the colloid with silica an ammonia solution (18.9 mL ethanol premixed with 0.84 mL of aqueous ammonia solution) was added immediately followed by addition of a TEOS solution (1.19 mL TEOS in 12.8 mL ethanol). The reaction mixture was stirred overnight at room temperature and then centrifuged (10000 rpm, 30 min) and washed (2 × water, 2 × ethanol). The intermediate material (Au/Ti, @SiO_2) was redispersed in 25 g ethanol in a 100 mL flask sealed with a septum and heated under vigorously stirring to 30 °C. Then 0.125 mL of an aqeous lutensol solution (430 mg lutensol in 11 g water) was added. After 1 h stirring 0.45 mL zirconium butoxide was added and the reaction was allowed to proceed overnight. The liquid phase was then exchanged for water by centrifugation and redispersion of the solid in water (25 mL) for four times. After aging the material at room temperature for 3 d the material was calcined in air by heating from room temperature to 900 °C with a heating rate of 2 K min^{-1} followed by natural cooling. Finally, the silica spacing layer was removed by treatment with 1 M NaOH solution at 50 °C. The resulting core-shell particles are washed for four times with water, once by ethanol and once by MTBE before drying at 50 °C.

Au, @TiO_2

The Au@SiO_2 intermediate material was prepared as described above. Specifically, millipore water was refluxed under stirring and 25 mL of a $HAuCl_4$ (2.54×10^{-3} M) solution was added, followed by addition 12.5 mL of a sodium citrate solution (10 mg mL^{-1}). The resulting solution was refluxed for 30 min and finally cooled to room temperature. Subsequently, 0.325 mL of an aqueous polyvinylpyrrolidone solution (12.8 mg mL^{-1}) was added and the resulting mixture was stirred overnight to allow complete adsorption of the polymer on the gold surface. The solution was than centrifuged (10000 rpm, 50 min) to remove the supernatant. The volume of the concentrated colloid was adjusted to 6 mL by dilution with water and vigorously stirred for 5 min. In the next step an ammonia solution (18.9 mL ethanol premixed with 0.84 mL of aqueous ammonia solution) was added immediately followed by addition of a TEOS solution (1.19 mL TEOS in 12.8 mL ethanol). The reaction mixture was stirred overnight at room temperature and than centrifuged (10000 rpm, 30 min) and washed (2 × water, 2 × ethanol). The resulting Au@SiO_2 intermediate material was dispersed in 25 g ethanol and lutensol was added as described above. After 1 h 6 mL titanium butoxide was added and the reaction was allowed to proceed overnight. Following, the material was washed four times with water and aged for up to 6 d before calcination in air by heating from room temperature to 900 °C with a heating rate of 2 K min^{-1} followed by natural cooling. Finally, the silica spacing layer was removed by treatment with 1 M NaOH solution at 50 °C. The resulting core-shell particles are washed for four times with water, once by ethanol and once by MTBE before drying at 50 °C.

Au/TiO_2

As mentioned in the manuscript, some modified Au/TiO_2 material was prepared for TEM investigation. Firstly, millipore water was refluxed under stirring and 25 mL of a $HAuCl_4$ (2.54×10^{-3} M) solution was added, followed by addition 12.5 mL of a sodium citrate solution (10 mg mL^{-1}). The resulting solution was refluxed for 30 min and finally cooled to room temperature. Subsequently, 0.325 mL of an aqueous polyvinylpyrrolidone solution (12.8 mg mL^{-1}) was added and the resulting mixture was stirred overnight to allow complete adsorption of the polymer on the gold surface. The solution was than centrifuged (10000 rpm, 50 min) to remove the supernatant. The volume of the concentrated colloid was adjusted to 6 mL by dilution with water and vigorously stirred for 5 min. The doping with titania was achieved by adding up to 3 mL titania precursor solution (0.1 ml titanium(IV)-propoxide, Aldrich, in 8 g EtOH) to the concentrated gold colloid solution under stirring for 30 min. The titania precursor was intended to adsorb and form a thin layer on the gold nanoparticle surface. For covering the colloid with silica an ammonia solution (18.9 mL ethanol premixed with 0.84 mL of aqueous ammonia solution) was added immediately followed by addition of a TEOS solution (1.19 mL TEOS in 12.8 mL ethanol). The reaction mixture was stirred overnight at room temperature and then centrifuged (10000 rpm, 30 min). Subsequently, the material was calcined in air by heating from room temperature to 900 °C with a heating rate of 2 K min^{-1} followed by natural cooling. Finally, the silica spacing layer was removed by treatment with 1 M NaOH solution at 50 °C. The resulting core-shell particles are washed for four times with water, once by ethanol and once by MTBE before drying at 50 °C.

