

Supporting Information

Graphene Microtubings: Controlled Fabrication and Site-specific Functionalization

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Experimental Section

Preparation of μ GT. GO was prepared from natural graphite powder *via* acid-oxidation according to a modified Hummers method as mentioned in our previous papers.^{s1-s3} The formation of μ GT is schematically shown in Figure 1. A glass pipeline with an inner diameter of *ca.* 0.4 mm was used as the reactor. 8 mg/mL GO suspension was filled in the glass pipeline, in which a Cu wire with a diameter of *ca.* 100 μ m has been intercalated in advance. After sealing the GO suspension within the glass pipeline by fast heating its two ends on alcohol burner, it was heated at 230°C for 2.5 h. During this process, GO is reduced and the hydrothermally converted

graphene enwraps the Cu wire. Then the wet graphene enwrapped Cu wire was taken out from glass pipeline, and densely packed graphene layer surrounding Cu wire was formed after drying naturally. Subsequently, meters of μ GTs with a diameter depending on the supporting Cu wire are collected after etching Cu wire in an aqueous 2.5 M FeCl_3 solution containing 0.5 M HCl and thoroughly washing with distilled water. The Cu wire induced the aggregation of hydrothermally reduced GO along it and acted as the support during the drying process. The μ GTs with diameters of *ca.* 150 and 40 μm were produced by choosing the Cu wires with corresponding diameters as supporting core.

Preparation of helical μ GTs and multichannel μ GTs. The formation of helical and multichannel μ GTs is similar to that illustrated in Figure 1 except the used supporting cores. For the synthesis of helical μ GTs, a twist of two Cu wires, instead of the single wire, is used as the supporting core (Figure 3c, inset). Two-channel, three-channel and four-channel μ GTs can be readily fabricated by utilizing two-, three-, and four-ply Cu wires without twist.

Outer-wall modification of μ GTs with Pt or Pd nanoparticles. To attach Pt nanoparticles onto the outer-wall surfaces of μ GTs, naturally dried Cu wire-embedded μ GT was immersed into an aqueous solution of 15.4 mM K_2PtCl_4 solution for *ca.* 2 min, followed by etching Cu wire in aqueous 2.5 M FeCl_3 solution containing 0.5 M HCl. Finally, the Pt outer-wall modified μ GT was obtained after thoroughly washing

with distilled water. Following the same procedure, Pd nanoparticles outer-wall modified μ GT was prepared by reaction of naturally dried Cu wire-embedded μ GT with 37.6 mM H_2PdCl_4 for *ca.* 2 min.

Inner-wall modification of μ GTs with Pt or Pd nanoparticles. To introduce Pt or Pd nanoparticles onto the inner-wall surfaces of the μ GTs, we first immersed the Cu wire into 15.4 mM K_2PtCl_4 solution or 37.6 mM H_2PdCl_4 for *ca.* 2 min to anchor Pt or Pd nanoparticles on the surface of Cu wires via SEED,^{s4} respectively, which then were used as the supporting core to prepare the μ GTs following the procedure in Figure 1. After removing the Cu wire, the Pt or Pd nanoparticle were decorated on the inner-wall surfaces of μ GTs.

Asymmetrical Out/inner-wall modification of μ GTs with Pt and Pd nanoparticles. The above-mentioned μ GT embedded with Pd nanoparticles modified Cu wire was further immersed into an aqueous solution of 15.4 mM K_2PtCl_4 solution for *ca.* 2 min to attach Pt nanoparticles onto the outer-wall surface of μ GT. Once removing the Cu wire, Pd nanoparticles will leave on the inner-wall surface, while Pt nanoparticles attach on the outer-wall surface of μ GT.

Within-wall modification of μ GTs with TiO_2 or Fe_3O_4 nanoparticles. TiO_2 nanoparticles (AEROXIDE P25, *ca.* 20 nm in diameter) were mixed into the 8 mg/mL GO aqueous solution with ultrasonication to form a *ca.* 0.5 mg/mL uniform suspension of TiO_2 , which was then filled in the glass pipeline with intercalated Cu

wire. After hydrothermal reduction, drying process, and removal of the Cu wire, a TiO_2 within-wall modified μGT was collected. Similarly, Fe_3O_4 nanoparticles within-wall modified μGT was synthesized by premixing Fe_3O_4 nanoparticles (Aladdin Chemistry Co. Ltd, 20 nm in diameter) in aqueous GO suspension at a concentration of *ca.* 0.5 mg/mL.

