

## Supporting Information:

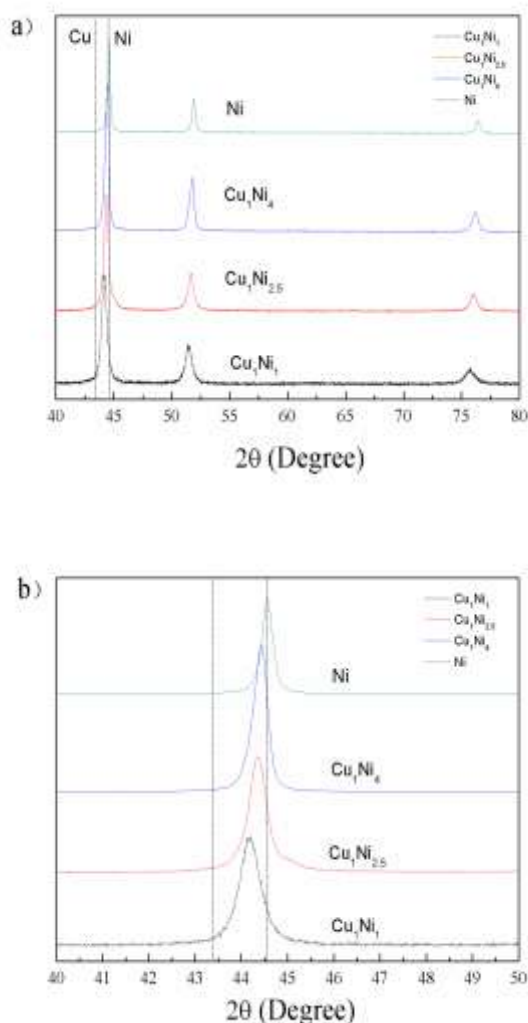
### Experimental Section

**Catalyst Preparation:** In a typical synthesis, a mixture of 6 g CTAB (Cetyltrimethyl Ammonium Bromide, Sonopharm), 15 ml of 1-butanol (Sonopharm), and 80 ml of cyclohexane (Sonopharm) was vigorously stirred and a solution containing 0.05 M  $\text{Cu}(\text{NO}_3)_2$  (Sonopharm) and 0.05 M  $\text{Ni}(\text{NO}_3)_2$  (4 ml, Sonopharm) was added to prepare microemulsion A. The aqueous phase of Microemulsion B was prepared using the solution of 0.5 ml hydrazine (98%, Sonopharm) and 1.5 ml NaOH (0.5M, Sonopharm). Microemulsion A was mixed with B at 70 °C. After 40 min, the solution was change into room temperature, TEOS (700 ul, Sonopharm) and  $\text{NH}_4\text{OH}$  (85%, 1 ml, Sonopharm) were added dropwise into the system under stirring, respectively. Hydrolysis and condensation of the silica precursors was allowed for 3 days at 25°C. After 3 days,  $\text{CuNi@SiO}_2$  was precipitated and washed by ethanol five times to remove CTAB. The  $\text{CuNi@SiO}_2$  was dried at 120°C and annealed at 500 °C in  $\text{H}_2$  for 5 h. The synthesis of CuNi control nanoparticle was identical to the above procedure without adding  $\text{SiO}_2$  precursor.

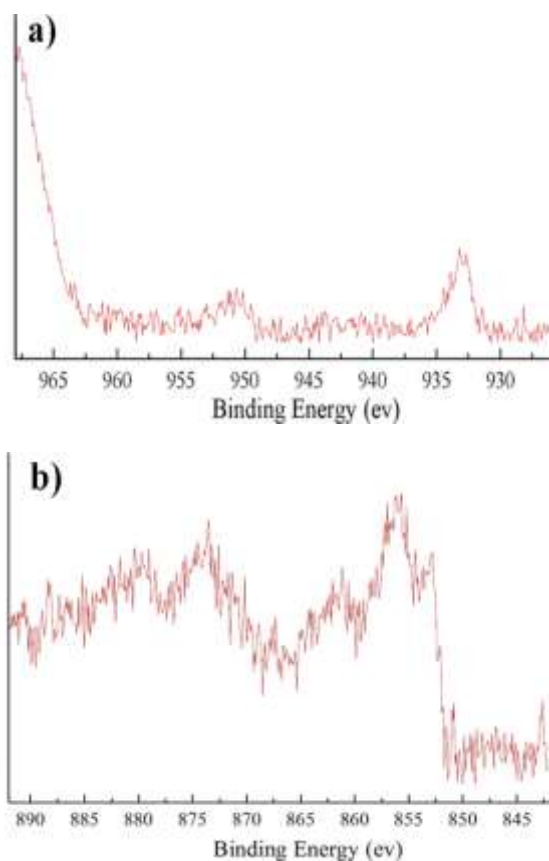
**Catalyst test:** Catalysis were performed in a fixed bed flow reactor (Fantai) at atmospheric pressure. In each experiment, 90 mg of the catalyst was installed in the fixed bed and reduced with  $\text{H}_2/\text{N}_2$  (50 ml/min) at 500 °C for 2 h. After the  $\text{H}_2$  pretreatment, a gas mixture of 20%  $\text{CH}_4$  and 20%  $\text{CO}_2$  in Ar at a total flow of 20 ml/min was introduced to test the activity of the catalyst in DRM reaction. The reaction temperature was ranged from 500 °C to 900 °C. The reactor effluent was analyzed using GC (Tianmei). The mass balance of the effluents was within 10% of the feed for most catalysts at reaction temperatures.

