# Electronic Supplementary Information

## Band Engineering of Perovskite-type Transition Metal Oxynitrides for Photocatalytic Overall Water Splitting

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**Experimental Methods**

**S1 Sample preparation for STEM analysis**

For *Cs*-corrected FE-STEM, a thinly sliced sample was used to ensure sufficient transmittance of the electron beam. The sample powder was mixed with a G2 epoxy resin, which was subsequently plasticized by drying at 353 K for 10 min and subsequent heating at 423 K for 1 h. Then, the embedded sample was thinly sliced by accelerated Ar ions using an ion slicer (EM-09100IS, JEOL Ltd.). For EDX analysis, the sample particles were spread on a carbon film supported by a molybdenum mesh.

**S2 ABF-STEM image simulation**

ABF-STEM image simulation was carried out with the QSTEM software package developed by Koch.[s1] The structures used for simulation are shown in the Fig. 1b inset. The values we used in QSTEM were: acceleration voltage, 200 kV; ABF collection angle, 0-40 mrad; defocus, −60 nm; Cs, 1 mm; Cc, 1.0 mm; convergence angle, 15 mrad; and 400 × 400 samples across a 50 × 50 Å sample size. The slice thickness was set at 1.927 Å. The QSTEM package offered the option of simulating a thermal diffuse scattering temperature of 300 K.

**S3 Theoretical calculation**

The DFT calculation was performed on CASTEP. The crystal parameters (such as the lattice constants, the space group, the positions for La, Mg/Ta and O/N atoms) used for the calculations are obtained from ref. s2 and s3. A 3 × 2 × 1 supercell with 120 atoms was built to perform optimization. According to the literature[s3], two types of B-sites are adjacently arranged in the $LaMg_{1/3}Ta_{2/3}O_2N$ structure. The occupancy of $Mg^{2+}/Ta^{5+}$ at each B-site is refined to be 0.356: 0.644 and 0.310: 0.690, respectively. In our supercell, in order to simplify calculations, $Mg^{2+}$ and $Ta^{5+}$ ions are symmetrically distributed over all B-sites, leading to occupancy of $Mg^{2+}/Ta^{5+}$ at each type of B-sites to be 1:2. The $O^{2-}$ and $N^{3-}$ ions are then manually added to all anionic sites to form a reported stable configuration[s4]. Namely, $Mg^{2+}$ ions are surrounded by six $O^{2-}$ ions, while the leftover $O^{2-}$ ions and all the $N^{3-}$ ions are symmetrically distributed between $Ta^{5+}$ ions. The Perdew-Burke-Ernzerh of generalized gradient approximation (PBE-GGA) was used to describe the exchange and correlation energy of the electrons. A 1 × 2 × 2 k-point sampling of the Brillouin zone was used. The calculations were done with designed nonlocal norm-conserving pseudopotentials. The cutoff energy was 380 eV.

**Reference**

s1 C. Koch, *Ph.D. Thesis*, Arizona State University, 2002.

s2 Y. Kim and P. Woodward, *J. Solid State Chem.,* 2007, **180**, 3224.

s3 Y. Kim, *Ph.D. Thesis*, The Ohio State University, 2005.

s4 H. Wolff, M. Lerch, H. Schilling, C. Bähtz and R. Dronskowski, *J. Solid State Chem.,* 2008, **181**, 2684.

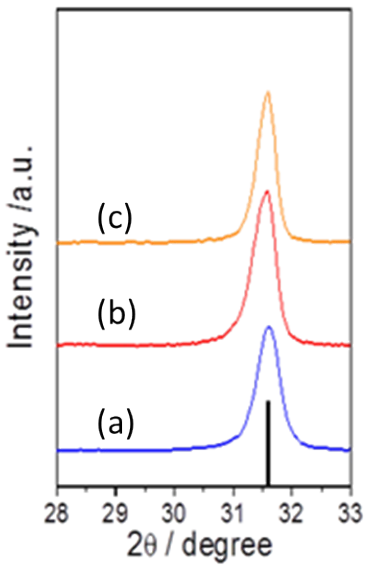


**Figure S1** Enlarged XRD patterns of Figure 1b. $LaMg_{0.33}Ta_{0.67}O_2N$ samples nitrided from oxide

precursors that was calcined at different temperatures (a) 973K, (b) 1073K, (c) 1173K.

