Using nickel manganese oxide catalysts for efficient water oxidation†

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Nickel–manganese oxides with variable Ni:Mn ratios, synthesised from heterobimetallic single-source precursors, turned out to be efficient water oxidation catalysts. They were subjected to oxidant-driven, photo- and electro-catalytic water oxidation showing superior activity and remarkable stability. In addition, a structure–activity relation could be established.

Splitting of water by an efficient catalyst is one of the major aspects of renewable energy research at present.1 Discovery of such highly active catalysts with scalable, abundant, robust, stable and low-cost materials is a promising solution for the sustainable production of clean energy.2 Over the years, first-row transition metal oxides, particularly those with manganese oxide based systems have been widely investigated for photocatalysis and electrocatalysis,3,4 not only due to their eco-economic and environmental benefits but also because of the fact that nature enables solar to chemical energy conversion with a superior activity and remarkable stability. In addition, a structure–activity relation could be established.

First of all, nickel manganese and nickel oxalate SSPs were prepared in micro-emulsions containing cetyltrimethylammonium bromide (CTAB) as a surfactant, 1-hexanol as co-surfactant and hexane as the lipophilic phase and mixed with aqueous solution containing Ni2+, Mn2+ and oxalate ions with tuneable ratios.13 The thus yielded oxalate SSPs were treated thermally in the presence of an oxidant-driven, photo- and electro-catalytic water oxidation.

In this context, several manganese oxides have been extensively explored for oxidant-driven, photo-catalytic and electro-catalytic water oxidation especially with nanocrystalline and amorphous manganese and calcium manganese oxides.6–11 Recently, we investigated different routes for the synthesis of various manganese oxides for efficient water oxidation.12,13 On the other hand, nickel based materials have drawn particular attention due to their earth abundant nature as well as their lower water oxidation potentials for efficient water oxidation catalysts.14–18 Although, we were successful in substitution of cobalt in manganese oxides for enhanced redox oxygen catalysis,19 the role of nickel in manganese oxide has been merely examined. This is indeed because of the difficulties involved in the synthesis and the precise control over the composition with a maximum of dispersion of the nickel and manganese on the atomic level, and of the oxidation states of the metals. A while ago, Fukuzumi et al. reported a NiMnO3 phase toward water oxidation20 but other Ni:Mn ratios (compositions) of nickel manganese oxides have not been studied as yet. Therefore, we opted for the single-source precursor (SSP) approach to gain access to a new class of heterobimetallic nickel manganese oxides versus nickel oxide as promising catalysts for efficient oxidant-driven, photo- and electro-catalytic water oxidation.

First of all, nickel manganese and nickel oxalate SSPs were prepared in micro-emulsions containing cetyltrimethylammonium bromide (CTAB) as a surfactant, 1-hexanol as co-surfactant and hexane as the lipophilic phase and mixed with aqueous solution containing Ni2+, Mn2+ and oxalate ions with tuneable ratios.13 The thus yielded oxalate SSPs were treated thermally in the presence of a Ni:Mn ratio and their presence in the phase was obtained by Inductively Coupled Plasma (ICP) Atomic Emission Spectroscopy (AES) and Energy Dispersive X-ray (EDX) analysis (Fig. S11 and Table S3, ESIF). Interestingly, just by tuning the nickel and manganese ratio, various morphologies have been realised. As shown in Fig. 1, the higher magnification Scanning Electron Microscopy (SEM) images of Ni2MnO8 showed a flower-type morphology (~1 μm) which consisted petals assembled from...
nanoparticles and MnNi$_2$O$_4$ displayed cubic type particles. NiMn$_2$O$_4$ forms small nanochains whereas NiO exhibits bricks (~400 nm) built of tiny nanoparticles (see also Fig. S12, ESIf). Further insights on the morphology and particles size were gathered by Transmission Electron Microscopy (TEM) and High Resolution (HR) TEM images (Fig. S13, ESIf). In all cases the particles were well crystalline with particle size of about 2–5 nm for Ni$_6$MnO$_8$, ~50 nm for MnNi$_2$O$_4$, ~10 nm for NiMn$_2$O$_4$, and ~5–10 nm for NiO, respectively. The Fourier Transform Infrared (FTIR) spectrum of all oxides is typical and characteristic for metal oxalates (Fig. S14, ESIf). The highest Brunauer–Emmett–Teller (BET) surface area was displayed for Ni$_6$MnO$_8$ (51.9 m$^2$ g$^{-1}$) followed by NiMn$_2$O$_4$ (39.6 m$^2$ g$^{-1}$), NiO (30.4 m$^2$ g$^{-1}$), and MnNi$_2$O$_4$ (29.3 m$^2$ g$^{-1}$), respectively (Fig. S15, ESIf).

