Materials and Methods

Preparation. The ZnGaNO nanorod was synthesized using a stoichiometric mixture of zinc chloride and potassium gallium as precursor. Typically, $0.2726g ZnCl_2$ and $0.2816g KGaO_2$ was put into a tube furnace with a continuously 250sccm NH₃ flow, and calcined at 750°C for 5 hours. The derived powders were washed with distilled water and centrifuged for a few times.

To enhance the kinetics of CO_2 reduction reaction, 0.5wt% Pt was loaded on the surface of derived ZnGaNO by immersing the as-prepared powder into a H₂PtCl₆ aqueous solution, and calcined at 400°C for 1h in a tube furnace with a continuously 250sccm NH₃ flow.

Characterization. The crystal phase of the derived sample was determined by an Xray diffractometer (XRD, Rigaku Ultima III, Japan) operated at 20kV and 40mA with Cu-K α radiation. Diffused reflectance spectrum was scanned by a UV-vis spectrophotometer (UV-2500, Shimadzu Co., Japan) and transformed into absorption spectrum with Kubelka–Munk relationship. The specific surface area was measured on nitrogen adsorption at -196°C by an automatic surface area analyzer (Micromeritics Tristar-3000, USA) after the samples had been dehydrated in the flow of N₂ at 150°C for 3h. The surface morphology was characterized by scanning electron microscope (SEM, FEI Nova Nano SEM 230, USA). TEM images and selected area electron diffraction patterns (SAED) was obtained by employing a transmission electron microscope (TEM, FEI Tecnai G2 F30 S-Twin, USA) operated at 200 kV.

Photocatalytic test. The photocatalytic CO_2 reaction was carried out in a glass reactor with an area of 4.2 cm². The light source was a 300W Xenon arc lamp, and to get a visible irradiation, a 420nm filter was employed. The volume of the reaction chamber was about 230ml. Before the reaction, the chamber was evacuated several times and then high purity CO_2 gas was introduced into the reaction chamber to achieve ambient pressure. 0.4ml deionized water was injected into the chamber as reactant. During the reaction, 1ml gas was extracted by a sampling needle from the chamber at given intervals for subsequent CH_4 concentration analysis with gas chromatography (GC-2014, Shimadzu Corp., Japan)



Figure S1 Elemental mapping of the ZnGaNO nanorod.



Figure S2 (a) XRD patterns of ZnGaNO synthesized from $KGaO_2$ and $Zn(OAc)_2$ (ZGNO-1), and ZnGaNO synthesized from Ga_2O_3 nanoplate and ZnCl₂ (ZGNO-2) and ZnGaNO nanorod (b) XRD patterns of washed and unwashed ZnGaNO nanorod, and peaks of KCl, GaN and ZnO JCPDS cards as comparison.



Figure S3 (a) SEM image of the final product $ZnGa_2O_4$ nanoparticles by heating the mixture of $ZnCl_2$ and $KGaO_2$ at 750°C in air. (b) SEM image of ZnGaNO nanorod synthesized from fluoride molten salt.



Figure S4 XRD patterns of ZnGaNO nanorod synthesized by heating the mixture of $KGaO_2$ and $ZnCl_2$ for 1h, 3h and 5h.

Table 1 Elements atom content percentage of ZnGaNO nanorod and ZnGaNO-SS derived from EDS analysis

	Zn atom%	Ga atom%	N atom%	O atom%
ZnGaNO nanorod	19.6%	29.0%	21.8%	29.7%
ZnGaNO-SS	9.2%	39.3%	37.3%	14.1%