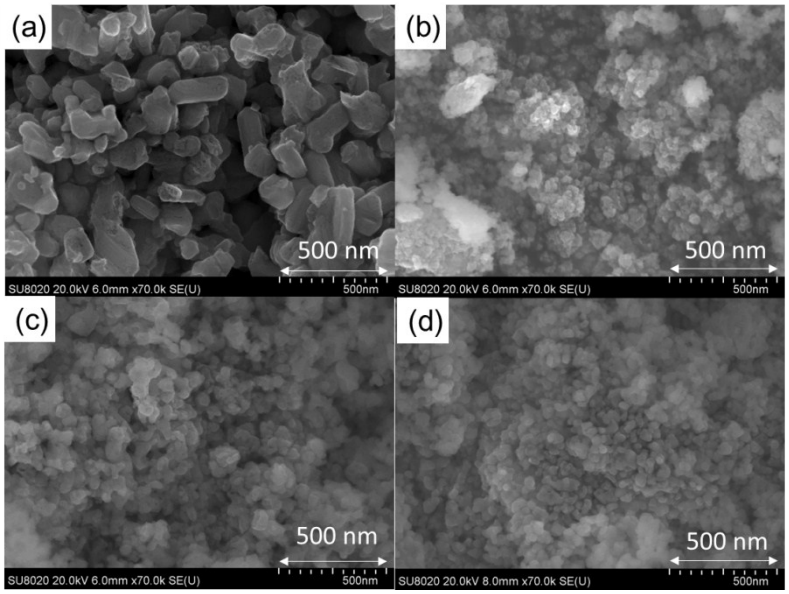


**Figure S2** SEM images of $LaMg_xTa_{1-x}O_{1+3x}N_{2-3x}$ (a) x=0, (b) x=0.1, (c) x=0.33, (d) x=0.5.

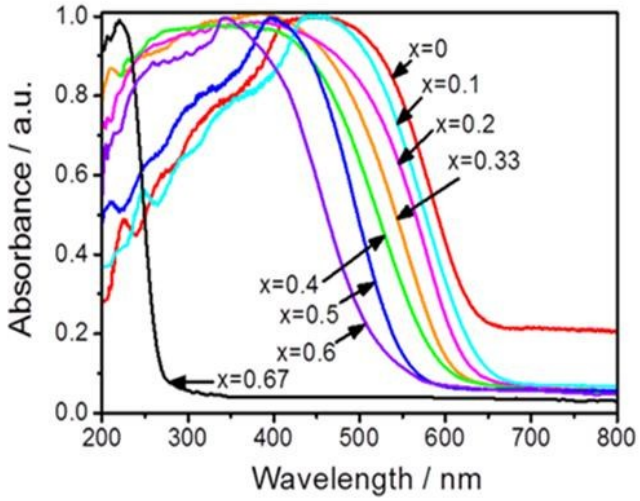


**Figure S3** UV-visible diffuse reflectance spectra of $LaMg_xTa_{1-x}O_{1+3x}N_{2-3x}$ series.

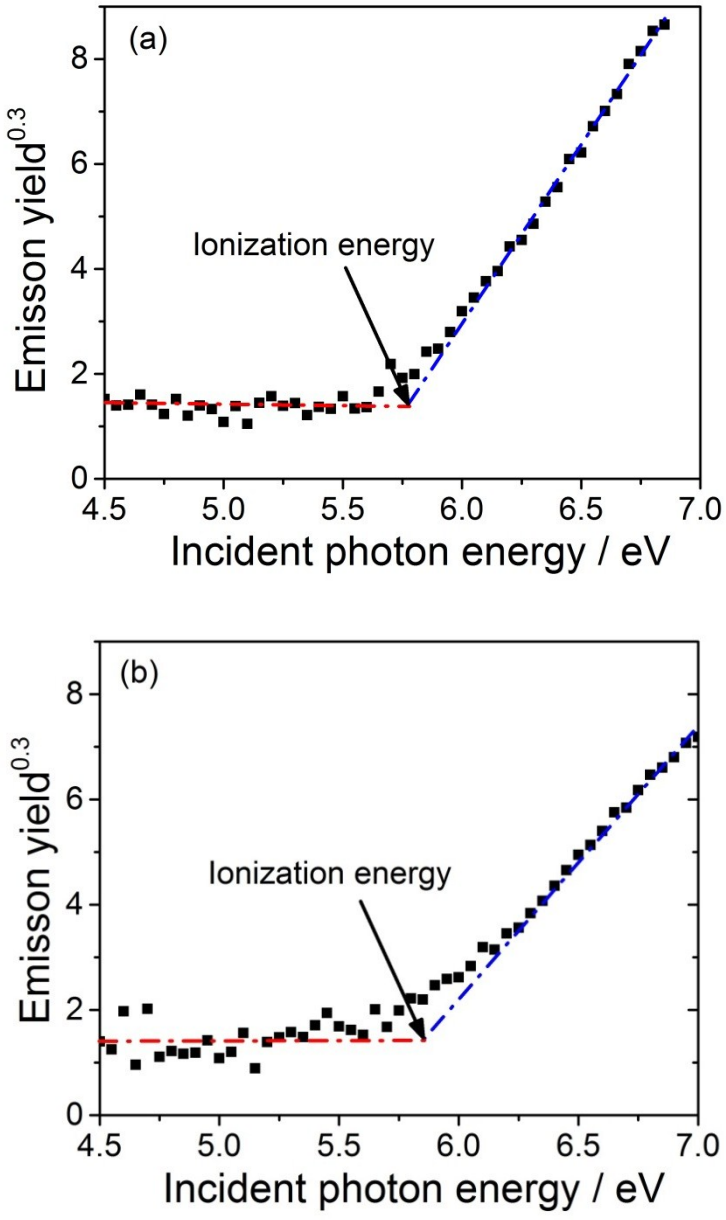


**Figure S4** PESA spectra of $LaTaON_2$ (a) and $LaMg_{0.33}Ta_{0.67}O_2N$ (b) electrodes fabricated by particle transfer method. The ionization potential which equal to VBM potential can be converted to