The detailed bonding states of Ni, Mn and O were further characterised by X-ray Photoelectron Spectroscopy (XPS). The XPS core level spectra of Ni$_2$P$_2$1/2 and Ni$_2$p$_3/2$ for Ni$_6$MnO$_8$, NiMn$_2$O$_4$ and NiO exhibited peaks at binding energy (BE) of ~854.5 eV and 872.2 eV corresponding to Ni$^{2+}$ while the peaks of MnNi$_2$O$_4$ shifted to the higher energy of 856 eV and 873.8 eV which can be assigned as the mixture of Ni$^{2+}$/3+ (Fig. S16, ESIf). The Mn$_2$p$_3/2$ and Mn$_2$p$_1/2$ at BE 643.5 eV and 655.0 eV that are consistent Mn$^{4+}$ species whereas for NiMn$_2$O$_4$, the peak positions were shifted to lower energy of 642.4 eV and 653.9 eV and are characteristic for Mn$^{3+}$ (Fig. S17, ESIf). The O1s spectrum for all oxides exhibited a major O$^{2-}$ peak assignable to bridging oxides with two smaller ones that could be attributed to the surface oxygen, physis- and chemisorbed water at or near the surface and to the hydroxide species (Fig. S18, ESIf).19

Oxidant-driven water oxidation experiments (see ESIf for details) were conducted with all catalysts (Fig. S19, ESIf) in deoxygenated aqueous solution of 0.5 M ceric ammonium nitrate (CAN) and the rate of the oxygen evolution was calculated from the slope of the linear fitting for the first 60 s. The Ni$_6$MnO$_8$ was found to be extremely active with a maximum rate of 1.41 mmol$_{O_2}$/mol$_{M}$ s$^{-1}$ considering both nickel and manganese atoms are active, and was approximately thrice higher than the MnNi$_2$O$_4$ (0.52 mmol$_{O_2}$/mol$_{M}$ s$^{-1}$). However, for NiMn$_2$O$_4$, the rate was far lesser with the value of 0.19 mmol$_{O_2}$/mol$_{M}$ s$^{-1}$ and is comparable with the pure NiO (0.15 mmol$_{O_2}$/mol$_{M}$ s$^{-1}$). The surface area and the total number of active sites present on the catalyst play a crucial role in water oxidation. Therefore, the correlation of surface area normalised plots is shown in Fig. S20 (ESIf) and follows the same trend as that of total mass activity.

The photo-catalytic water oxidation was performed in a phosphate buffer solution of pH 7 in the presence of [Ru(bpy)$_3$]$_2^{2+}$ (bpy = 2,2'-bipyridine) as a photosensitiser and S$_2$O$_8^{2-}$ as two electron acceptor (Scheme S1, ESIf). In a similar trend to the oxidant-driven water oxidation, the highest rate of oxygen evolution was exhibited by the nickel-rich Ni$_6$MnO$_8$ with a value of 1.00 mmol$_{O_2}$/mol$_{M}$ s$^{-1}$ that was again 1.5 times higher than the other nickel-rich MnNi$_2$O$_4$ phase (0.69 mmol$_{O_2}$/mol$_{M}$ s$^{-1}$) (Fig. 2). The rate of oxygen evolution for the nickel-diluted NiMn$_2$O$_4$ was 0.44 mmol$_{O_2}$/mol$_{M}$ s$^{-1}$ while NiO showed only a limited activity (0.07 mmol$_{O_2}$/mol$_{M}$ s$^{-1}$). To compare the photo-catalytic activity, the commercial manganese oxides and nickel oxide were measured as standards that again showed that as-synthesised catalysts are highly active and of interest (Fig. S21, ESIf). Surface normalisation discloses that the values for MnNi$_2$O$_4$ are superior to Ni$_6$MnO$_8$ > NiMn$_2$O$_4$ > NiO due to their lower surface area (Fig. S22, ESIf). Comparison of the mass and surface normalised activity with other reported catalysts confirmed that the diluted-manganese oxide based Ni systems produced higher oxygen evolution than most of the known active nickel and manganese based catalysts (Table S4, ESIf).7–10,20

After the Clark electrode experiments, a set of experiments for longer duration was also carried out separately (see ESIf) and the oxygen gas was collected in the head space of the reaction mixture was quantitatively analysed by a gas chromatograph (GC). A maximum oxygen yield of 0.08 mL h$^{-1}$ of O$_2$ was detected for Ni$_6$MnO$_8$ and 0.07 mL h$^{-1}$ for MnNi$_2$O$_4$ (Table S5, ESIf). Moreover, it is not enough to have catalysts that are extremely active but one of the indispensable criteria is also to know the fate of the catalyst after the photo-catalytic experiments, and therefore, PXRD and HRTEM investigation were conducted on high performance Ni$_6$MnO$_8$ and MnNi$_2$O$_4$ catalysts. From PXRD and HRTEM images (Fig. S23, ESIf),
it is clear that the crystallinity and the morphology of the nickel-rich manganese oxides catalysts were preserved and stayed intact unveiling the enhanced stability.