Characterization. The morphology of the graphene sheets and functionalized graphene sheets on the corresponding μGTs were determined by JEM-2010 high resolution transmission electron microscopy (HR-TEM) at an acceleration voltage of 120 kV. Field-emission scanning electron microscope (FE-SEM) images and EDS data of the samples were taken on JSM-7001F SEM unit. X-ray diffraction (XRD) patterns were obtained by using a Netherlands 1,710 diffractometer with a Cu $K\alpha$ irradiation source ($\lambda = 1.54 \text{ \AA}$), and a self-calibration process was performed with a SiO_2 internal standard sample prior to target measurement. Raman spectra were recorded using a RM 2000 Microscopic Confocal Raman Spectrometer (Renishaw PLC, England) with an Ar laser at a wavelength of 514.5 nm. Mechanical property test of μGT was conducted with an Instron material testing system (Instron 3342). The strain rate for a centimeter gauge length is 1mm/min with a preload of 0.5 N. The electrical resistance of graphene fiber was measured by using a four-probe resistance tester (Model ST2258A, Suzhou, China).

Electrochemical investigation. The electrochemical ethanol oxidation was conducted in a three-electrode cell by using a CHI760D electrochemical workstation. Pt nanoparticles outer-wall modified μ GT with a length of *ca.* 1 cm was used as working electrode and catalyst. A saturated calomel electrode (SCE) and a platinum foil (1 cm²) were used as the reference and counter electrodes, respectively. The activity evaluation for ethanol oxidation reaction was carried out in 1 M KOH electrolyte containing 1 M CH₃CH₂OH. Cyclic voltammetry curves (CV) was recorded by applying a linear potential scan at a sweep rate of 50 mV s⁻¹. The cycling was repeated until reproducible CV curves were obtained before the measurements were recorded.

Photocurrent test. The photocurrent response of TiO₂ within-wall modified μ GT was measured by applying a bias of 0.1 V to the μ GT with about 1 cm electrode distance, and the current was recorded by CHI 760D electrochemical workstation upon exposure to a daylight lamp (100 W).

μ GT micromotor. The inner-wall modified μ GT (*ca.* 6 mm in length and *ca.* 100 μ m in diameter) with Pt nanoparticles is used as a transporter, one end of which is sealed with super glue. The fast motion of a μ GT micromotor was observed in 20 wt% H₂O₂ solution. The ejected O₂ bubbles from the other side will drive the μ GT moving in the contrary direction. The corresponding result was recorded in the Supporting Movies.