Catalytic measurements

The catalytic properties of the material were investigated in a fixed-bed reactor. Prior to catalytic measurement, the catalyst was stored under vacuum over night at $1\cdot10^{-2}$ mbar to remove the adsorbed water. The catalyst was introduced into a tube (5 mm internal diameter) and fixed with quartz glass wool at the bottom. The temperature was measured inside the catalyst bed by means of a thermocouple. The temperature inside the reactor was adjusted by flowing air through the reactor shell. The air is preliminary cooled by a bath of dry ice in isopropanol and subsequently electrically heated to the desired temperature. The catalytic measurements were carried out by heating the reactor from 0 °C to the final temperature with a heating rate of 2 K min^{-1}. During the temperature program, the composition of the product gas was permanently (interval of 5 s) analyzed by nondispersive IR absorption spectroscopy (EL3020, ABB). Three measurement runs were performed to activate the catalyst and reproduce the results of the activated catalyst. The first run was performed up to a temperature of 300 °C, while the following runs were stopped when a conversion close to 1 is reached.

Table S.1 Material composition from SEM-EDX (rest ZrO_2), temperature for 50 % conversion T_{50} and reaction rate at 60 °C r_{60}.

	composition				
sample ID	Au wt%	TiO_2 wt%	Ti/Au mol/mol	T_{50} °C	r_{60} $mol_{CO}\ kg^{-1}_{Au}\ s^{-1}$
	Au/TiO_2, @ZrO_2 material				
1	9.8	0	0	119	2.21
2	10.2	0	0	83	2.47
3	7.8	0	0	126	1.65
4	7.5	0.14	0.074	119	2.30
5	6.3	0.27	0.171	61	7.06
6	8.9	0.34	0.156	56	5.51
7	7.5	0.35	0.192	63	5.82
8	8.8	0.43	0.196	77	4.48
9	6.5	0.62	0.396	106	4.95
10	7.2	0.83	0.475	65	5.84
11	8.3	1.07	0.536	49	6.99
12	7.5	1.74	0.963	61	6.03
13	6.7	1.77	1.097	37	9.34
14	7.0	2.41	1.417	53	7.58
15	5.7	3.09	2.237	29	15.2
	Au, @TiO_2 material				
16	1.4	rest	162	86	25.6
17	2.2	rest	95	123	14.1
	heat treated material				
7ht	7.5	0.35	0.192	167	0.99
16ht	1.4	rest	162	165	6.71
17ht	2.2	rest	95	248	0.41

