

Supporting Information

Materials

Multiwalled carbon nanotubes (MWNTs, $\phi = 10\text{-}30$ nm) were purchased from Nanotech Port Co. Ltd. (Shenzhen, China). Tetraethylorthosilicate (TEOS, >98 %), Triton X-100 and 1,3-dicyclohexylcarbodiimide (DCC) were purchased from Sigma-Aldrich. Propargylamine hydrochloride and (3-chloropropyl)trimethoxysilane (CTMS, >95 %) were obtained from Alfa (Ward Hill, MA). Tetramethylbenzidine (TMB), sodium azide (NaN_3) and sodium ascorbate were purchased from BBI (Ontario, Canada). Glutathione (GSH) was obtained from Genview Corp (Houston, TX). $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, H_2O_2 , cyclohexane, *n*-hexanol, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, NH_4OH (25%) and triethylamine were obtained from Beijing Chemicals Inc (Beijing, China). All other reagents were of analytical reagent grade. Aqueous solutions were prepared using distilled water pre-treated with nitrogen gas.^[1]

Preparation of acetylene-functionalization of MWNTs (MWNT-al).

The carboxyl-modified MWNTs were prepared by sonicating the primitive MWNTs in a 3:1 v/v solution of concentrated sulfuric acid (98%) and concentrated nitric acid (70%) for 6 h (MWNT-6h) or 24 h (MWNT-24h) at 35–40 °C and washed with copious water, then dried in vacuum at 40 °C for 24 h.^[2-3]

For preparation of MWNT-al, 25 mg MWNT-COOH (MWNT-6h) were dispersed in 10 mL DMF solutions containing 20 mg DCC, and 0.1 mL triethylamine.^[4] This mixture solution was sonicated for 1 h, followed by addition of 15 mg propargylamine hydrochloride. After stirring at room temperature for 72 h, 20 mL chloroform was added. The products were obtained by centrifugation, followed by a wash three times with 20 mL chloroform and two times with 10 mL water.

Preparation of magnetic silica nanoparticles (MSNs).

The Fe_3O_4 nanoparticles were prepared as previously reported and in size 5 nm in diameter.^[5] Magnetic silica nanoparticles were synthesized by the reverse microemulsion method. Briefly, the nanoparticles were synthesized by adding 8.85 g of Triton X-100, 37.5 mL of cyclohexane, and 8 mL of *n*-hexanol to a 100 mL glass vial with continuous magnetic stirring. Next, 2 mL of ddH₂O and 25 mg Fe_3O_4 nanoparticles were added. Followed by the addition of 600 μL of TEOS, the materials were stirred

for 40 min. To initiate silica polymerization, 400 μL of NH_4OH was added. This polymerization was allowed to proceed for 18 h. The particles were obtained by magnetic separation, followed by a wash three times with 20 mL ethanol and two times with water.

Preparation of 3-chloropropyl-functionalized magnetic silica nanoparticles (MSN-Cl).

Magnetic silica nanoparticles (100 mg) were dried at 110°C under vacuum conditions for 90 minutes. Afterwards, the amount of 15 mL dry toluene was added under nitrogen atmosphere. After addition of 3-chloropropyltrimethoxysilane (200 μl), the reaction mixture was allowed to stir for overnight under reflux conditions.^[6] The functionalized MSN-Cl was separated by centrifugation and washed with each 30 mL of toluene, methanol and water before being dried at 60°C for 12 hours.

Preparation of azide-functionalized magnetic silica nanoparticles (MSN-N₃).

The amount of 50 mg MSN-Cl was added to 10 mL of a saturated solution of sodium azide in DMF.^[6] The resulting mixture was stirred at 90°C for overnight. The material was obtained by magnetic separation followed by two times with 30 mL of water and ethanol before being dried at 60°C for 12 hours.

Preparation of magnetic silica nanoparticles decorated multiwalled-carbon nanotubes (MWNT-MSN).

To a solution containing 100 $\mu\text{g}\cdot\text{ml}^{-1}$ of MWNT-al and 100 $\mu\text{g}\cdot\text{ml}^{-1}$ of MSN-N₃ in ddH₂O, a freshly prepared aqueous solution of $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ and ascorbic sodium was added.^[6,7] The final concentration of Cu^{2+} was keeping at 0.5 mM, while ascorbic sodium was added at five times the concentration of Cu^{2+} . The resulting mixture was allowed to keep at room temperature for 24 h. The magnetic silica nanoparticles decorated multiwalled-carbon nanotubes were recovered by magnetic separation and washed three times with water.