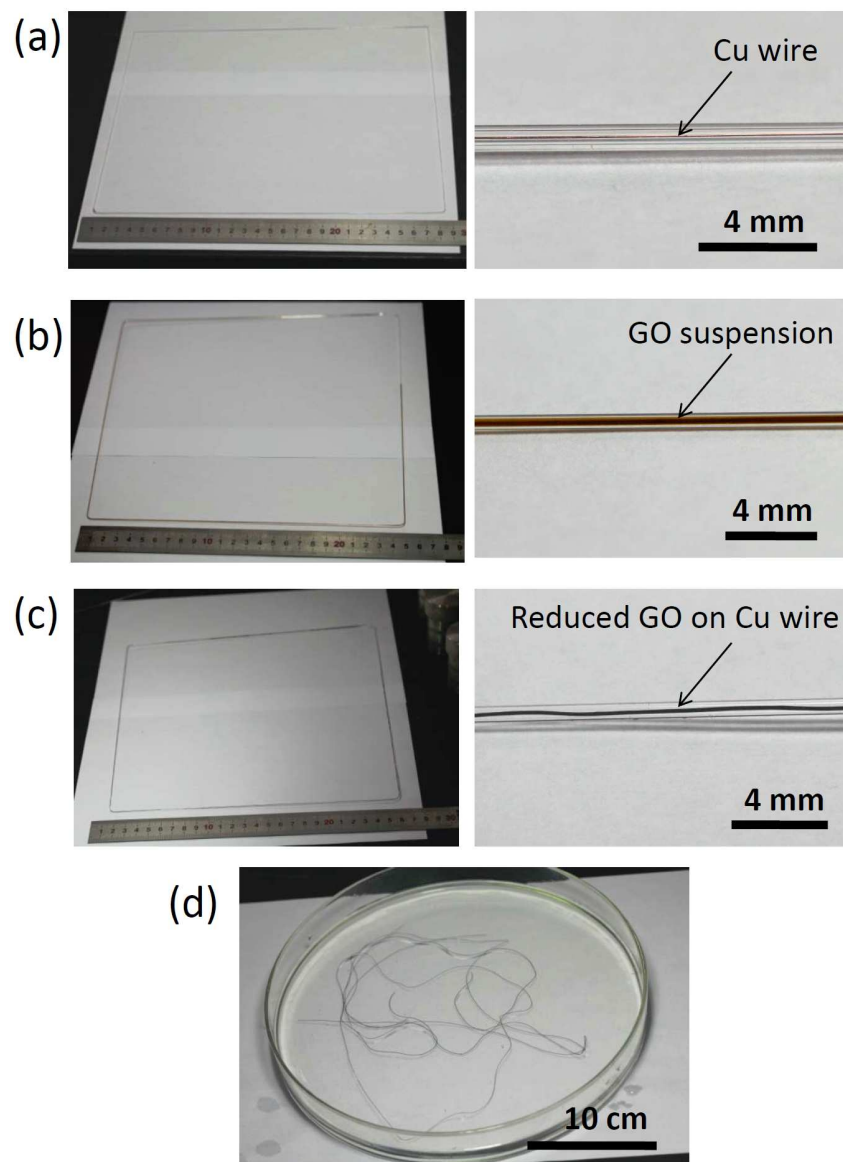


Figure S1. Preparation of μ GTs. (a) A one-meter long glass pipeline with Cu wire inside. (b) The glass pipeline filled with aqueous GO suspension (8 mg/mL). (c) Hydrothermally reduced GO aggregated along Cu wire within the glass pipeline after heating at 230°C for 2.5 h. (d) The released Cu wire covered with reduced GO.

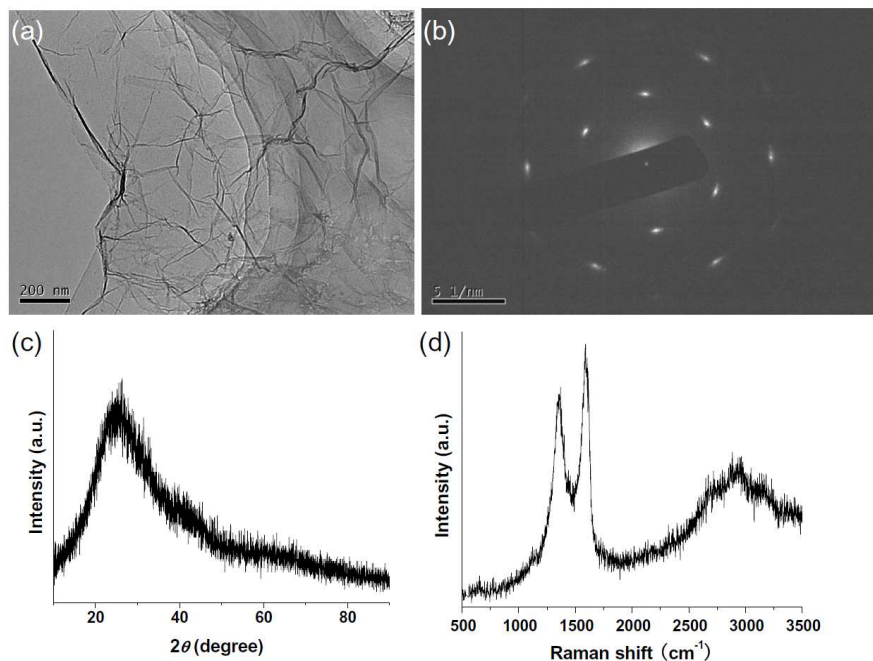


Figure S2. Characterization of reduced GO within μ GTs. (a) TEM image of graphene sheets within μ GTs, and the corresponding electron diffraction (b), XRD pattern (c) and Raman spectrum (d).

The graphene sheets within μ GTs were confirmed by TEM image (Figure S2a) and the corresponding electron diffraction (Figure S2b). In addition, XRD pattern (Figure S2c) and Raman spectra (Figure S1d) also indicate the formation of graphene by the hydrothermal process.

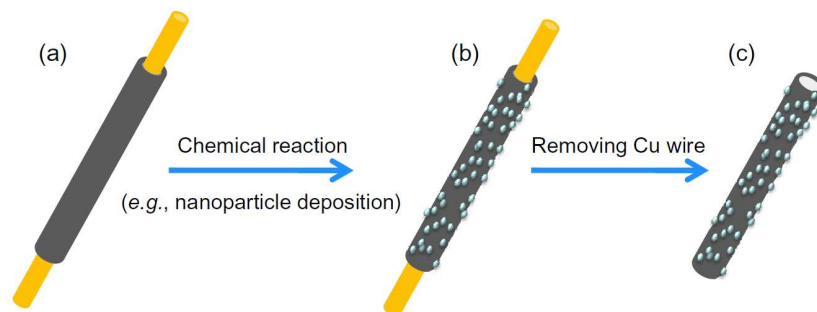


Figure S3. Schematic diagram of the outer-wall modification of a μ GT.

