Ca-assisted nitrogen-rich molecular approach for the synthesis of monodisperse tantalum oxide and (oxy)nitride nanocrystals for visible light–induced water oxidation

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1. Introduction

Photoelectrochemical and photocatalytic water splitting using transition metal (oxy)nitrides has attracted considerable attention due to its potential application to produce H₂ from water splitting by utilizing visible light provided by solar energy. To prepare a photocatalytic material that efficiently works under visible light, it is primarily important to control the band energy structure, i.e., the semiconductor has to have sufficient negative conduction band to H₂ production while keeping a narrow band gap (<3.0 eV) for visible light absorption. Although various kinds of (oxy)nitrides have been reported to date for water splitting, only a few have been demonstrated to operate under visible light.1 Among them, Ta₃N₅ and TaON have shown to be suitable candidates. The electronic structures of TaON and Ta₃N₅ were theoretically studied by Fang et al.2 and found that the valence band of TaON and Ta₃N₅ is composed mainly of (O 2p) N 2p orbitals hybridized with Ta 5d states. The top of their valence band is dominated by N 2p states while the bottom of the conduction band is mainly composed of Ta 5d states. Due to the higher potential energy of N 2p than O 2p, tantalum (oxy)nitrides have smaller bandgap than tantalum oxides. Both TaON and Ta₃N₅ are semiconductors with indirect band gaps varying from around 2.0 eV (Ta₃N₅) to 2.5 eV (TaON). The absolute position of the conduction band minimum and valence band maximum of semiconductors is one of the most crucial physical entities affecting the performance of these materials as visible light absorbers for water splitting applications. Chun et al.3 studied the conduction and valence band edges for band gaps and Fermi levels of Ta₂O₅, TaON and Ta₃N₅, and the results confirmed that the positions of the band edges of (oxy)nitrides are suitable for water oxidation due to the shift of maxima of the valence bands to higher potential energy from Ta₂O₅ to TaON and Ta₃N₅, whereas the minima of the conduction bands are kept in the range −0.3 to −0.5 V.

The synthesis of (oxy)nitride-based materials is less straightforward than that for oxides because of their lesser stability. A rigorous control of nitrogen concentration during the synthesis is needed in order to avoid decomposition in oxides at high temperatures. The conventional synthesis for (oxy)nitrides is ammonolysis.4,5) However, the classical approach has the following drawbacks: a) the reactions are usually slow, i.e. many reaction cycles have to be carried out to achieve pure oxynitrides, b) the nitridation process is difficult to control due to the complexity involved in the rigid control of gas composition, flow rate, and pressure, and c) the approach involves the use of NH₃ at high temperature which can be dangerous.6−8) Therefore, great efforts are going into finding synthetic routes being faster and safer than ammonolysis. These so-called non-conventional synthesis routes are, e.g. the reactions of TaON with alkaline earth oxides,9) plasma nitridation,10) and the use of azides11) or nitrogen-rich organic molecules as nitrogen source.12−15) Recently, a Ca-assisted urea route has been demonstrated as a controllable, efficient, safe, and low-cost approach to synthesize nanostructured tantalum (oxy)nitrides.16) In this approach, nanoparticles of TaON and Ta₂O₅ were easily synthesized through the calcination of Ta-urea gel precursors from suitable urea/Ta ratios in the presence of calcium ions. Ca⁺⁺ are known to stabilize urea by complexation...
 facilitating the controlled synthesis of pure tantalum (oxy)nitride nanoparticles at relatively low temperatures (<800°C).

In the present work, we report on the synthesis of monodisperse TaON and Ta3N5 nanoparticles by the Ca-assisted urea route. The specific aim of this study is to determine the efficiency of the as-synthesized nanocrystals for visible-light-induced water oxidation. The characterization of optical properties of the as-synthesized (oxy)nitrides confirmed that both materials possess suitable band gaps, 2.27 eV for TaON and 2.08 eV for TaN, suggesting that they can be used as visible light-active photocatalysts. The photocatalytic activity for water oxidation of both samples was evaluated without any cocatalyst under visible light irradiation.