TEM was performed using a JEOL 1011 transmission electron microscope at an accelerating voltage of 100 kV. SEM and EDX were carried out using a HITACHI S-4500 instrument. FTIR characterization was carried out on a BRUKE Vertex 70 FTIR spectrometer.

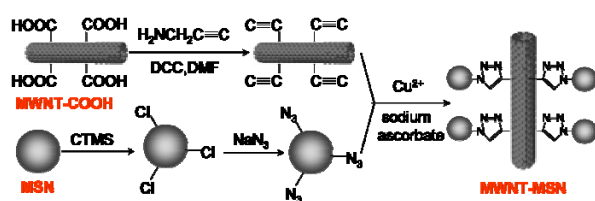
Assay: Kinetic measurements were carried out in time course mode by monitoring the absorbance change at 652 nm^[8, 9] on a Jasco-V550 UV-Vis spectrophotometer. Experiments were carried out at room temperature using 50 $\mu\text{g}\cdot\text{ml}^{-1}$ MWNT-al, 50 $\mu\text{g}\cdot\text{ml}^{-1}$ MSN-N₃ or MWNT-MSN (prepared from 50 $\mu\text{g}\cdot\text{ml}^{-1}$ MWNT-al and 50 $\mu\text{g}\cdot\text{ml}^{-1}$ MSN-N₃) in a reaction volume of 500 μL buffer solution (25 mM Na₂HPO₄, pH 4.0) with 800 μM TMB as substrate, and H₂O₂ concentration was 5 mM, unless otherwise stated.

For sensing of Cu(II), different concentration of CuSO₄·5H₂O was added to a solution containing 50 $\mu\text{g}\cdot\text{ml}^{-1}$ of MWNT-al and 50 $\mu\text{g}\cdot\text{ml}^{-1}$ of MSN-N₃ in ddH₂O. Sodium ascorbate at five times the concentration of Cu²⁺ was also added.^[7] After keeping at room temperature for 24 h, the composite was collected by using an external magnetic field and then washed three times with water. With addition of 5 mM H₂O₂ and 800 μM TMB, kinetic studies were performed to quantitatively evaluate the catalytic ability of the composite. In control experiments, 0.5 mM Al³⁺, Cr²⁺, Ni²⁺, Ba²⁺, Ca²⁺, Co²⁺, Mn²⁺, Zn²⁺, K⁺, Na⁺, Ag⁺ were used instead of Cu²⁺ for the experiment.

For sensing of Cu(I), a solution of Cu(I)-GSH (premixed from 2 mM Cu²⁺ and 20 mM glutathione) was added to the solution containing 50 $\mu\text{g}\cdot\text{ml}^{-1}$ of MWNT-al and 50 $\mu\text{g}\cdot\text{ml}^{-1}$ of MSN-N₃ in water.^[1] After keeping at room temperature for 24 h, the composite was collected by using an external magnetic field and then washed three times with H₂O. With addition of 5 mM H₂O₂ and 800 μM TMB, kinetic studies were performed to quantitatively evaluate the catalytic ability of the composite.

Reference

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Scheme S1. Synthetic Scheme of magnetic silica nanoparticles clicked on multiwalled-carbon nanotubes.

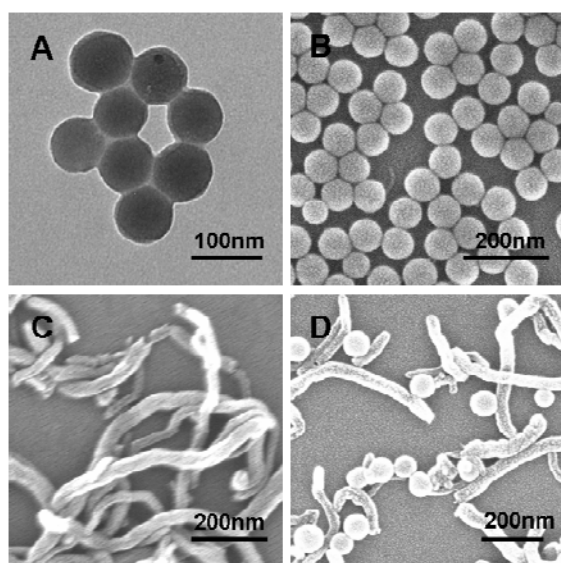


Figure S1. TEM image of A) MSN-N₃; SEM images of B) MSN-N₃, C) MWNT-al and D) MWNT-MSN.