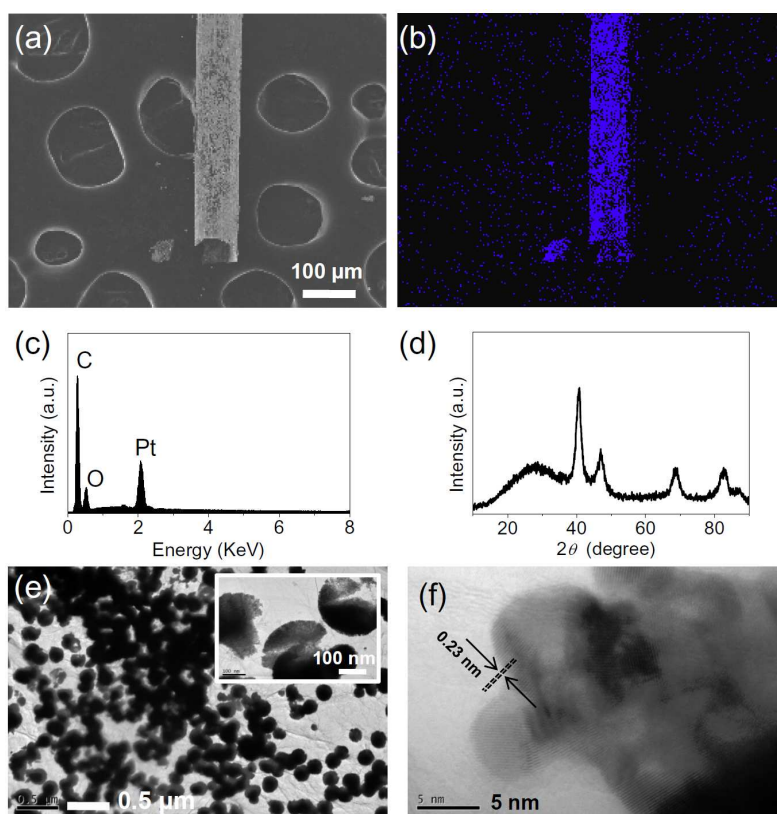


Figure S4. Outer-wall modification of μ GTs with Pt nanoparticles. (a,b) SEM image and Pt element mapping. (c,d) EDS spectrum and XRD pattern of Pt outer-wall modified μ GTs, respectively. (e,f) TEM images of Pt nanoparticles on graphene sheets.

Figure S4a and b are the SEM image of a μ GT outer-wall modified with Pt nanoparticles and the corresponding energy dispersive spectroscopy (EDS) mapping, respectively. EDS (Figure S4c) confirms the C, Pt and plus O associated with the hydrothermally reduced graphite oxide. X-ray diffraction (XRD) pattern of the μ GTs outer-wall modified with Pt nanoparticles further verified the composition profile (Figure S4d). The broad peak located at $2\theta \approx 23^\circ$ is assigned to the (002) plane of stacked graphene sheets within μ GTs.^{s5} A series of typical peaks of the face-centered cubic (fcc) structure of Pt, corresponding to the planes of Pt (111), Pt (200), Pt (220), Pt (311) and Pt(222) at *ca.* 40° , 47° , 68° , 82° , and 86° , respectively, are observed, in agreement with those of a standard Pt (refer to JCPDS ICDD card NO. 01-1194). Figures. S4e and f are TEM images of Pt nanoparticles on graphene layer at different magnifications. Pt particles have the diameter of *ca.* 200-300 nm (Figure S4e) in consistent with the SEM observation (Figures. 4j,k,o). The high resolution TEM (HR-TEM) image in Figure S4f reveals the lattice spacing of 0.23 nm, corresponding to the (111) interplanar distance of standard Pt crystalline lattice.^{s6}

