Supplementary Material (ESI) for Chemical Communications

Supporting Information

Room Temperature Oxidation of Methyl Orange and Methanol over Pt-$HCa_2Nb_3O_{10}$ and Pt-WO_3 Catalysts without Light.

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Experimental section

Synthesis of Catalysts

a) Preparation of $KCa_2Nb_3O_{10}$ and its protonated form, $HCa_2Nb_3O_{10}$

The starting $KCa_2Nb_3O_{10}$ Dion Jacobson phase was prepared by solid state reaction of K_2CO_3, $CaCO_3$ and Nb_2O_5 in 1.1:2:3 molar ratio (1200°C). The protonated form was obtained by treating the starting compound with 5M HNO_3, for 3 days at RT and replacing the acid solution daily.[1] The resulting solid was separated by vacuum filtration and washed abundantly with distilled water, followed by drying at 80°C overnight.

b) Platinum loading

The catalyst (0.1g) was suspended in 100ml of aqueous 20 vol% methanol solution and purged with nitrogen for 15minutes. After the addition of 0.02ml of 8wt% H_2PtCl_6, the reaction mixture was irradiated with UV light leading to the reduction of Pt^{4+} and the formation of fine platinum nanoparticles on catalyst surface.

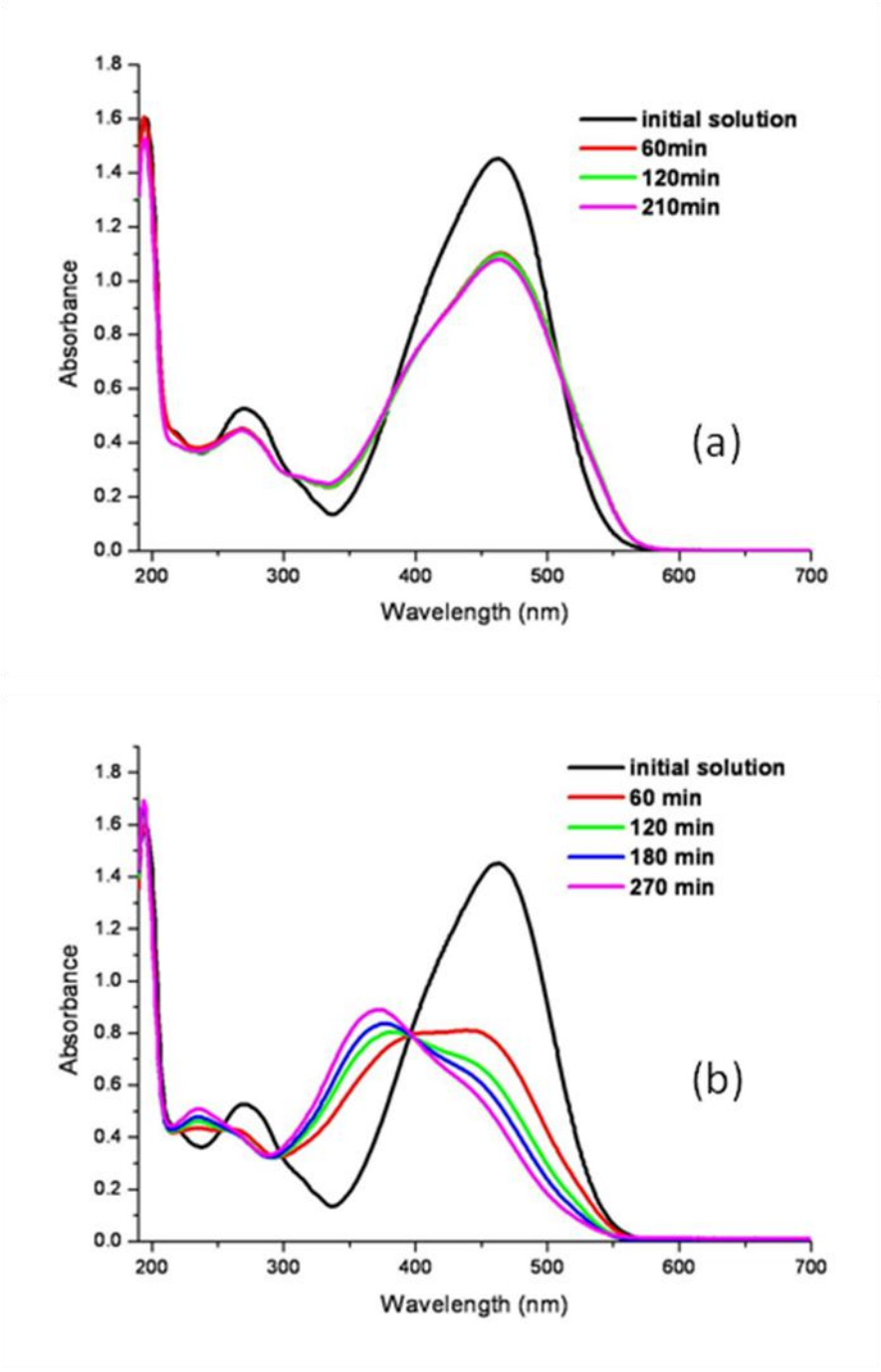
Catalytic Reactions

a) Oxygen Reduction - was followed using a temperature controlled Clark Electrode (Rank Bros 50mL glass electrode) as previously described.[2] 0.01 g of catalysts were dispersed in water and various amounts of methanol (1 – 10%) were introduced into the reaction mixture.

