## Facile Method to Attach Transition Metal Ions to the Surface of Anatase TiO2 Nanorods

Choumini Balasanthiran and James D. Hoefelmeyer

## **Supporting Information**

Table of Contents

1.0. Experimental Section
1.1 Synthesis of TiO2 nanorods and determination of mass TiO24
1.2 Synthesis of metalated TiO <sub>2</sub> nanorods4
Table 1. Experimental conditions for the attachment of different metal ion on TiO <sub>2</sub> NR surface
Figure S1. Mn(II)-TiO <sub>2</sub> and Fe(II)-TiO <sub>2</sub> dispersions exposed to air
Figure S2. Powder XRD for metalated $TiO_2$ nanorods. In all samples the ratio M: $TiO_2 = 0.07.6$
Figure S3. TEM images for metalated $TiO_2$ nanorods (scale bar 50nm). Top row, from left to right: $Cr(III)$ - $TiO_2$ , $Mn(II)$ - $TiO_2$ , $Fe(II)$ - $TiO_2$ ; bottom row, from left to right: $Co(II)$ - $TiO_2$ , $Ni(II)$ - $TiO_2$ , $Cu(II)$ - $TiO_2$ ). In all samples the mole ratio $M:TiO_2 = 0.07$
1.3 Determination of optimum OLAM:M mole ratio in the synthesis of M-TiO <sub>2</sub> nanorods8
Figure S4. Optimization of OLAM concentration for synthesis of Cr(III)-TiO <sub>2</sub>
Figure S5. Optimization of OLAM concentration for synthesis of Mn(II)-TiO <sub>2</sub>
Figure S6. Optimization of OLAM concentration for synthesis of Fe(II)-TiO <sub>2</sub> 9
Figure S7. Optimization of OLAM concentration for synthesis of Co(II)-TiO <sub>2</sub> 10
Figure S8. Optimization of OLAM concentration for synthesis of Cu(II)-TiO <sub>2</sub> 10
Figure S9. Optimization of OLAM concentration for synthesis of $Ni(II)$ -TiO <sub>2</sub> 11
1.4 Determination of maximum loading percentage for M-TiO <sub>2</sub> nanorods11
Table 2. Experimental design for different percentage of Co(II) loadings on the TiO <sub>2</sub> NR surface with optimized oleylamine concentration
Figure S10. Actual (from elemental analyses) versus theoretical $Cr:TiO_2$ mass ratio (inset is the linear fit of the actual $Cr:TiO_2$ mass ratio up to the surface saturation limit ~8.75%)12
Figure S11. Actual (from elemental analyses) versus theoretical $Mn:TiO_2$ mass ratio (inset is the linear fit of the actual $Mn:TiO_2$ mass ratio up to the surface saturation limit ~9.5%)13
Figure S12. Actual (from elemental analyses) versus theoretical $Fe:TiO_2$ mass ratio (inset is the linear fit of the actual $Fe:TiO_2$ mass ratio up to the surface saturation limit ~13.5%)13
Figure S13. Actual (from elemental analyses) versus theoretical Ni:TiO <sub>2</sub> mass ratio (inset is the linear fit of the actual Ni:TiO <sub>2</sub> mass ratio up to the surface saturation limit $\sim$ 8.0%)14
Figure S14. Actual (from elemental analyses) versus theoretical Cu:TiO2 mass ratio (inset is the linear fit of the actual Cu:TiO <sub>2</sub> mass ratio up to the surface saturation limit $\sim 6.0\%$ )14

Figure S15. UV-visible absorbance spectra of Co(II)-TiO <sub>2</sub> for samples with varyir mole ratio.	ng Co:TiO <sub>2</sub>
Figure S16. Powder XRD (top) and TEM (bottom, left to right: $Co:TiO_2 = 0.01$ , 0.09, $Co:TiO_2 = 0.17$ ) data of $Co(II)$ -TiO <sub>2</sub> NR.	Co:TiO <sub>2</sub> =16
1.5 Synthesis and characterization of Co(II)-OLAM as a control experiment	17
Figure S17. UV-Vis spectra of Co(II)-TiO <sub>2</sub> and CoCl <sub>2</sub> -OLAM complex.	17
1.6 Calculation of dispersion of anatase TiO <sub>2</sub> NRs	18
References	19