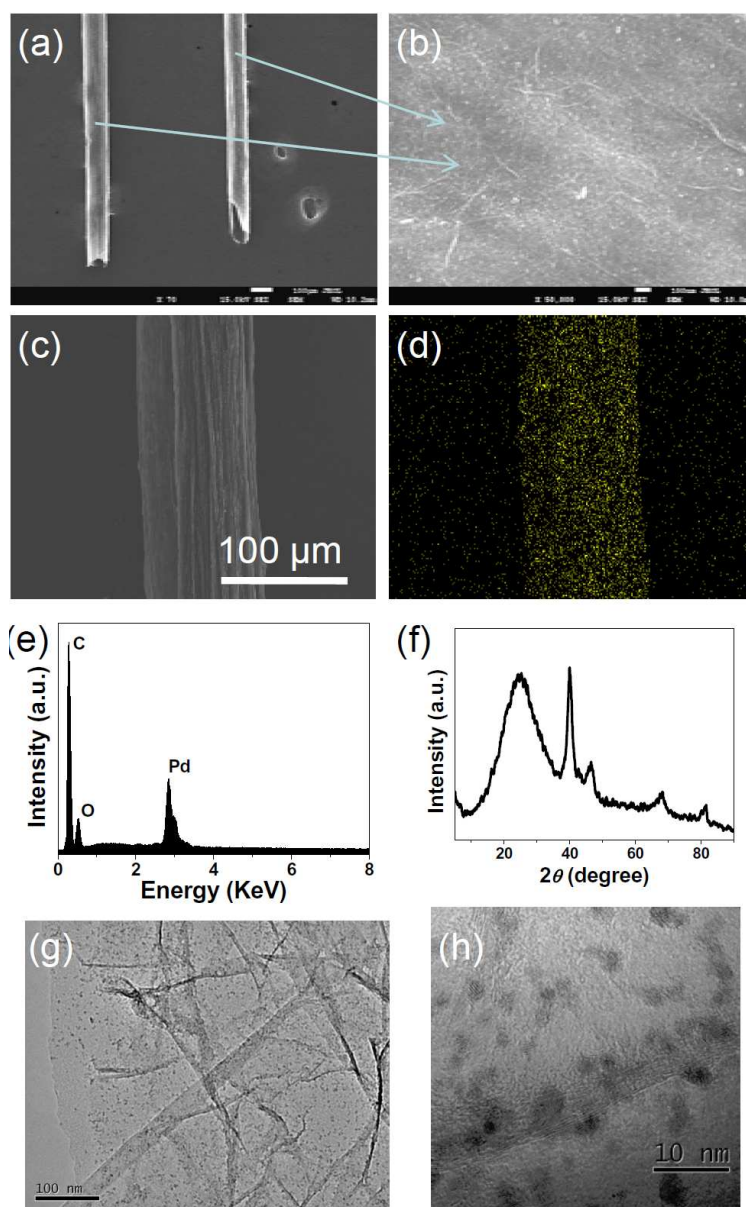


Figure S5. Outer-wall modification of μ GTs with Pd nanoparticles. (a,b) SEM image of Pd outer-wall modified μ GTs and the high magnification view of the surface. (c,d) SEM image of Pd outer-wall modified μ GT and corresponding EDS mapping of Pd element. (e, f) EDS spectrum and XRD pattern of Pd outer-wall modified μ GTs. (g, h) TEM images of Pd nanoparticles on graphene layers. Scale bars: a, 100 μ m; b, 100 nm; g, 100 nm; h, 10 nm.

Figure S5a shows a low magnification SEM image of two μ GTs outer-wall modified with Pd nanoparticles. The close view in Figure S5b reveals that Pd nanoparticles anchored on the surface of μ GT, which have a much small size of less than 10 nm. Figures S5c and d are SEM image and the corresponding Pd EDS mapping of μ GT outer-wall modified with Pd nanoparticles, showing the relatively uniform distribution of Pd along μ GT. The EDS spectrum in Figure S5e reveals that the sample is mainly composed of C, Pd, and O elements within the sample. XRD pattern of the μ GTs outer-wall modified with Pd nanoparticles (Figure S5f) further verified the composition profile in combination with Pd and μ GTs. The broad peak located at $2\theta \approx 23^\circ$ is assigned to the (002) plane of stacked graphene sheets within μ GTs.^{s5} A series of the typical peaks in agreement with those of a standard face-center cubic Pd (refer to JCPDS ICDD card NO. 48-1551) are observed. TEM image (Figure S5g) further confirms that the formation of the small nanoparticles and their good dispersion around graphene sheets. The HR-TEM image demonstrates that the size of Pd nanoparticles is of *ca.* 4 nm (Figure S5h).