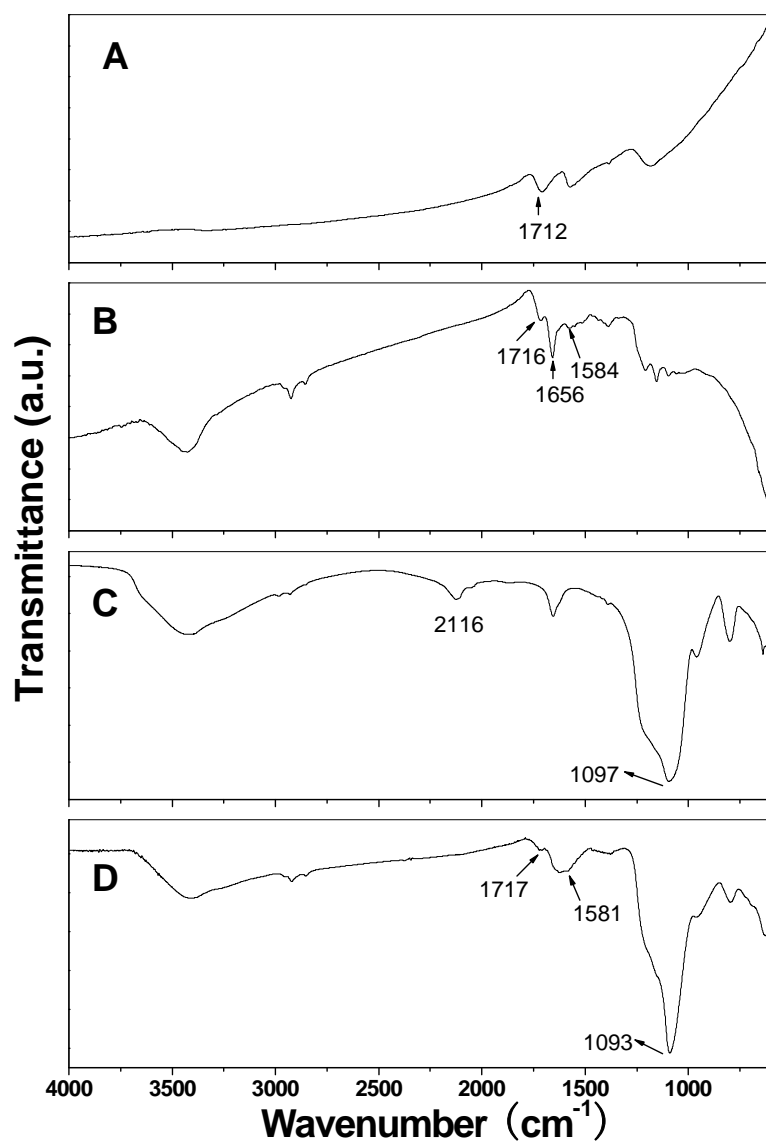


Figure S2. FTIR spectra of (A)MWNT-COOH, (B) MWNT-al, (C) MSN-N₃ and D) MWNT-MSN.

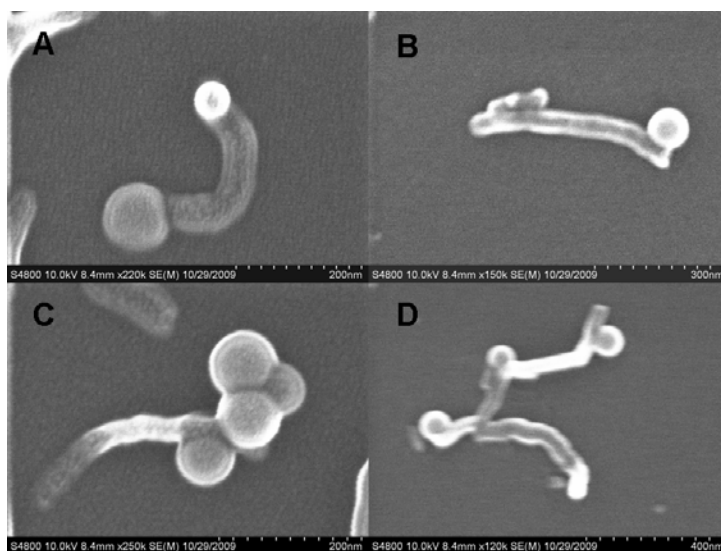


Figure S3. Different morphologies of MWNT-MSN: A) MSNs at the ends of MWNT; B) MSN at the sidewalls of MWNT; C) MSNs aggregates on MWNTs; (D) End-to-end array of MWNTs linked by MSNs.