### **1.0 Experimental Section**

All preparations were carried out under an atmosphere of N<sub>2</sub> by using both Schlenk line technique and glove box. UV-Visible absorption spectra were recorded with Cary 50-Bio UV- Visible spectro photometer. Transmission electron microscopy (TEM) data was obtained using a Technai Spirit G2 Twin (FEI Company) transmission electron microscope fitted with LaB<sub>6</sub> filament operated at 120kV. Samples were dispersed in hexanes, and then drop cast onto carbon film (20-30 nm) on 200 mesh copper grid (Electron Microscopy Sciences) and allowed to dry in the air. Electron micrographs were obtained by projection onto Gatan US1000 or Orius SC200 CCD Digital Camera and recorded with Digital Micrograph software.

Chromium(III) chloride hexahydrate, iron(II) chloride tetrahydrate, copper(II) chloride dihydrate, manganese(II) chloride tetrahydrate, cobalt(II) chloride hexahydrate, nickel(II) chloride hexahydrate, oleic acid (97%, Fisher Catalog # A195-500), oleylamine (OLAM; manufactured by TCI, 50+%, Fisher Catalog # 50-014-43281), octadecene (ODE; 90%, technical grade, Fisher Catalog # AC12931-0025), isopropanol, and hexanes were purchased from Fischer and used without purification. Titanium(IV)tetraisopropoxide (TTIP), 98+%, was manufactured by Acros Organics. The phases present in the powdered samples were characterized by using Rigaku Ultima IV powder X-ray diffractometer. The X-ray tube produced Cu K<sub>a</sub> radiation ( $\lambda = 1.54$  Å), and the generator was set to 40 kV and 44 mA during data collection. Data was collected from 20–80° (20). Dry TiO<sub>2</sub> nanorod powders and metalated TiO<sub>2</sub> nanorod powders were prepared by evacuating the solvent under vacuum at room temperature.

### 1.1 Synthesis of TiO<sub>2</sub> nanorods and determination of mass TiO<sub>2</sub>.

The anatase TiO<sub>2</sub> nanorods were synthesized as previously reported.<sup>[1]</sup> Briefly, 50 g oleic acid was evacuated at 120°C for one hour to remove volatiles. Then 60 mmol TTIP was combined with the 50 g of oleic acid in a 500 mL three neck flask at room temperature in glove box. The mixture was heated to 270°C (10°C/min) and held at this temperature for 2 hours while refluxing. The product was isolated by addition of excess isopropanol and centrifugation and was found to consist of a mixture of nanorods and nanospheres. The nanorods were separated from spheres by selective precipitation. The isolated nanorods were dispersed in hexane (40 mL). The mass of the TiO<sub>2</sub> in the nanorods sample was calculated by finding the mass of a calcined portion of the sample (1mL dispersion) at 450°C for 6 hours. The mass of TiO<sub>2</sub> nanorods in this synthesis (average over multiple reactions) was approximately 3.2 g (compared to 4.8 g theoretical yield TiO<sub>2</sub>). The quantitative portions (0.079 g, 1 mL dispersions) were used in the synthesis of metalated TiO<sub>2</sub> nanorods.

### 1.2 Synthesis of metalated TiO<sub>2</sub> nanorods.

The M-TiO<sub>2</sub> nanorods can be prepared with varying metal ion loading, and each metal ion requires optimized parameters of OLAM:M (ESI section 1.3) and reaction temperature. These are summarized in the table below:

Metal source	OLAM:M	Temperature (°C)
	mole ratio	
CrCl <sub>3</sub> .6H <sub>2</sub> O	10	250
MnCl <sub>2</sub> .4H <sub>2</sub> O	6	200
FeCl <sub>2</sub> .4H <sub>2</sub> O	6	180
CoCl <sub>2</sub> .6H <sub>2</sub> O	10	250
NiCl <sub>2</sub> .6H <sub>2</sub> O	10	150
CuCl <sub>2</sub> .2H <sub>2</sub> O	12	80