the potential against a normal hydrogen electrode (NHE) by $E$ / V vs. NHE = $E$ / V vs. vacuum level -4.44 / V.

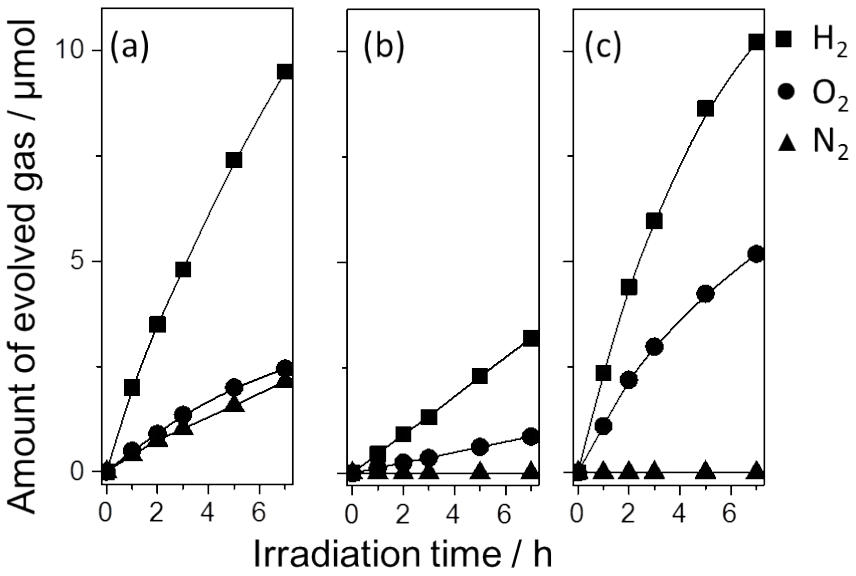


**Figure S5** Time courses of water splitting on (a) $CoO_z/RhCrO_y/LaMg_{0.33}Ta_{0.67}O_2N$, (b) $TiO_2/CoO_z/RhCrO_y/LaMg_{0.33}Ta_{0.67}O_2N$ and (c) $TiO_2/RhCrO_y/LaMg_{0.33}Ta_{0.67}O_2N$. Reaction conditions: catalyst, 0.2 g; reaction solution, pure water (250 mL); light source, Xe lamp (300 W, $\lambda \geq 300$ nm); side irradiation-type reaction vessel made of Pyrex.