b) Methyl Orange degradation without light – all catalytic reactions were carried out using a 1g catalyst/1L solid-liquid ratio. Briefly, 20mg of catalyst was dispersed in 20ml Methyl Orange (20mg/L) aqueous solution and sonicated for 5 minutes. A syringe was used to remove samples from the solution using a 2μm membrane to remove particles from the sample and analyzed using a Perkin Elmer (LAMBDA 650S) UV/Visible spectrophotometer. Figure 1S (a) shows the spectral changes for Methyl Orange in the dark when the solution is purged with nitrogen. This shows that there is an initial loss of dye due to adsorption onto the Pt-$HCa_2Nb_3O_{10}$ catalyst but no further oxidation in the absence of oxygen. Figure 1S (b) shows that the reaction with oxygen at 40^{o}C which is

faster than the result at 25°C (shown in main paper). In this figure the appearance of the new peak at 374nm is clearly visible.

Figure 1S (a) Methyl Orange and Pt-$HCa_2Nb_3O_{10}$ in water purged with nitrogen and (b) Methyl Orange and Pt-$HCa_2Nb_3O_{10}$ in water with air at 40°C.



Characterisation of Catalysts

The X-ray powder diffraction (XRD) patterns of all samples were recorded with a Panalytical X'pert Pro diffractometer using Co Kα radiation (λ = 1.7889 Å). Powder X-ray diffractions patterns of the pristine $KCa_2Nb_3O_{10}$ and its protonated form were indexed on the basis of tetragonal unit cells, with a=7.727Å, c=29.466Å and a=3.849(7)Å, c=16.213Å, respectively, these values being in good agreement with literature data[1].

Figure. 2S. XRD patterns of $KCa_2Nb_3O_{10}$ and $HCa_2Nb_3O_{10}$.