**Table 1.** Experimental conditions for the attachment of different metal ion on $TiO_2$  NR surface.

As an illustrative example, we describe the synthetic procedure for  $0.07:1 \text{ Co(II)}:TiO_2$  mole ratio. The appropriate metal source and amount, OLAM:M mole ratio, and temperature should be substituted as needed in order to prepare M-TiO<sub>2</sub> at the desired metal loading. A heating rate of 10°C/min was used for all of the reactions, and all reactions were kept at 3 hours at the temperature setpoint.

A dispersion of oleic acid stabilized TiO<sub>2</sub> nanorods (1 mmol) in hexane, OLAM (228  $\mu$ L, 0.7 mmol) and ODE (3.77g to bring total volume 5 mL) were combined in a 100 mL three neck flask and evacuated at 120°C for 30 minutes to remove volatiles. The flask was allowed to cool to room temperature and filled with N<sub>2</sub>. To this mixture, CoCl<sub>2</sub>.6H<sub>2</sub>O (16.5 mg, 0.07 mmol) was added under N<sub>2</sub> atmosphere with magnetic stirring. The flask was fitted with a reflux condenser and thermocouple-temperature controller relay. Under N<sub>2</sub> blanket, the mixture was heated to 250°C with a heating rate of 10°C/min (the solution turned to blue colour at ~80°C), kept at this temperature for 3 hours, then allowed cool to room temperature. On addition of approximately 15 mL isopropanol to the blue mixture, a blue precipitate was observed. The blue precipitate was separated by centrifugation at 3500 rpm for 8 minutes. The precipitate was redispersed in non-polar solvents such as hexane to give transparent blue dispersion.

Notes:

The Fe<sup>2+</sup> and Mn<sup>2+</sup> -TiO<sub>2</sub> NR samples are air sensitive! The Mn<sup>2+</sup>-TiO<sub>2</sub> sample undergoes oxidation in air over several hours, and the dispersion changes from yellow to brown without loss of solubility. The Fe<sup>2+</sup>-TiO<sub>2</sub> sample undergoes oxidation in air much more rapidly (minutes), and the dispersion changes from brown to yellow without loss of solubility. UV-

vis spectra were recorded in sealed cuvettes. The color changes are shown in photographs of the samples before and after exposure to air in figure S1.



Figure S 1. Mn(II)-TiO<sub>2</sub> and Fe(II)-TiO<sub>2</sub> dispersions exposed to air.



Figure S2. Powder XRD for metalated  $TiO_2$  nanorods. In all samples the ratio M:TiO<sub>2</sub> = 0.07.



**Figure S3.** TEM images for metalated TiO<sub>2</sub> nanorods (scale bar 50nm). Top row, from left to right: Cr(III)-TiO<sub>2</sub>, Mn(II)-TiO<sub>2</sub>, Fe(II)-TiO<sub>2</sub>; bottom row, from left to right: Co(II)-TiO<sub>2</sub>, Ni(II)-TiO<sub>2</sub>, Cu(II)-TiO<sub>2</sub>). In all samples the mole ratio  $M:TiO_2 = 0.07$ .

# 1.3 Determination of optimum OLAM:M mole ratio in the synthesis of M-TiO<sub>2</sub> nanorods.

The generalized procedure (ESI section 1.2) was followed. There are 6 series of reactions in which the optimum OLAM:M was determined for each metal ion. For each reaction series there are 7 reactions in which OLAM:M was varied while keeping [M] constant. For each reaction, the M-TiO2 product was isolated (ESI section 1.2), calcined at 450°C for 6 hours in air, then sent to Galbraith Laboratories, Inc. (Knoxville, TN) for metal analysis. Data are shown in figure S4-9 below. The elemental analyses provide actual M:TiO<sub>2</sub> mass ratio (left y-axis) versus OLAM:M mole ratio (x-axis). For reference, the theoretical M:TiO<sub>2</sub> mass ratio (if all metal ion introduced were adsorbed onto the TiO<sub>2</sub> nanocrystal surface) is plotted as a horizontal line equivalent to a constant value on the right y-axis. The maxima represent optimum OLAM:M mole ratio at which metal ion was adsorbed with highest yield.