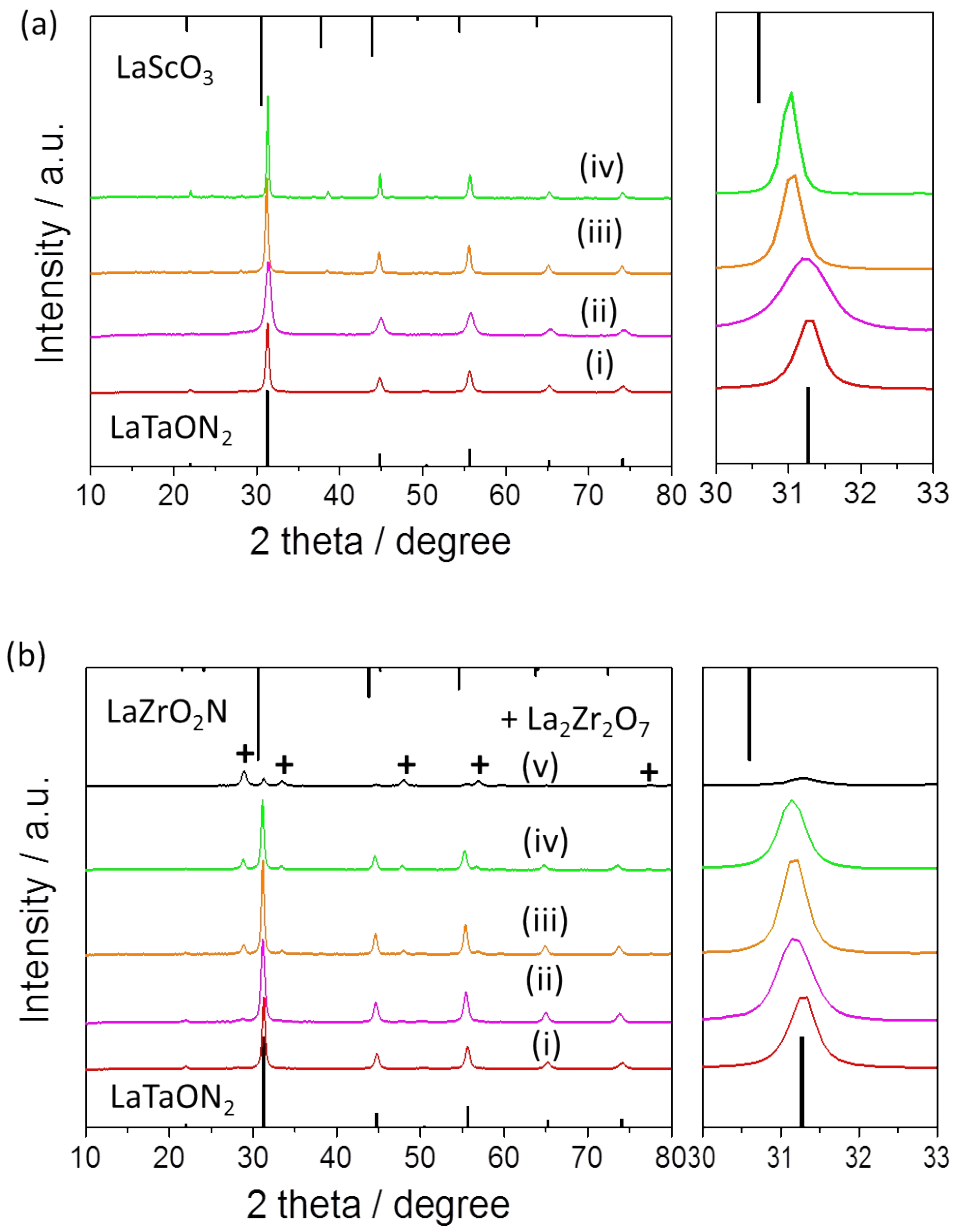


**Figure S6** XRD of (a) $LaSc_xTa_{1-x}O_{1+2x}N_{2-2x}$ with different Sc content(x), (i) 0.25, (ii) 0.33 (iii) 0.5, (iv) 0.75; and (b) $LaZr_xTa_{1-x}O_{1+x}N_{2-x}$ with different Zr content(x), (i) 0.05, (ii) 0.25 (iii) 0.33, (iv) 0.50, (v) 0.75.