The electro-catalytic measurements (see ESI†) were performed in alkaline 0.1 M KOH solution using Cyclic Voltammetry (CV) at a scan rate of 20 mV s⁻¹. The current for all electrodes were initially increased during the first few cycles and reached a steady value after 50 cycles (Fig. S24, ESI†), and then stayed stable and were unchanged even after additional cycling. As shown in Fig. 3, For Ni₆MnO₈, the anodic current started growing at 1.54 (vs. the reversible hydrogen electrode, RHE). The maximum current density of 5.85 mA cm⁻² was attained at 1.87 V. Similarly, for the MnNi₂O₄ and NiMn₂O₄, the current started increasing at 1.58 and 1.60 V, and the highest current density was achieved at 2.83 mA cm⁻² and 1.25 mA cm⁻² at 1.87 V, respectively. Interestingly, for NiO, the current started growing at 1.40 V itself and the CV’s featured a pair of anodic and cathodic peaks centred ~1.5 V vs. RHE corresponding to the oxidation of NiO (NiO + OH⁻ → O₂ + O₂⁻ → NiOOH), followed by a current due to O₂ evolution.23 Electrodes were also preconditioned and forward and backward scans were performed, with respect to the NiO/NiOOH redox reaction of NiO (Fig. S25, ESI†). It could also be seen that for the Ni₆MnO₈, MnNi₂O₄ and NiMn₂O₄, a small redox peak exists, suggesting the partial oxidation of NiO to NiOOH in the nickel manganese catalysts.

The estimated overpotential for water oxidation at 1 mA cm⁻² for NiO was 395 mV while Ni₆MnO₈ and NiMn₂O₄ displayed current density was achieved at 2.83 mA cm⁻² and 1.25 mA cm⁻² at 1.87 V, respectively. Interestingly, for NiO, the current started growing at 1.40 V itself and the CV’s featured a pair of anodic and cathodic peaks centred ~1.5 V vs. RHE corresponding to the oxidation of NiO (NiO + OH⁻ → O₂ + O₂⁻ → NiOOH), followed by a current due to O₂ evolution.23 Electrodes were also preconditioned and forward and backward scans were performed, with respect to the NiO/NiOOH redox reaction of NiO (Fig. S25, ESI†). It could also be seen that for the Ni₆MnO₈, MnNi₂O₄ and NiMn₂O₄, a small redox peak exists, suggesting the partial oxidation of NiO to NiOOH in the nickel manganese catalysts.

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The situation is partly reversed in the electrochemical water oxidation. The NiO exhibits highest activity followed by nickel manganese oxides. This is due to a large amount of amorphous NiOOH, where Ni$^{II}$ is hexa-coordinated (Fig. 4d), and is formed on the surface of the electrodes (as shown by TEM and XPS) under electrochemical conditions and the resulting amorphous phase is known to be active for water oxidation by making the system very efficient and has been already well established for other nickel oxide and hydroxides.\textsuperscript{16,23,25} Interestingly, for MnNi$_2$O$_4$, NiMn$_2$O$_4$) with various Ni : Mn ratios and morphologies, and photo-catalytic water oxidation Ni$_6$MnO$_8$ is efficient due to the oxygen generated depending on the amount of nickel present in the catalysts. Therefore, it can be concluded that for oxidant-driven and photo-catalytic water oxidation Ni$_6$MnO$_8$ is efficient due to the higher amount of Ni active sites stabilised by manganese and higher structural-hole density whereas amorphous NiOOH seems to be crucial for electro-catalytic water oxidation due to its structural features.

In conclusion, we investigated for the first time, the oxidant-driven, photochemical and electrochemical water oxidation employing nickel manganese oxide-based catalysts (Ni$_x$Mn$_{1-x}$O$_y$, Mn$_x$Ni$_{1-x}$O$_y$, Ni$_x$Mn$_{1-x}$O$_y$) with various Ni : Mn ratios and morphologies, starting from well-defined heterobimetallic nickel manganese SSSPs; their activities were compared with NiO. Nickel-rich manganese oxides were found to be highly efficient with very high activity for oxidant-driven and photo-catalytic water oxidation whereas NiO exhibited higher performance and remarkable stability for electro-catalytic water oxidation.

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