2. Experimental

2.1 Synthesis

The tantalum oxide and (oxy)nitride nanocrystals were synthesized by a Ca-assisted nitrogen-rich molecular approach using urea, reported previously elsewhere.16) The molar quantities of reactants used in the synthesis–TaCl5 (Sigma Aldrich, Germany), urea (Sigma Aldrich, Germany), and CaCO3 (Sigma Aldrich, Germany)—are given in Table 1. Note that the molar ratio of urea/tantalum was kept to 5 in all the synthesis, while the ratio of Ca2+/urea was varied from 0.10 to 0.50. The reactants were thoroughly mixed in ethanol and the suspension was directly calcined at 800°C for 5 h under N2 atmosphere.

2.2 Characterization

The powder X-ray diffraction (XRD) patterns of the synthesized samples were recorded on a STADI P X-ray diffractometer (STOE&Cie GmbH), equipped with a position-sensitive detector, using Cu Kα (λ = 0.793 Å) radiation under 60 kV voltage and 50 mA current in the 2θ range of 5°–40°. The Fourier transform infrared (FTIR) spectroscopy measurement was performed. The FTIR spectra of the TaON nanocrystals synthesized with Ca2+/urea molar ratio of 0.25 (red line) and pure urea (black line) are comparatively represented in Fig. 2. As shown, the characteristic vibrations of the N–H group were detected at 3489 and 3444 cm⁻¹ (H) in the FTIR spectrum of the TaON nanocrystals. No peaks attributable either to the C–O or C–N vibrations were identified, indicating that urea was completely transformed to ammonia during the calcination process. The presence of ammonia in the sample even after acid treatment suggests that these molecules were strongly adsorbed on the surfaces of the synthesized nanocrystals.

3. Results and discussion

The crystalline phases of the as-synthesized samples were identified by XRD, and the results are shown in Fig. 1. Depending on the content of CaCl2, the color of the final product varies: (i) black for the molar ratio of Ca2+/urea of 0.10, (ii) red for 0.25, and (iii) brownish for 0.50. The XRD pattern of the black-colored sample synthesized with molar ratio of Ca2+/urea of 0.10 ([Ca2+/urea]=0.10, Fig. 1(a)) shows a mixture of predominating tantalum oxide (Ta2O5), oxinitride (TaON) and nitride (Ta2N5, Ta2N5 and TaN) phases, indicating that the Ca2+ content was too low to control the reaction over urea (i.e., the kinetics of NH3 release was too fast). Consequently, multiple crystalline phases with different amounts of nitrogen were formed in the final product. On the contrary, when the molar ratio of Ca2+/urea was set to 0.50 ([Ca2+/urea]=0.50, Fig. 1(c)), the Ca2+ content was excessive, inhibiting the NH3 release from urea, and as a result, multiple crystalline phases with different amounts of nitrogen (TaON and Ta2N5 in a proportion close to 50% and TaN) were formed again in the final product. Interestingly, the Ta2N5 was only formed as a main phase along with TaN in the red-colored sample synthesized with the molar ratio of Ca2+/urea of 0.25 ([Ca2+/urea]=0.25), as shown in Fig. 1(b).

For the synthesis of monodisperse tantalum oxide and (oxy)nitride nanocrystals by a Ca-assisted nitrogen-rich molecular approach, an excess amount of urea has to be used, and the sub-products generated from the decomposition of urea during the reaction will eventually be present in the final products. In order to confirm this, the Fourier transform infrared (FTIR) spectroscopy measurement was performed. The FTIR spectra of the Ta2N5 nanocrystals synthesized with Ca2+/urea molar ratio of 0.25 (red line) and pure urea (black line) are comparatively represented in Fig. 2. As shown, the characteristic vibrations of the N–H group were detected at 3489 and 3444 cm⁻¹ (σ N–H) and at 1628 and 1612 cm⁻¹ (β N–H) in the FTIR spectrum of the Ta2N5 nanocrystals. No peaks attributable either to the C–O or C–N vibrations were identified, indicating that urea was completely transformed to ammonia during the calcination process. The presence of ammonia in the sample even after acid treatment suggests that these molecules were strongly adsorbed on the surfaces of the synthesized nanocrystals.