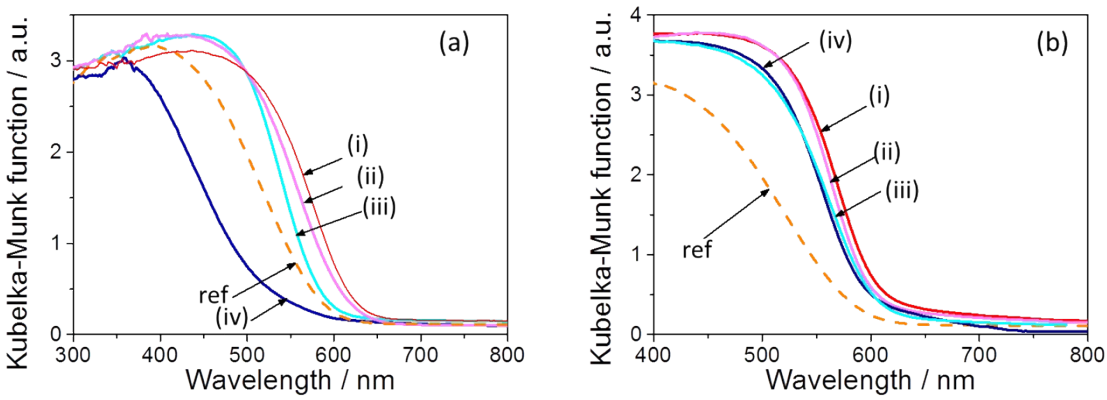


**Figure S7** UV-Vis DRS of (a) $LaSc_xTa_{1-x}O_{1+2x}N_{2-2x}$ with different Sc content(x), (i) 0.25, (ii) 0.33 (iii) 0.5, (iv) 0.75; and (b) $LaZr_xTa_{1-x}O_{1+x}N_{2-x}$ with different Zr content(x), (i) 0.05, (ii) 0.25 (iii) 0.33, (iv) 0.50. Ref. is the absorption spectrum of $LaMg_{0.33}Ta_{0.67}O_2N$.

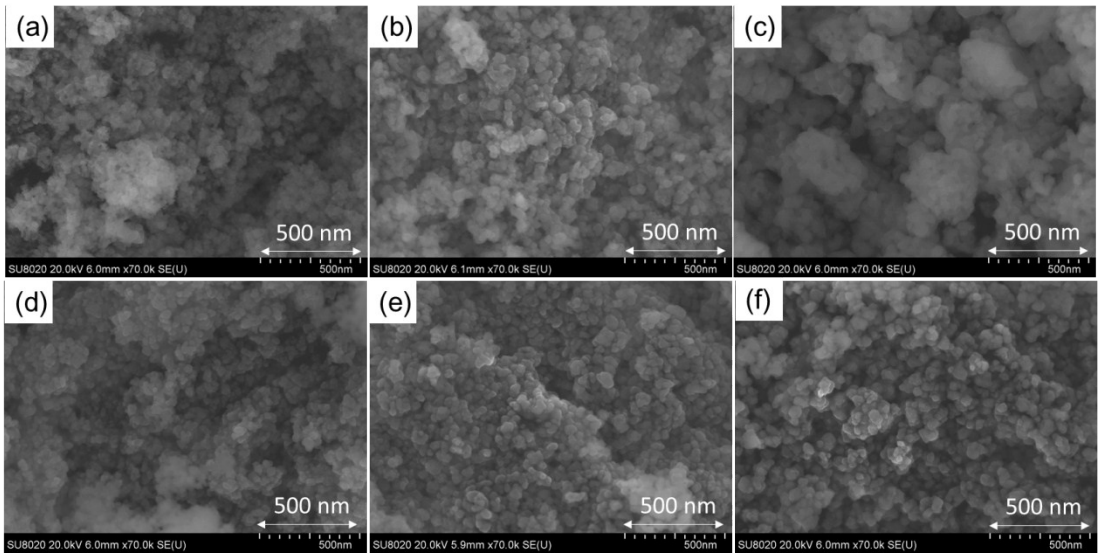


**Figure S8** SEM images of $LaSc_xTa_{1-x}O_{1+2x}N_{2-2x}$ (a-c): (a) x=0.33, (b) x=0.5, (c) x=0.75; and $LaZr_xTa_{1-x}O_{1+x}N_{2-x}$ (d-f): (d) x=0.25, (e) x=0.33, (f) x=0.5.