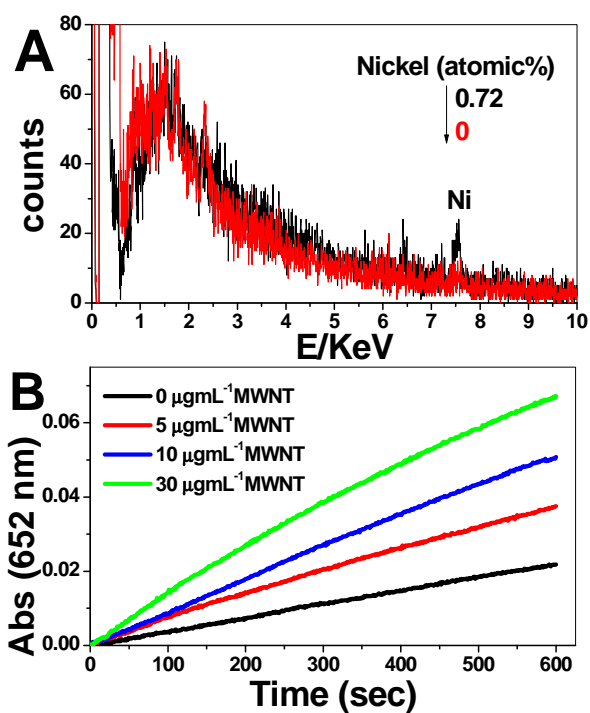


Figure S4. (A) EDX spectra of pristine MWNTs (black) and MWNT-24h (red). (B) The time-dependent absorbance changes at 652 nm in the absence (black) or presence of MWNT-24h: 5 (red), 10 (blue), and 30 $\mu\text{g}\cdot\text{mL}^{-1}$ (green) in phosphate buffer (25 mM Na_2HPO_4 , pH 5.0) at room temperature. 800 μM TMB and 50 mM H_2O_2 were added to 500 μL buffer solution to perform the experiment.

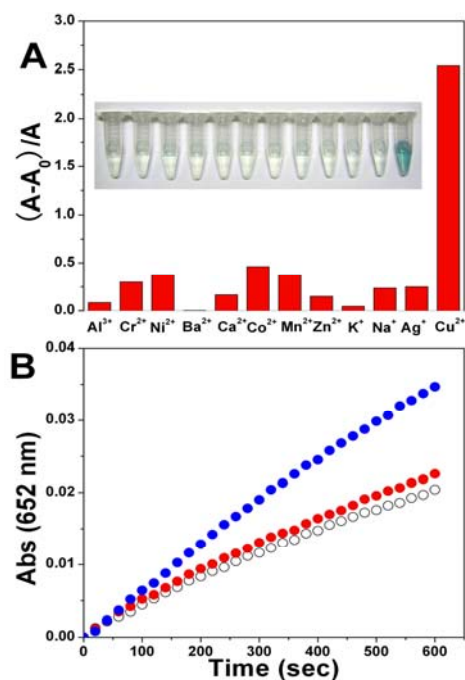


Figure S5. A) Selectivity analysis for Cu²⁺ detection by monitoring the relative absorbance. Ion concentration of Al³⁺, Cr²⁺, Ni²⁺, Ba²⁺, Ca²⁺, Co²⁺, Mn²⁺, Zn²⁺, K⁺, Na⁺ and Ag⁺ is 0.5 mM. [Cu²⁺] = 200 μM. Sodium ascorbate at five times the concentration of ions was also added. Inset: Typical photographs for Cu²⁺ detection with the colorimetric method developed using click chemistry and peroxidase-like catalytic reaction. (from left to right: 0.5 mM Al³⁺, Cr²⁺, Ni²⁺, Ba²⁺, Ca²⁺, Co²⁺, Mn²⁺, Zn²⁺, K⁺, Na⁺, Ag⁺ and 200 μM Cu²⁺, sodium ascorbate at five times the concentration of ions was also added). B) The time-dependent absorbance changes at 652 nm in the absence (black) or presence of 10 μM (red) and 50 μM (blue) Cu (I)-GSH complex (prepared from 2 mM Cu²⁺ and 20 mM glutathione).