**Table 1.** The size of the alloy nanoparticles estimated by the XRD peak broadening using Scherrer's equation. The result of ICP show some difference to the precursor concentration.

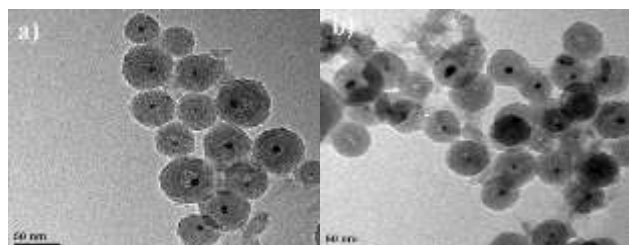
catalyst	d (nm)	precursor concentration (Ni:Cu)	ICP(Ni:Cu)
$\text{Cu}_1\text{Ni}_1$	14.3	50:50	55:45
$\text{Cu}_1\text{Ni}_{2.5}$	16.7	71:29	76:24
$\text{Cu}_1\text{Ni}_4$	18.9	80:20	87:13



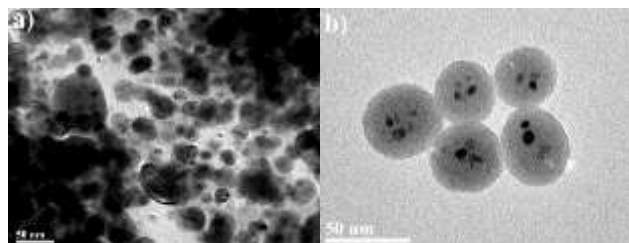
**Figure S1.** (a) XRD patterns of  $\text{CuNi}_x\text{@SiO}_2$  with  $x = 0, 1, 2.5,$  and  $4$ . (b) Shifts of the diffraction peaks of the alloy nanoparticles relative to the pure Ni nanoparticles. All of the samples were annealed in  $\text{H}_2$  (500 °C, 3h).



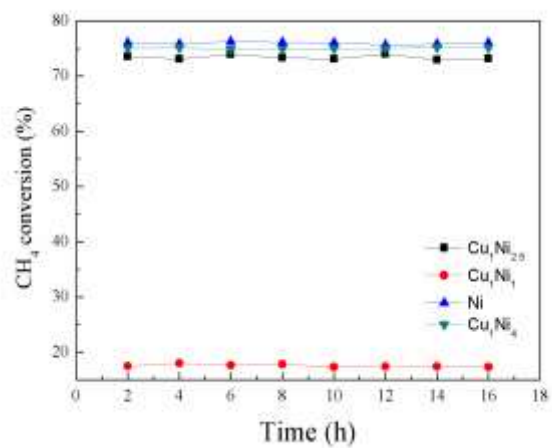
**Figure S2**a,b. XPS of Cu 2p and Ni 2p of the  $\text{CuNi}_{2.5}@SiO_2$  catalyst. The binding energy of Cu 2p 932.8 eV can be ascribed to  $\text{Cu}^0$  binding energy in CuNi nanoalloy.<sup>[11]</sup> The binding energy of Ni 2p 855.6 eV can be assigned to  $\text{NiSiO}_3$ , which can be ascribed to the oxidation of surface Ni atoms and the bonding with the silica shell. Similar phenomenon has been reported by Chen.<sup>[11]</sup>



**Figure S3.** The morphology of  $\text{Cu}_1\text{Ni}_{2.5}@SiO_2$  (a) and  $\text{Cu}_1\text{Ni}_4@SiO_2$  (b) nanostructure.



**Figure S4.** The morphology of CuNi nanoparticles synthesized without silica shells (a) and  $\text{CuNi}@SiO_2$  nanostructure with more than one metal cores encapsulated in one silica shell (b).



**Figure S5.** The stability of Cu-Ni@SiO<sub>2</sub> tested at 700 °C for 16 h.