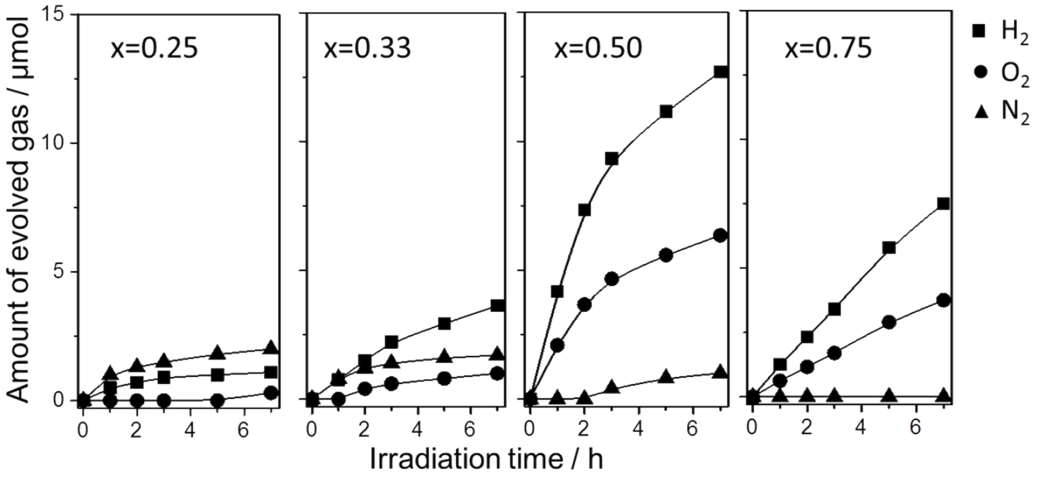


**Figure S9** Time courses of water splitting on $TiO_2/RhCrO_y/LaSc_xTa_{1-x}O_{1+2x}N_{2-2x}$. Reaction conditions: catalyst, 0.2 g; reaction solution, pure water (250 mL); light source, Xe lamp (300 W, λ≥300 nm); side irradiation-type reaction vessel made of Pyrex.

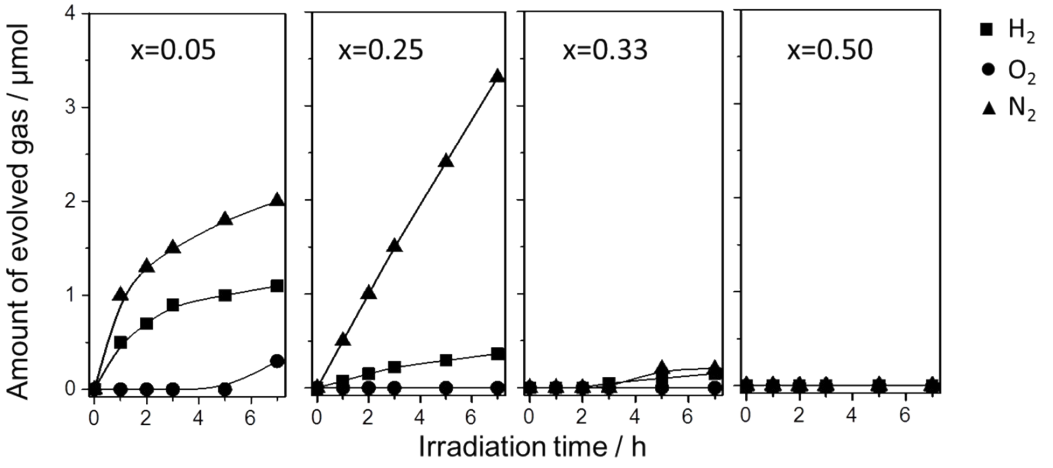


**Figure S10** Time courses of water splitting on $TiO_2/RhCrO_y/LaZr_xTa_{1-x}O_{1+x}N_{2-x}$. Reaction conditions: catalyst, 0.2 g; reaction solution, pure water (250 mL); light source, Xe lamp (300 W, λ≥300 nm); side irradiation-type reaction vessel made of Pyrex.