Figure S4. Optimization of OLAM concentration for synthesis of Cr(III)-TiO<sub>2</sub>.



Figure S5. Optimization of OLAM concentration for synthesis of Mn(II)-TiO<sub>2</sub>.



Figure S6. Optimization of OLAM concentration for synthesis of Fe(II)-TiO<sub>2</sub>.



Figure S7. Optimization of OLAM concentration for synthesis of Co(II)-TiO<sub>2</sub>.



Figure S8. Optimization of OLAM concentration for synthesis of Cu(II)-TiO<sub>2</sub>.



Figure S9. Optimization of OLAM concentration for synthesis of Ni(II)-TiO<sub>2</sub>.

## 1.4 Determination of maximum loading percentage for M-TiO<sub>2</sub> nanorods.

The syntheses were carried out according to the experimental procedure from section 1.2. For illustrative purposes, we show the parameters used for the determination of maximum cobalt loading on the  $TiO_2$  nanocrystal surface in table 2.

TiO <sub>2</sub> NRs	OLAM (µL)	CoCl <sub>2</sub> .6H <sub>2</sub> O	ODE (g)	Theoretical Loading
(g, mmol)		(mg, mmol)		(moles $Co:TiO_2$ )
0.079, 1.0	33	2.4, 0.01	3.92	0.01
0.079, 1.0	163	11.8, 0.05	3.82	0.05
0.079, 1.0	293	21.2, 0.09	3.71	0.09
0.079, 1.0	423	30.6, 0.13	3.61	0.13
0.079, 1.0	553	40.0, 0.17	3.51	0.17
0.079, 1.0	683	49.4, 0.21	3.41	0.21
0.079, 1.0	814	58.8, 0.25	3.30	0.25
0.079, 1.0	976	70.6, 0.30	3.17	0.30
0.079, 1.0	1139	82.4, 0.35	3.05	0.35
0.079, 1.0	1302	94.1, 0.40	2.92	0.40
0.079, 1.0	1627	117.7, 0.50	2.66	0.50
0.079, 1.0	3254	235.4, 1.00	1.38	1.00

**Table 2.** Experimental design for different percentage of Co(II) loadings on the $TiO_2$  NR surface with optimized oleylamine concentration.

The metal content of each sample was determined using ICP-AES elemental analysis (Galbraith Laboratories, Inc.) of calcined samples (450°C, 6 hours in air). At the saturation limit, the approximate mass fraction of Cr:TiO<sub>2</sub>= 0.09, Mn:TiO<sub>2</sub> = 0.10, Fe:TiO<sub>2</sub> = 0.14, Co:TiO<sub>2</sub> = 0.11, Ni:TiO<sub>2</sub>= 0.08, and Cu:TiO<sub>2</sub> = 0.06 (see figures S10-S14 and Figure 3).



Figure S10. Actual (from elemental analyses) versus theoretical  $Cr:TiO_2$  mass ratio (inset is the linear fit of the actual  $Cr:TiO_2$  mass ratio for data well below the saturation limit; surface saturation limit ~8.75%).



Figure S11. Actual (from elemental analyses) versus theoretical  $Mn:TiO_2$  mass ratio (inset is the linear fit of the actual  $Mn:TiO_2$  mass ratio for data well below the saturation limit; surface saturation limit ~9.5%).



Figure S12. Actual (from elemental analyses) versus theoretical Fe:TiO<sub>2</sub> mass ratio (inset is the linear fit of the actual Fe:TiO<sub>2</sub> mass ratio for data well below the saturation limit; surface saturation limit ~13.5%).



Figure S13. Actual (from elemental analyses) versus theoretical Ni:TiO<sub>2</sub> mass ratio (inset is the linear fit of the actual Ni:TiO<sub>2</sub> mass ratio for data well below the saturation limit; surface saturation limit  $\sim 8.0\%$ ).