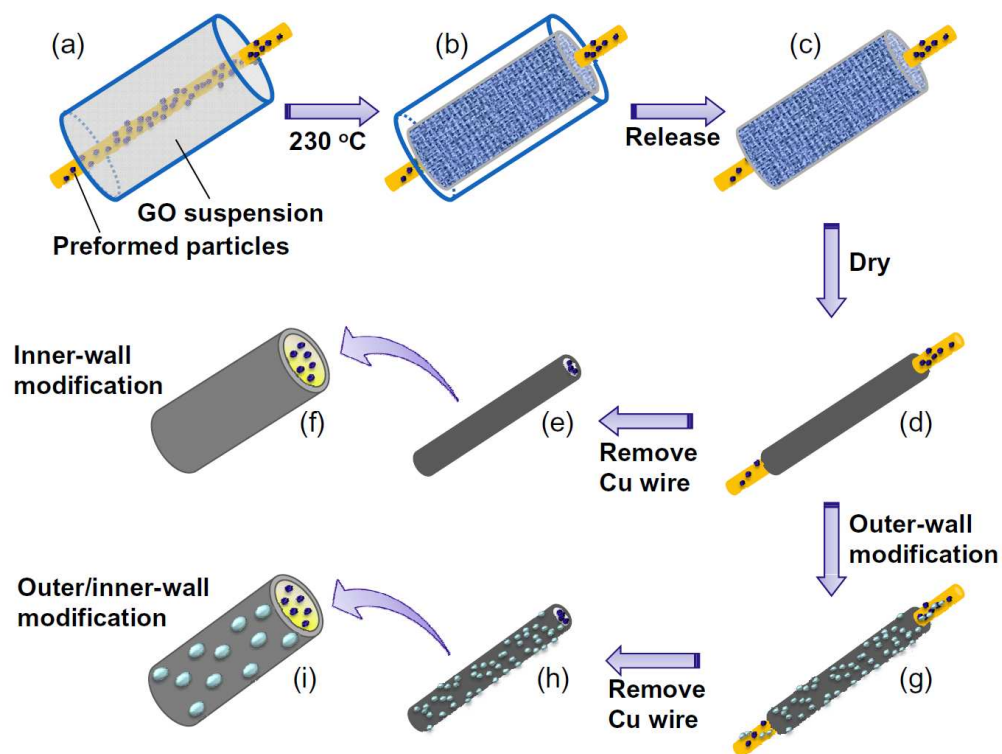


Figure S6. Schematic diagram of the inner-wall and outer/inner-wall modification of a μ GT.

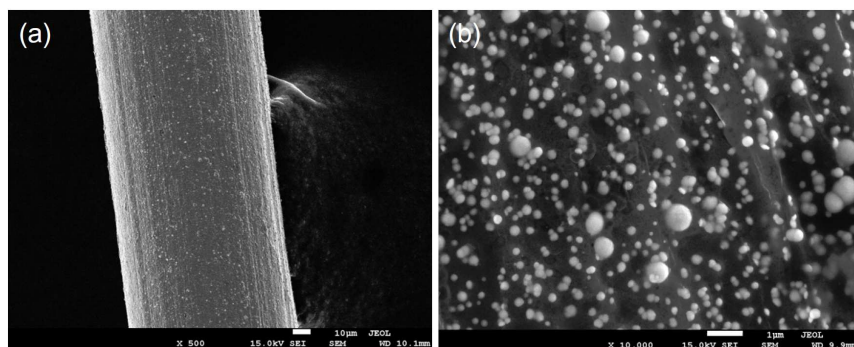


Figure S7. SEM images of Pt nanoparticles on Cu wire by immersing the Cu wire into 15.4 mM K_2PtCl_4 solution for *ca.* 2 min.

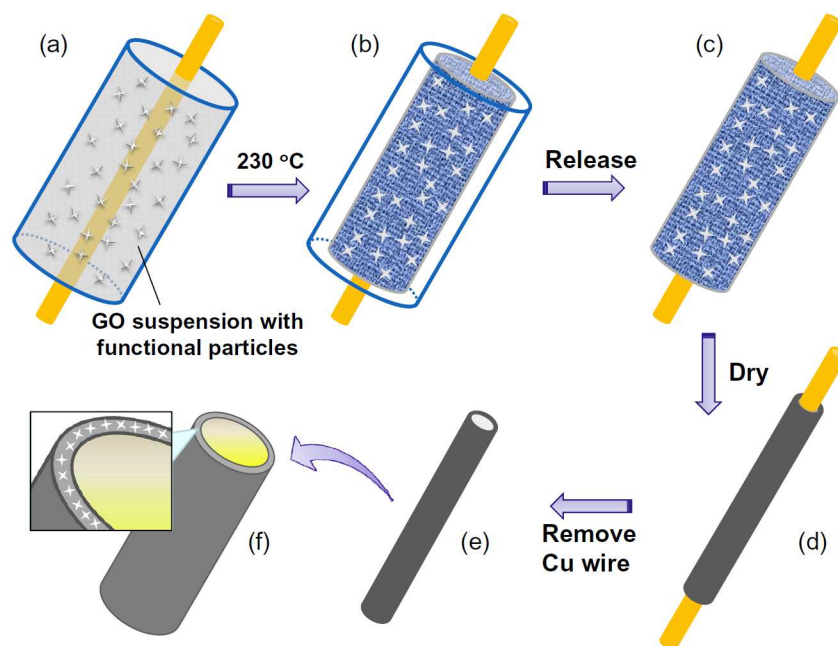


Figure S8. Schematic diagram of the within-wall modification of a μ GT.