Table 1. Molar quantities of reactants used in the synthesis of tantalum oxide and (oxy)nitride nanocrystals by the Ca-assisted nitrogen-rich molecular approach

<table>
<thead>
<tr>
<th>Sample</th>
<th>TaCl5 (mol)</th>
<th>Urea (mol)</th>
<th>CaCO3 (mol)</th>
<th>Ca2+/urea</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca2+/urea-0.10</td>
<td>0.002</td>
<td>0.010</td>
<td>0.001</td>
<td>0.10</td>
</tr>
<tr>
<td>Ca2+/urea-0.50</td>
<td>0.002</td>
<td>0.010</td>
<td>0.005</td>
<td>0.50</td>
</tr>
<tr>
<td>Ca2+/urea-0.25</td>
<td>0.002</td>
<td>0.010</td>
<td>0.002</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Fig. 1. XRD patterns of the samples synthesized with Ca2+/urea molar ratio of (a) 0.10, (b) 0.25 and, (c) 0.50.
The TEM image of the Ta₃N₅ nanocrystals synthesized with Ca²⁺/urea molar ratio of 0.25 is shown in Fig. 3(a). As shown, the spherically-shaped, well-defined Ta₃N₅ nanocrystals have a low degree of agglomeration. The low degree of agglomeration can be explained by taking into account the high quantity of ammonia molecules strongly attached on the surface of the Ta₃N₅ nanocrystals which stabilized the nanocrystals electrostatically facilitating their dispersion, i.e., keeping the nanocrystals separated after ultrasonication. The HRTEM image of the Ta₃N₅ nanocrystals is shown in Fig. 3(b). The spherically-shaped and well-defined nanocrystals have an average diameter of ca. 7.1 ± 0.5 nm, and no clear defects were noted. In Fig. 3(b), the interplanar distance was estimated to be 0.51 nm which correspond to the (200) lattice distance of Ta₃N₅, indicating that the nearly monodisperse Ta₃N₅ nanocrystals with high crystallinity can be obtained by applying the current approach.

The UV–Vis diffuse reflectance spectra of the nanocrystals synthesized by a Ca-assisted nitrogen-rich molecular approach with Ca²⁺/urea molar ratios of 0.50 and 0.25, are shown in Fig. 4. Figure 4(a) shows the Kubelka–Munk absorption coefficients calculated from the measured reflectance (R%) according to the formula: F(R) = (1 − R²)/2R. The absorption edge of the Ca²⁺/urea-0.50 nanocrystals appeared at ca. 590 nm, whereas the Ca²⁺/urea-0.25 nanocrystals also had an absorption edge in the visible light region but extended to ca. 620 nm. The band gap energies were determined from the Tauc’s plots of the diffuse reflectance spectra of the samples, shown in Figs. 4(b) and 4(c). From the Tauc’s plots, the band gaps for the Ca²⁺/urea-0.50 and Ca²⁺/urea-0.25 nanocrystals were estimated to be 2.27 and 2.08 eV for indirect allowed transitions, respectively. A broad tailing beyond the band gap was also observed in the Tauc’s plots of the indirect transitions of the Ca²⁺/urea-0.50 nanocrystals (mixture of TaON and Ta₃N₅ nanocrystals in a proportion of 50%) compared to that of the Ca²⁺/urea-0.25, which is formed mainly by Ta₃N₅ nanocrystals (valence band dominated by fully filled N 2p states), due to the allowed transitions from the valence band of TaON formed by N 2p and O 2p states to the conduction band formed by empty Ta 5d states.