Figure S14. Actual (from elemental analyses) versus theoretical Cu:TiO<sub>2</sub> mass ratio (inset is the linear fit of the actual Cu:TiO<sub>2</sub> mass ratio for data well below the saturation limit; surface saturation limit ~6.0%).



Figure S15. UV-visible absorbance spectra of Co(II)-TiO<sub>2</sub> for samples with varying Co:TiO<sub>2</sub> mole ratio. This data correlates to figure 3, right y-axis points.



Figure S16. Powder XRD (top) and TEM (bottom, left to right:  $Co:TiO_2 = 0.01$ , Co:TiO<sub>2</sub> = 0.09, Co:TiO<sub>2</sub> = 0.17) data of Co(II)-TiO<sub>2</sub> NR. Bar = 100 nm.

### 1.5 Synthesis and characterization of Co(II)-OLAM as a control experiment.

Large excess of metal ion loading gave rise to new absorption bands at 485 nm and 630 nm due to a Co(II)-OLAM complex. We carried out a control experiment in which Co(II) and OLAM in 1-octadecene were heated to 250°C for three hours. After cooling to room temperature, isopropanol was added that resulted in a blue-green precipitate. The solubility of the Co(II)-OLAM complex and Co(II)-TiO<sub>2</sub> nanorods is similar; however, the Co(II)-OLAM complex becomes insoluble in non-polar solvents after four cycles of precipitation with isopropanol, centrifugation, and redispersion in hexanes. This allowed us to separate the metalated TiO<sub>2</sub> NRs from the Co(II)-OLAM complex in experiments with Co:TiO<sub>2</sub> > 0.18. Our observation suggests that the metal ion attaches on the TiO<sub>2</sub> NR until the surface becomes saturated; thereafter, the metal ion reacts with OLAM and forms the Co(II)-OLAM complex.



Figure S17. UV-Vis spectra of Co(II)-TiO<sub>2</sub> and CoCl<sub>2</sub>-OLAM complex.

#### 1.6 Calculation of dispersion of anatase TiO<sub>2</sub> NRs

The nanorod geometry was assumed to be a cylinder with a diameter of 3.3 nm and a height of 43.3 nm. Therefore the volume of the cylinder is  $V = \pi r^2 h = 367.9 \text{ nm}^3$ .

The unit cell parameters of anatase are a = 3.7845 Å, c = 9.5143 Å, *Volume* = 0.1362 nm<sup>3</sup> and **Z** = **4**. Therefore, there are 2699 anatase unit cells per nanorod and 10799 TiO<sub>2</sub> formula units per nanorod.

The anatase nanocrystal consists of the  $\{101\}$  facet, which has an area of 0.39 nm<sup>2</sup> per unit cell.

The surface area of the nanorod is  $2\pi rh + 2\pi r^2$ . The surface area of a single nanorod with a diameter of 3.3 nm and a height of 43.3 nm is 463.08 nm<sup>2</sup>.

There are 1195 (101) 'unit planes' per nanorod, and each (101) 'unit plane' contains 4 Ti atoms.

We estimate there are 4781 surface Ti atoms per nanorod. Two of the Ti atoms in the 'unit plane' are  $Ti_{5c}$  sites, which corresponds to a surface density of 5.12  $Ti_{5c}/nm^2$  that is in accordance with figures previously reported. <sup>[2]</sup>

The dispersion, *D* or the ratio of the number of surface Ti atoms to the total number of Ti atoms is 4781/10799 = 0.44

### **References:**

- [1] J. Joo, S. G. Kwon, T. Yu, M. Cho, J. Lee, J. Yoon, T. Hyeon, J. Phys. Chem. B. 2005, 109, 15297-15302.
- [2] a) U. Diebold, N. Ruzycki, G. S. Herman, A. Selloni, *Catal. Today.* 2003, *85*, 93-100;
  b) K. S. Kim, M. A. Barteau, W. E. Farneth, *Langmuir* 1988, *4*, 533-543.