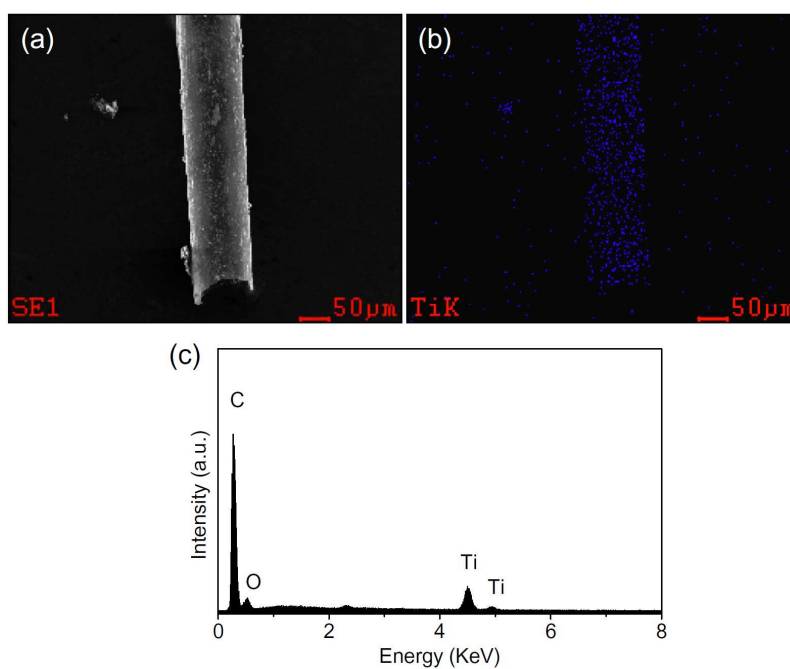


Figure S9. TiO₂ within-wall modified μ GT. (a, b) SEM image and corresponding EDS mapping of Ti element. (c) The EDS of this TiO₂ within-wall modified μ GT.

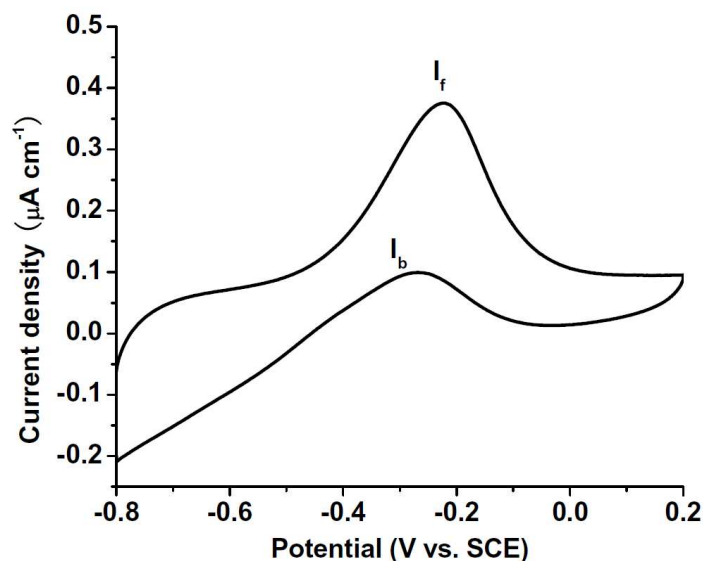


Figure S10. Catalytic ethanol oxidation of Pt outer-wall modified μ GT. CV of the Pt outer-wall modified μ GT with about 1 cm length in 1 M $\text{CH}_3\text{CH}_2\text{OH}$ + 1 M KOH aqueous solution. The scan rate: 50 mV s^{-1} .

To evaluate the catalytic activity of Pt outer-wall modified μ GT, we investigated the electrooxidation reaction of ethanol in basic medium. Figure S10 shows the CV of ethanol oxidation in a 1.0 M KOH + 1.0 M $\text{C}_2\text{H}_5\text{OH}$ solution at a scan rate of 50 mV s^{-1} . The onset potential for the ethanol oxidation on the Pt outer-wall modified μ GT electrode is *ca.* -0.5 V, which is even slightly lower than that of previously reported result -0.47 V.^{s7} The reduction in the onset anodic potential shows the enhancement in the kinetics of the ethanol oxidation reaction. Ethanol oxidation is characterized by separated anodic peaks in the forward and reverse scans. It is well known that the ratio of the forward anodic peak current (I_f) to the backward anodic peak current (I_b), I_f/I_b , could be used to describe the catalyst tolerance to incompletely oxidized species.^{s8-s10} The I_f/I_b of Pt outer-wall modified μ GT is high, indicating the better

tolerance to the intermediate species during the oxidation reaction. Therefore, the Pt outer-wall modified μ GT is suitable for the electrooxidation of ethanol.

