they are similar in pyridinic N content, NGQDs tend to have higher density of pyridinic N at edge sites than NRGOs. The pyridinic N at the edge site is believed to be more active to induce C–C bond formation than those at the basal plane, which leads to a higher yield of C2 and C3 products on NGQDs electrode than on NRGOs electrode[32].

Production rate of CO_2 reduction products. In addition to the promising selectivity with respect to the formation of multi-carbon hydrocarbons and oxygenates, the NGQDs electrode also exhibits a high CO_2 reduction current density of $100\ mA\ cm^{-2}$ at relative low potentials (Supplementary Fig. 12). The partial current densities for production of CO, C_2H_4 and C_2H_5OH reach 23, 46 and $21\ mA\ cm^{-2}$ at $-0.86\ V$, respectively (Fig. 3a), which are on the same order of magnitude compared with corresponding partial current densities observed for commercial Cu nanoparticles (around 20–40 nm) under identical testing conditions[9]. Accordingly, CO, C_2H_4 and C_2H_5OH could be produced at rates of 4.2, 1.4 and $0.7\ mol\ h^{-1}\ m^{-2}$ at $-0.86\ V$, respectively (Supplementary Fig. 13). In contrast, the GQDs exhibit a partial current density or production rate for C_2H_4 that is at least one order of magnitude lower at comparable potentials (Fig. 3b and Supplementary Fig. 13).

Discussion

A metal-free catalyst comprising NGQDs is discovered to exhibit extraordinary activity towards CO_2 reduction. Interestingly, NGQDs show predominant selectivity to the production of multi-carbon hydrocarbons and oxygenates, whereas GQDs and NRGOs primarily yield CO and $HCOO^-$. Detailed characterization reveals that the unique nanostructure in combination with utmost exposure of edge sites and heteroatom N doping grants NGQDs the unprecedented activity and selectivity. This finding expands the horizon for the design of high-performance electrocatalysts for CO_2 reduction. However, the reaction mechanism of electroreduction of CO_2 over NGQDs remains elusive and the unravelling requires further work. The combination of high-sensitive operando spectroscopy and first-principle calculation would be an efficient way to provide insight into the reaction intermediates to reveal the reaction pathways. In addition, the activity difference between the zig-zag and armchair edge necessitates exploration as well in the future.

Methods

GQD synthesis. NGQDs were synthesized by heat treating the GO dispersion in DMF in a PTFE-lined autoclave at 200 °C for 10 h. The pristine GQDs were prepared in a similar way, except using a mixture of isopropanol and water (1:1 by volume) as the solvent. The NRGO was prepared by doping GO in a tube furnace at 800 °C, while flowing ammonia for 1 h. More details about the synthesis and characterization are in the Supplementary Information.

Materials characterization. The morphology and crystallinity of N-doped and pristine GQDs was characterized by high-resolution field-emission gun TEM (JEOL 2,100 FEG TEM). The TEM samples were prepared by dropping the QDs solution onto the ultrathin carbon film TEM grid followed by vacuum drying at 100 °C. The thickness of QDs was measured by atomic force microscopy with tapping mode (Bruker Multimode 8). The atomic force microscopy samples were prepared by dropping the QDs solution onto the Mica substrate. The morphology of NRGOs was analysed by scanning electron microscope (FEI Quanta 400 FEG ESEM). The Raman spectra were taken with a Renishaw inVia Raman microscope with 514 nm laser excitation. XPS measurements were performed to analyse the element component and oxide state of QDs and NRGOs at ambient temperature using PHI Quantera with Al-Kα X-ray source. The Cu content in the NGQDs was determined by using inductively coupled plasma optical emission spectroscopy (PerkinElmer-Optima 2000DV). One millilitre of original liquid sample that is dissolved in DMF was diluted with 5 ml water, then one drop (~0.05 ml) of concentrated HNO_3 was used to adjust the pH to be <7. Two different emission lines: $\lambda = 224.7000\ nm$ and $\lambda = 213.5970\ nm$ were used to detect the Cu element. The detection limit for Cu is 10 p.p.b.

Electrochemical measurement of CO_2 reduction. The CO_2 reduction reaction was conducted in an electrochemical flow cell composed of targeted quantum dots or NRGO-based gas diffusion electrodes (see Supplementary Fig. 4). The electrochemical measurement was carried out at ambient pressure and temperature. The electrolysis was performed under potentiostatic mode with a full cell voltage ranging from -1.6 to $-3.5\ V$ controlled by a potentiostat (Autolab PGSTAT-30, EcoChemie). Both the catholyte and anolyte were 1 M KOH (pH 13.48, as calibrated by a pH meter (Thermo Orion, 9106BNWP). Individual electrode potentials were recorded using multimeters (AMPROBE 15XP-B) connected to each electrode and a reference electrode (Ag/AgCl; RE-5B, BASi) placed in the electrolyte exit stream. The measured potentials after iR compensation were rescaled to the RHE by E (versus RHE) = E (versus Ag/AgCl) + 0.209 V + 0.0591 V/pH × pH. The current reported here was obtained by averaging the span of time (at least 180 s) for each applied voltage.

For each applied voltage, after the cell reached steady state, 1 ml of the effluent gas stream was periodically sampled and diverted into a gas chromatograph (Thermo Finnegan Trace GC) equipped with both the thermal conductivity and flame ionization detector, and a Carboxen 1,000 column (Supelco). Meanwhile, the exit catholyte was collected at each applied voltage followed by identifying and quantifying using ^{1}H NMR (nuclear magnetic resonance, UI500NB, Varian).

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