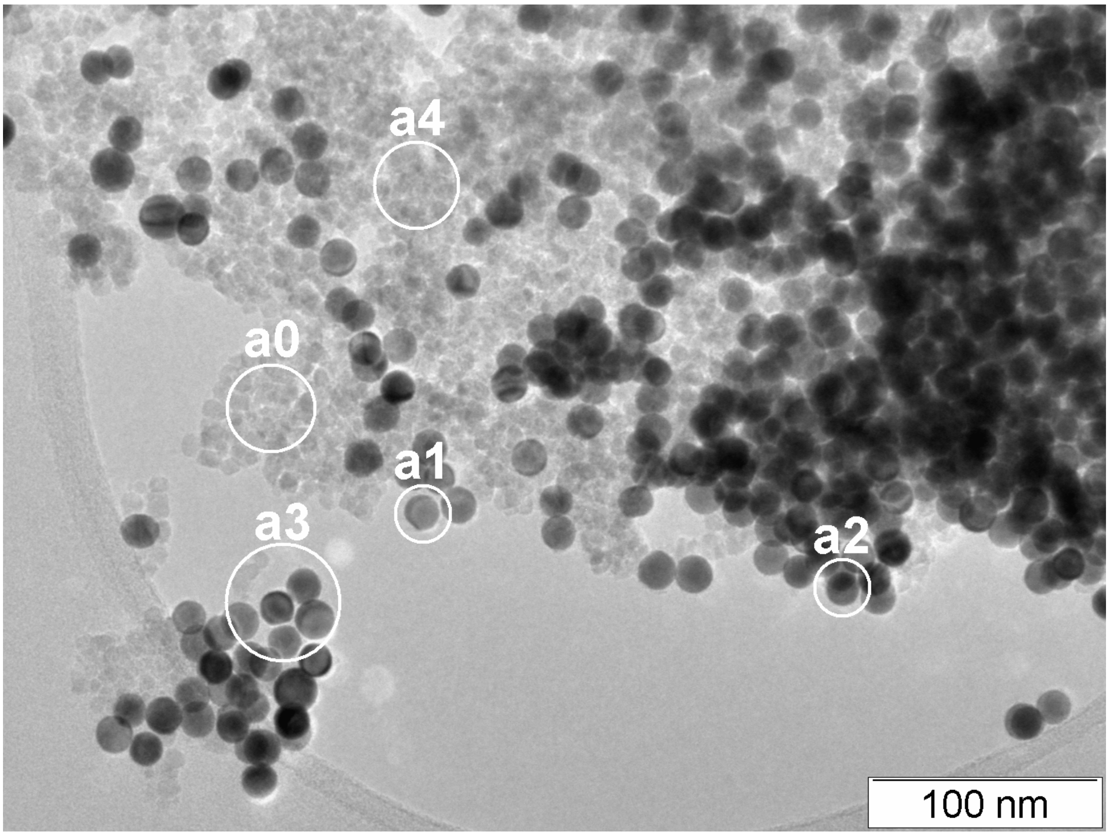

Figure S.1 Overview TEM image for TEM-EDX measurements of Au/TiO_2 material; section (a3) refers to Fig. 3d.

Table S.2 sample composition (in atom%) from TEM-EDX measurements (samples prepared on copper-grid).

Element	a0	a1	a2	a3	a4
O	63.3 ± 3.65	17.91 ± 3.80	0	16.51 ± 4.50	62.31 ± 3.97
Si	3.81 ± 0.68	6.91 ± 1.54	2.60 ± 1.49	3.18 ± 1.30	3.67 ± 0.50
Ti	22.20 ± 1.19	0	2.90 ± 0.64	5.12 ± 0.81	23.64 ± 1.27
Au	0	33.38 ± 2.53	41.08 ± 2.98	33.32 ± 2.88	1.23 ± 0.31
Cu (from grid)	10.70 ± 1.04	41.79 ± 3.30	53.41 ± 3.53	41.87 ± 2.46	9.15 ± 0.87