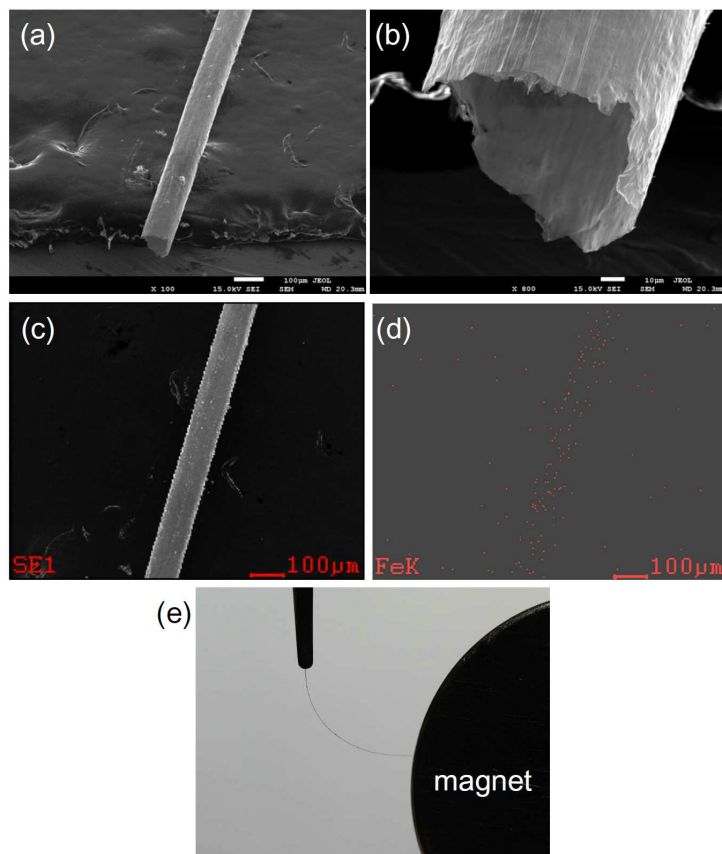


Figure S11. μ GT within-wall modified with Fe_3O_4 nanoparticles. (a–c) SEM images and (d) Fe element mapping corresponding to (c) for a μ GT within-wall modified with Fe_3O_4 nanoparticles ($\mu\text{GT}@\text{Fe}_3\text{O}_4$). (e) A photo showing the $\mu\text{GT}@\text{Fe}_3\text{O}_4$ attracted to the magnet.

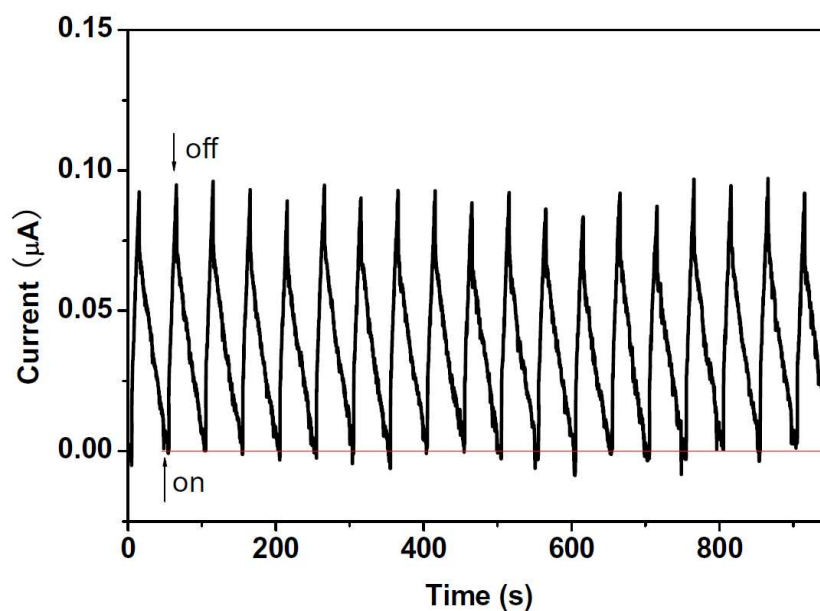


Figure S12. Photocurrent response. A typical photocurrent response for a *ca.* 6 wt% TiO₂ immobilized μ GT upon exposure to on/off light at room temperature. The tested sample length is 1 cm.

The photocurrent response of the TiO₂ immobilized μ GT was measured by applying a bias of 0.1 V to the μ GT with about 1 cm electrode distance, while the current was recorded by CHI 760D electrochemical workstation upon exposure to a daylight lamp (100 W). TiO₂-immobilized μ GT exhibits a fast photocurrent pulse with good repeatability (Figure S12).

Captions for Supporting Movies

Movie S1. The slow motion of an inner-wall modified μ GT with Pt nanoparticles micromotor (12 mm in length and 100 μ m in diameter) in 2 wt % H₂O₂ aqueous solution.

Movie S2. The fast motion of an inner-wall modified μ GT with Pt nanoparticles micromotor (6 mm in length and 100 μ m in diameter) in 20 wt% H₂O₂ aqueous solution.

References

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