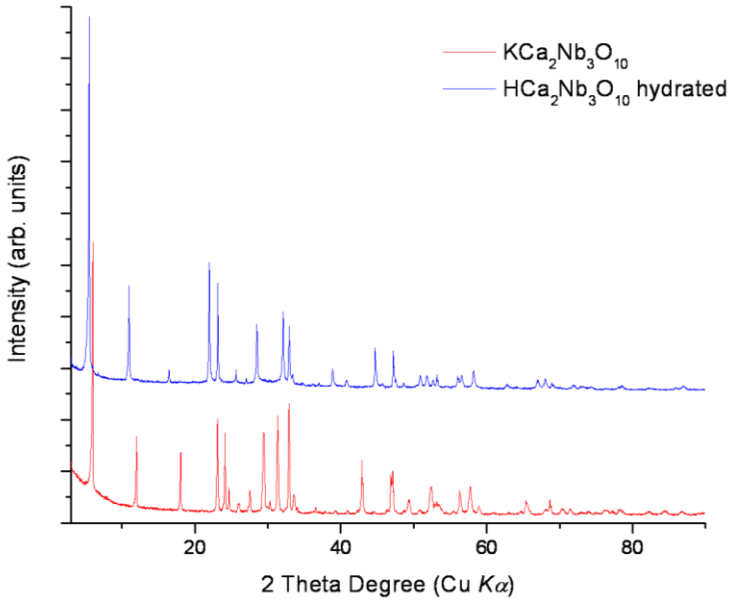
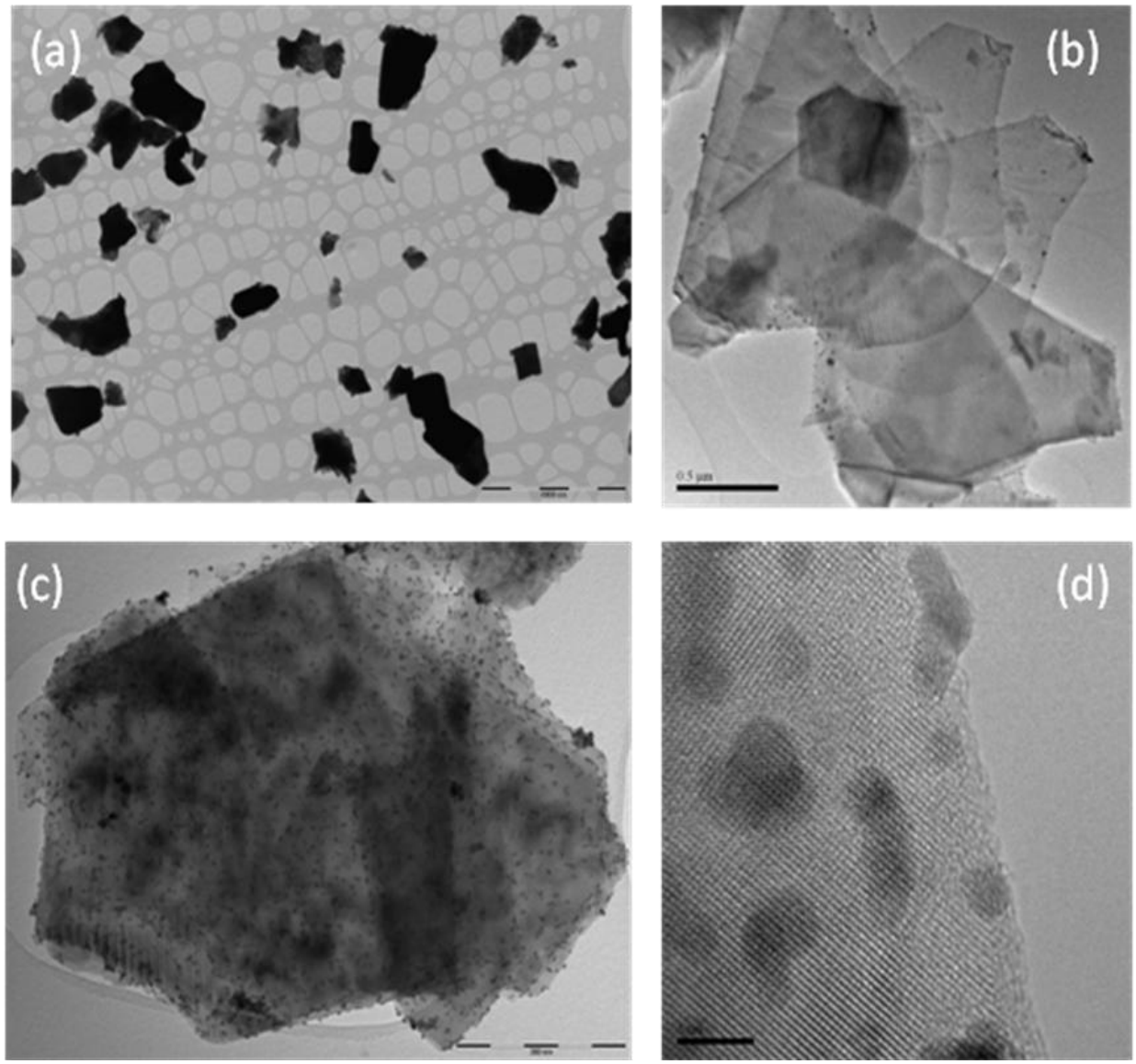


Figure 3S. TEM and HRTEM images of Pt-$HCa_2Nb_3O_{10}$ [Scale bar = 5000nm (a), 500nm (b), 200nm (c), 5nm (d)]



The TEM images and analysis shows that $HCa_2Nb_3O_{10}$ is a poly-disperse mixture of sheets and particles ranging up to 10 microns with an average size of 1.4 microns. When Platinum is photodeposited onto the material some large (>10nm) Pt particles are seen on the edge of $HCa_2Nb_3O_{10}$ and many islands of Pt are seen across the surface and sheets with an average size of 3.4nm. A representative SAED pattern is given in Figure 4(b) in the main text.