The water oxidation half-reaction time courses of samples performed without any cocatalyst under visible light are shown in Fig. 5. Upon visible light irradiation, the O₂ evolution rate is gradually increased and reached the maximum values of 2.01, 3.32, and 4.66 μmol·h⁻¹ for the samples synthesized with Ca²⁺/urea molar ratio of 0.10 (black triangles), 0.50 (brown rectangles) and 0.25 (red circles), respectively. As shown, the samples synthesized with Ca²⁺/urea molar ratio of 0.25 and 0.50 showed
higher \( \text{O}_2 \) evolution rates compared with the sample synthesized with \( \text{Ca}^{2+}/\text{urea} \) molar ratio of 0.10 due to their smaller band gaps achieved by a partial or complete replacement of oxide ions with nitride ions in the \( \text{Ta}_2\text{O}_3 \) lattice. As mentioned above, the reported band gaps of \( \text{Ta}_2\text{O}_3 \), TaON, and \( \text{Ta}_3\text{N}_5 \) are 3.9, 2.4, and 2.1 eV, respectively.\(^3\) The sample synthesized with \( \text{Ca}^{2+}/\text{urea} \) molar ratio of 0.25 showed higher \( \text{O}_2 \) evolution rate (4.66 \( \mu \text{mol h}^{-1} \)) compared to the sample synthesized with \( \text{Ca}^{2+}/\text{urea} \) molar ratio of 0.50 due to the dominance of \( \text{Ta}_3\text{N}_5 \) as the main crystal phase with smaller band gap in the former one. However, first-principles quantum calculations of (oxy)nitride photocatalysts revealed that \( \text{Ta}_3\text{N}_5 \) is a good candidate only for \( \text{H}^+ \) reduction, pure TaON is a good candidate for water oxidation, and non-stoichiometric \( \text{Ta}_{x-\delta}\text{N}_5\text{O}_{5+\delta} \) (for \( x \leq 0.16 \)) between TaON and \( \text{Ta}_3\text{N}_5 \) was predicted to be a good candidate for visible-light-driven overall water splitting reactions.\(^7\) The visible light-driven photooxidation of water on non-stoichiometric and defective TaON was reported to proceed very efficiently.\(^19\) Moreover, Higashi et al.\(^19\) also reported the incident photon to charge carrier efficiencies (IPCEs) of the \( \text{IrO}_2 \)-loaded TaON and \( \text{Ta}_3\text{N}_5 \) photoanodes to be ca. 76\% at 400 nm and ca. 31\% at 500 nm, respectively, at 1.15 V vs. reversible hydrogen electrode (RHE) in aqueous \( \text{Na}_2\text{SO}_4 \) solution. However, Chen et al.\(^20\) recently reported the visible-light-driven photocatalytic oxygen evolution rate of the \( \text{CoO}_2/\text{MgO}(\text{in})-\text{Ta}_3\text{N}_5 \) photocatalyst to be ca. 23 times higher than that of the pristine \( \text{Ta}_3\text{N}_5 \) with a new apparent quantum efficiency record of 11.3\% under 500–600 nm illumination. Although the \( \text{O}_2 \) evolution rate without any cocatalyst of the \( \text{Ta}_3\text{N}_5 \) nanoparticles synthesized in this study (sample synthesized with \( \text{Ca}^{2+}/\text{urea} \) molar ratio of 0.25) is low, further surface and interface modification will be beneficial to achieve higher efficiency.

4. Conclusions

In summary, we have demonstrated the Ca-assisted nitrogen-rich molecular approach for the facile synthesis of tantalum (oxy)nitrides (TaON and \( \text{Ta}_3\text{N}_5 \)) nanocrystals. Monodisperse TaON and \( \text{Ta}_3\text{N}_5 \) nanocrystals were formed by applying suitable urea/Ta ratios in the presence of \( \text{Ca}^{2+} \) ions. Spherically-shaped and well-defined TaON and \( \text{Ta}_3\text{N}_5 \) nanocrystals have an average diameter of ca. 7 nm. Both nanocrystals showed absorption edges in the visible region. From the Tauc’s plots of the UV–Vis diffuse reflectance spectra, the determined band gap energies of \( \text{Ca}^{2+}/\text{urea}-0.50 \) nanocrystals (mixture of TaON and \( \text{Ta}_3\text{N}_5 \) nanocrystals in a proportion of 50\%) and \( \text{Ca}^{2+}/\text{urea}-0.25 \) nanocrystals (formed mainly by \( \text{Ta}_3\text{N}_5 \)) are 2.27 and 2.08 eV for indirect allowed transitions, respectively. The photocatalytic activity for water oxidation of both samples was evaluated without any cocatalyst under visible light irradiation. The \( \text{O}_2 \) evolution rate was increased and reached the maximum in the following order: 2.01, 3.32, and 4.66 \( \mu \text{mol h}^{-1} \) for the samples synthesized with \( \text{Ca}^{2+}/\text{urea} \) molar ratio of 0.10, 0.50, and 0.25, respectively, due to the decrease in the optical band gap.

Acknowledgements

The authors thank Kenta Kawashima and Manli Yang for their assistance in water oxidation experiment and synthesizing the nanoparticles, respectively. The assistance given by Dr. Stefan Lauterbach and Elmar Kersting for HRTEM and optical absorption measurements is also greatly acknowledged.

References