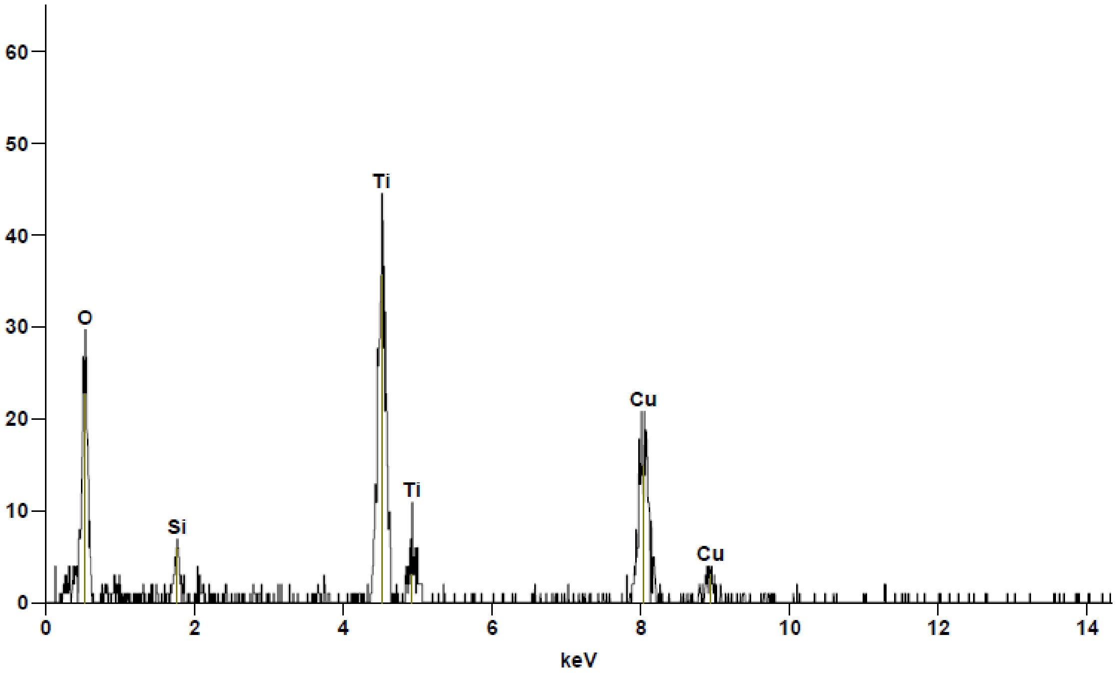

Figure S.2 TEM-EDX spectra Figure S.1a0.

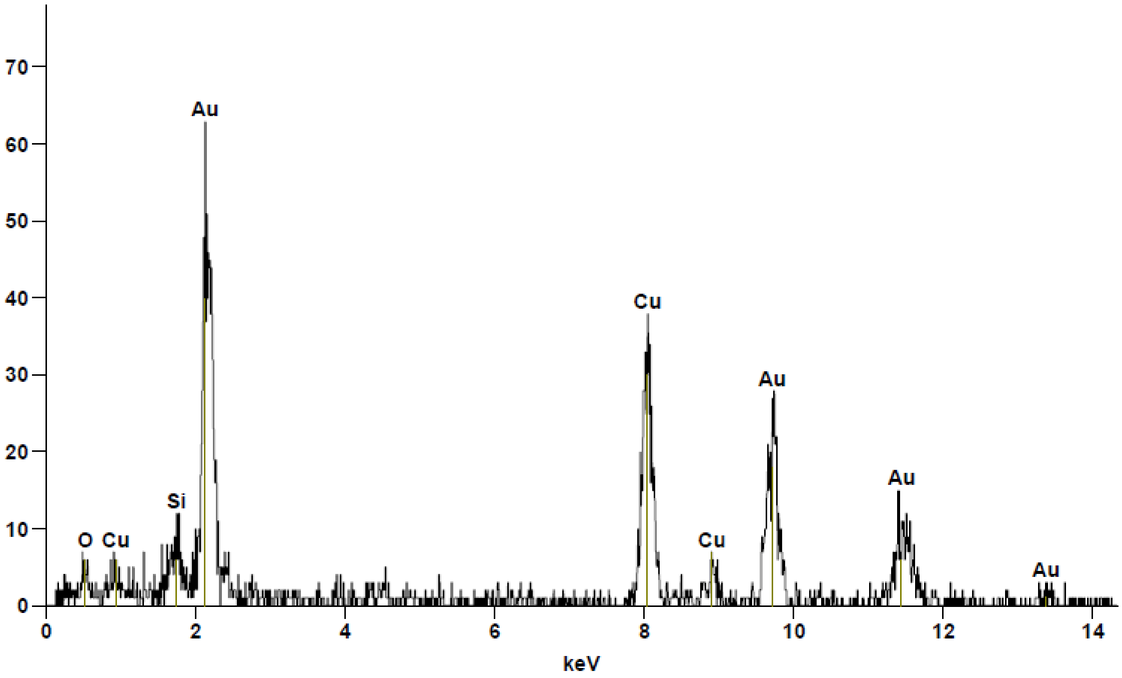

Figure S.3 TEM-EDX spectra Figure S.1a1.