Fig. 4S.Analysis of particle sizes of Pt and $HCa_2Nb_3O_{10}$ in Pt-$HCa_2Nb_3O_{10}$.

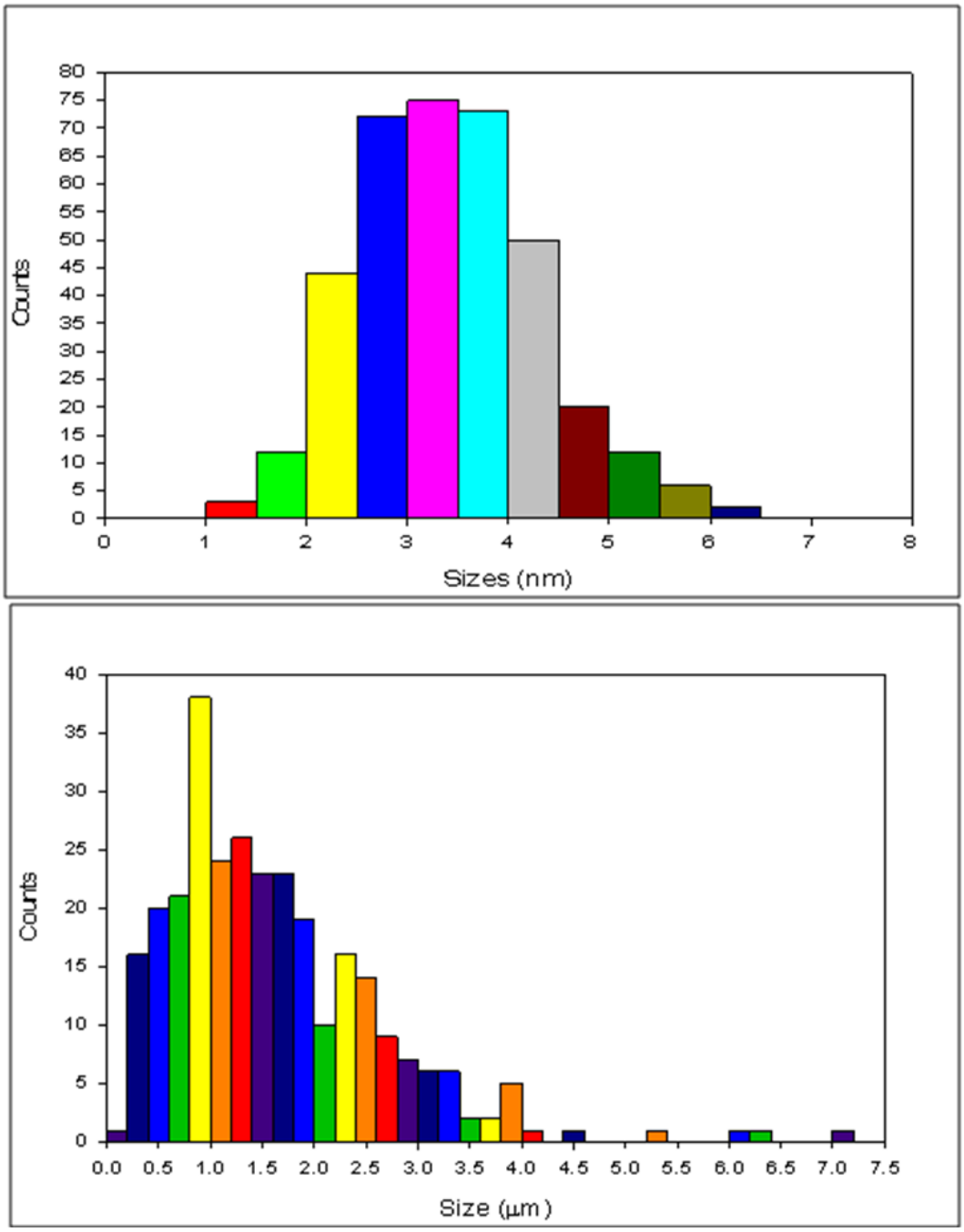
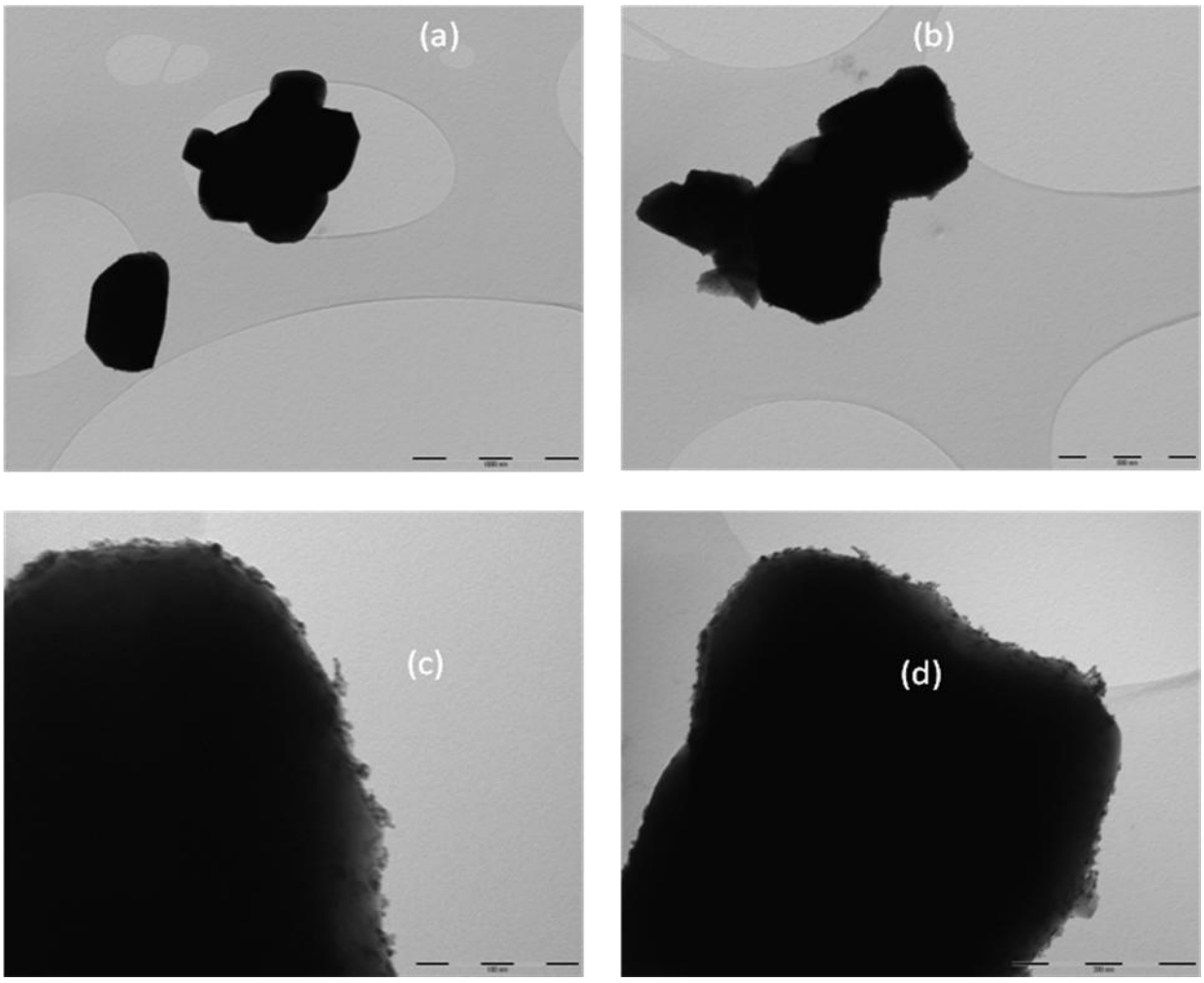