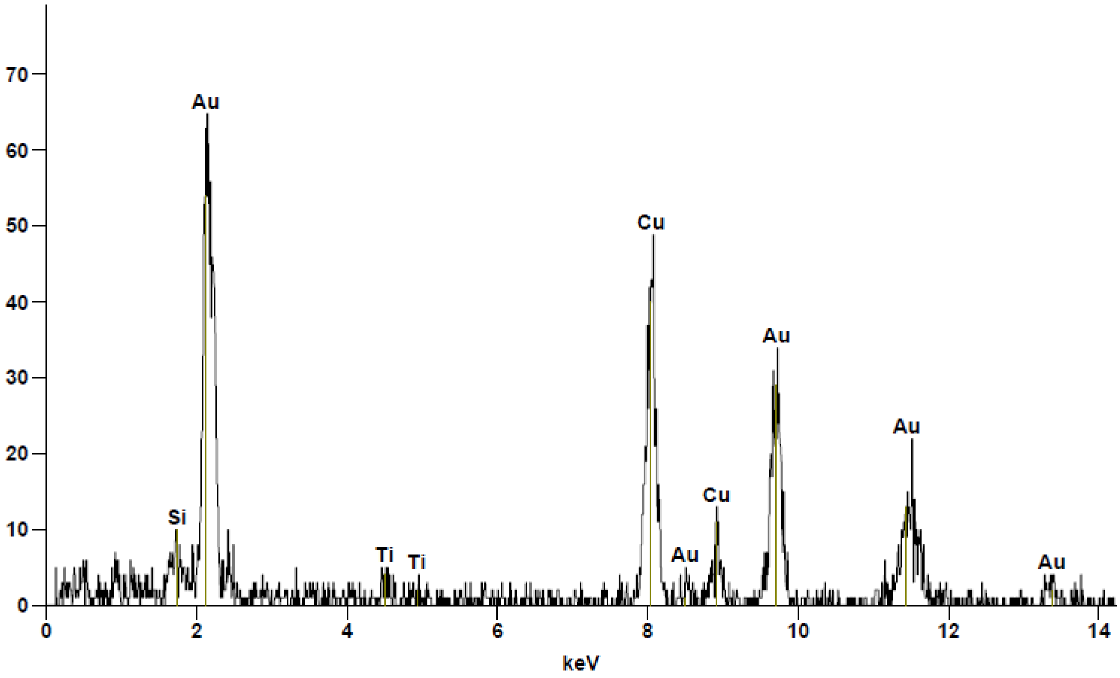

Figure S.4 TEM-EDX spectra Figure S.1a2.