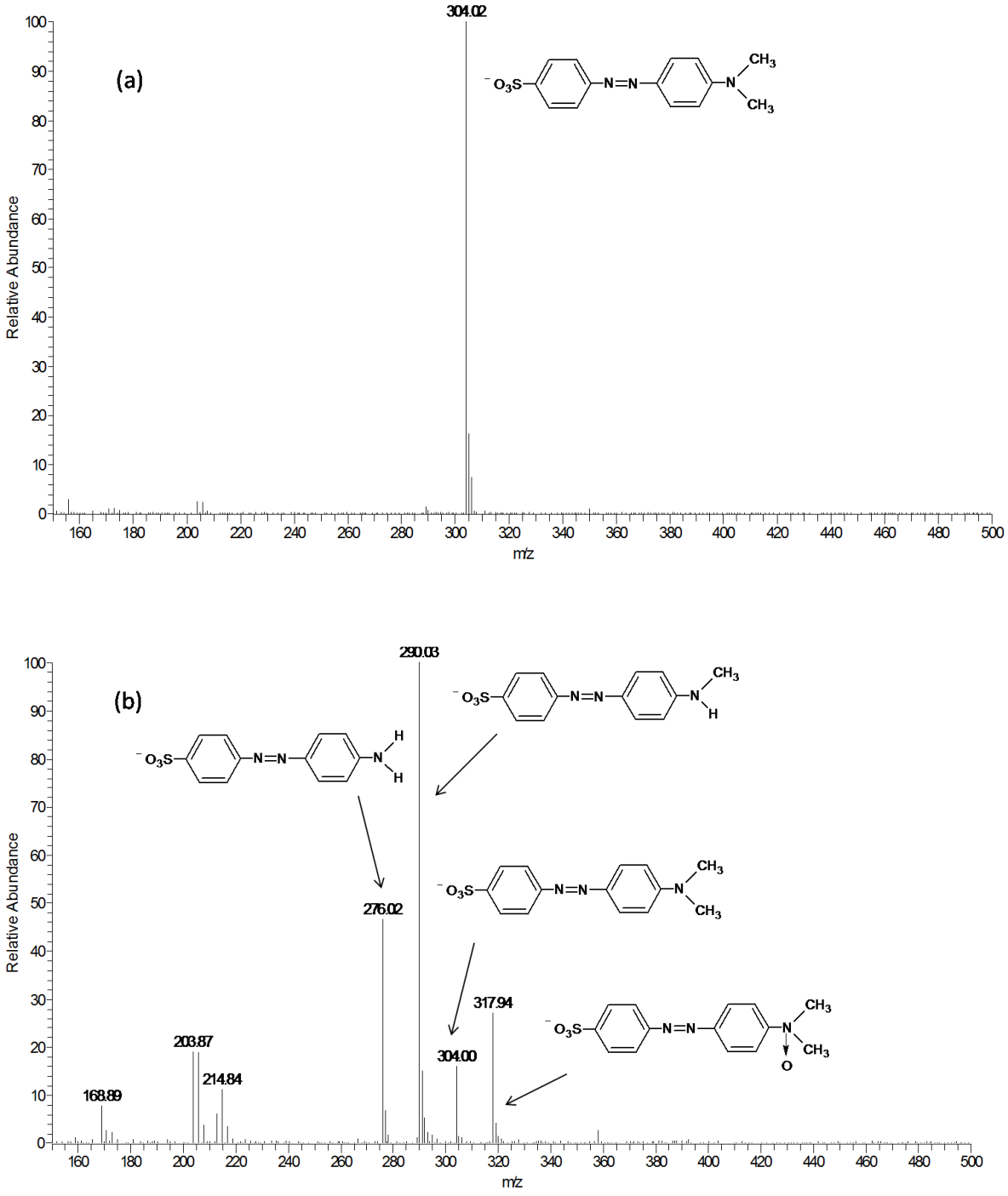
Figure 5S. Pt-WO_3 TEM images [Space Bar = 1000nm (a), 500nm (b), 100nm (c), 200nm (d)]



LC/MS analysis of Methyl Orange Oxidation

The experiment was carried out with a Surveyor MSQ Plus Mass Spectrometer using an 12mM ammonium formate/acetonitrile solution (pH=6.8) as eluent. The results are shown in Figure 6S.

Figure 6S. LC/MS results for Methyl Orange oxidation in water catalyzed by Pt-$HCa_2Nb_3O_{10}$ after t=0 (a) and t=2 hours (b).



Materials

Methanol (HPLC grade), hexachloroplatinic acid ($H_2PtCl_6.6H_2O$, 8 wt% solution) and Methyl Orange were purchased from Aldrich. Bulk WO_3 was purchased from Aldrich. The metal based oxides with high purity (99,9%) used for layered materials synthesis have been purchased from Alfa-Aesar.

References

1. A. J. Jacobson, J. T. Lewadowski, J. W. Johnson, Ion exchange of the layered perovskite $KCa_2Nb_30_{10}$ by protons, *J. Less-Common Metals*, 1986, **116**, 137 – 146.
2. A. Harriman, A. Mills and G. Porter, *Anal. Chem.*, 1981, **53,** 1254-1257.