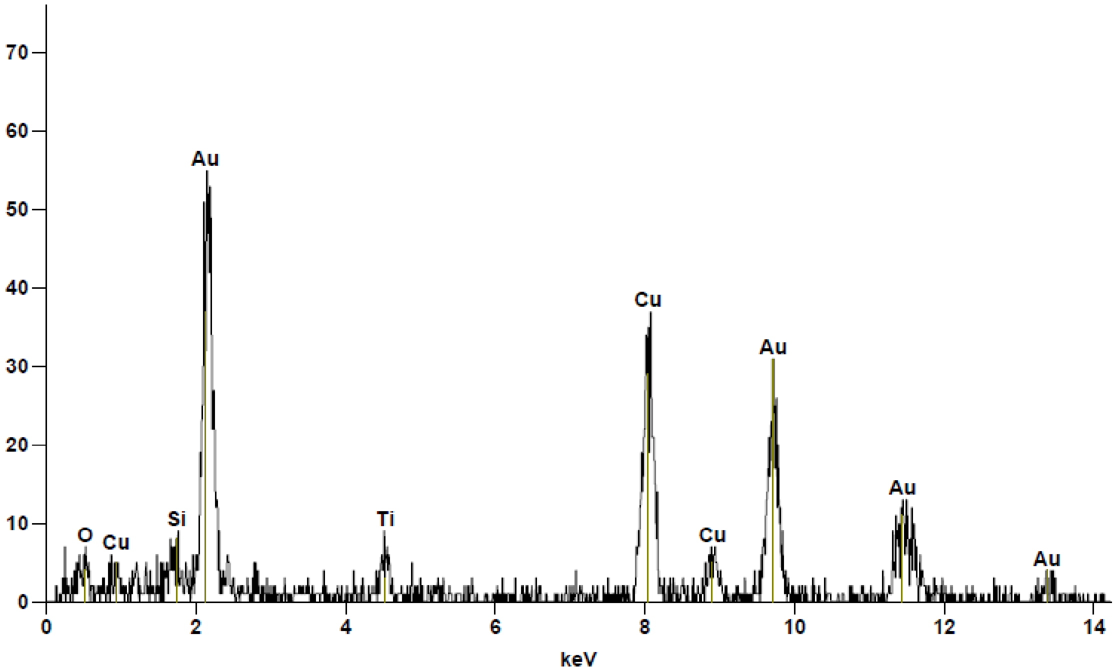

Figure S.5 TEM-EDX spectra Figure S.1a3.

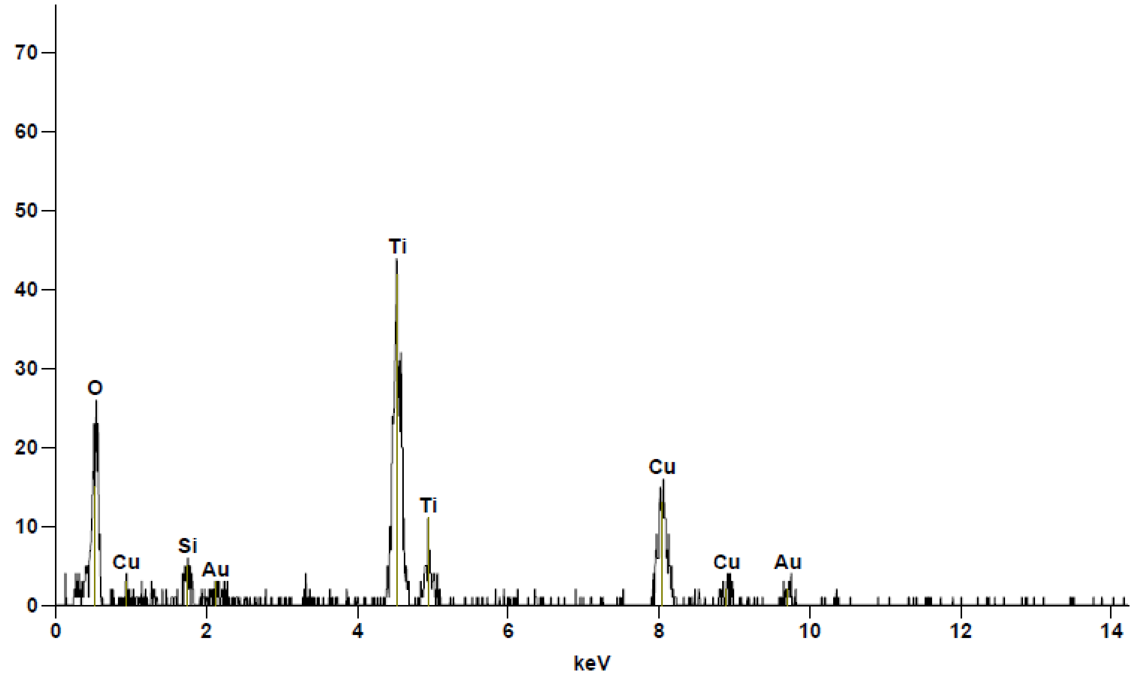

Figure S.6 TEM-EDX spectra Figure S.1a4.